NORTHWESTERN UNIVERSITY

Processing and Properties of Advanced Metallic Foams

A DISSERTATION

SUBMITTED TO THE GRADUATE SCHOOL
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

for the degree

DOCTOR OF PHILOSOPHY

Field of Materials Science and Engineering

By

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EVANSTON, ILLINOIS

December 2006
ABSTRACT

Processing and Properties of Advanced Metallic Foams

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Since the development of the first aluminum foams in the middle of the 20th century [178], great advances have been made in the processing and fundamental understanding of metallic foams. As a result of these advances, metallic foams are now penetrating a number of applications where their unique suite of properties makes them superior to solid materials, such as lightweight structures, packaging and impact protection, and filtration and catalysis [3]. The purpose of this work is to extend the use of metallic foams in such applications by expanding their processing to include more sophisticated base alloys and architectures.

The first four chapters discuss replacement of conventional crystalline metal foams with ones made from high-strength, low-melting amorphous metals, a substitution that offers potential for achieving mechanical properties superior to those of the best crystalline metal foams, without sacrificing the simplicity of processing methods made for low-melting crystalline alloys. Three different amorphous metal foams are developed in these chapters, and their structures and properties characterized. It is shown for the first time that amorphous metal foams, due to stabilization of shear bands during bending of their small strut-like features, are capable of compressive ductility comparable to that of ductile crystalline metal foams. A two-fold improvement
in mechanical energy absorption relative to crystalline aluminum foams is shown experimentally to result from this stabilization.

The last two chapters discuss modifications in foam processing that are designed to introduce controllable and continuous gradients in local foam density, which should improve mass efficiency by mimicking the optimized structures found in natural cellular materials [64], as well as facilitate the bonding and joining of foams with solid materials in higher-order structures. Two new processing methods are developed, one based on replication of nonuniformly-compressed polymer precursors, and the other based on nonuniform chemical milling of uniform foams, and each method is demonstrated through the production of low-density aluminum foams having simple model density gradients.
Acknowledgements

I would like to first acknowledge the generous support of my funding sources, specifically the Department of Defense via the DARPA-SAM Project (under ARO Contract No. DAAD 19-01-1-0525) for supporting the amorphous metal foam project, and Lawrence Livermore National Laboratories (with extra thanks to supervisor Dr. Andrea Hodge, for providing this support when I needed it most) for supporting the graded metallic foam project. I am further indebted to the Northwestern University Society of Fellows, both for generous fellowship support, and for all the good people it has allowed me to meet.

Thanks are also due to those whose help went into the work described here, most importantly Drs. Chris San Marchi (for help at the beginning of the amorphous metals project), David Prine (for invaluable assistance with acoustic emissions experiments), Yoshihisa Matsumoto (for doing a lion’s share of the work in the dissolution-grading project), and Stuart Stock (for all his help with tomographic experiments and analysis), and to my helpful undergraduate students Richard Scheunemann and Benjamin Mangrich. I would also like to thank all the other generous folks who provided me with both materials and brain power for my work, especially Marko and Dr. K. Stair, and to those who helped keep everything running: Peggy Adamson and Joanna Gwinn. Extra special thanks are due to the extraordinary people at the machine shop, especially Jeff and Thang, who by all rights should be coauthors on this thesis, after all the help they gave me. Thank you for your creativity, your punctuality, and your constant willingness to help. You will be missed.
Personally, I would above all like to thank my advisor, David Dunand, for his help and support throughout my stay at Northwestern. Most importantly, I am grateful for his support through the difficult early years of this work. It would have been easy (as well as unsettlingly logical) to cut the early losses from this project at that time; for the opportunity he gave me to see the project through, I will always be grateful. The same appreciation must also extend to the rest of my committee, Profs. Katherine Faber and Gregory Olson, and Dr. Charles Kuehmann, who showed their faith in me in this same difficult period and afterwards.

I am also grateful, and duly apologetic, to the rest of the Dunand group who had to help keep me going back then, including Chris and Aria, Dorian, Emmanuelle, Andrea, and Naomi. Thanks to you, and to my other groupmates and friends, John and Scott (1021 FTW), Heeman, Marsha, Rick, Keith, Marcus, Justin, and Ampika, who patiently listened to my lighter-hearted, but no less painfully-long, conversation over the years. For those who have been my friends inside and outside the group, who are too many to name (even in something that I have written), I consider myself blessed. I hope you all know who you are, and that I will see all of you in the future; to Dimitris and Neil, in particular, all my best. And to Apple: your patience and selflessness have been an inspiration to me. I hope you know that the part you play in my life could not be played by anyone else. My thoughts will stay with you, wherever I go.

Finally, I am eternally grateful to my family, especially Mom, Dad, and Eric, for their love and support, which they have given freely for so many years. Whatever success I have had, or may have in the future, you must know it is really your success. I love you all, and I hope that the next two hundred pages or so will convince you that, despite all appearances, I did not fall off the planet a month ago...
# Table of Contents

ABSTRACT 3

Acknowledgements 5

List of Tables 10

List of Figures 11

Chapter 1. Introduction 24

1.1. Porous and Foam Materials 24

1.2. Amorphous Metals 37

1.3. Next-Generation Metallic Foams 51

Chapter 2. Amorphous Metal Foams 55

2.1. Motivation 55

2.2. Origins of Compressive Ductility in Amorphous Metal Foams 58

2.3. The State of the Art 62

Chapter 3. Replicated Amorphous Metal Foams 68

3.1. Processing 68

3.2. Structure 85

3.3. Mechanical Properties 91

3.4. Damage Evolution 108

Chapter 4. Syntactic Amorphous Metal Foams 131
Appendix B. Scripts for Calculations Described in the Text

B.1. Scripts for Density Profile Analysis from Radiographic Images 236

B.2. Scripts for Density Profile Analysis from 3D Microtomographic Data 239
List of Tables

3.1 Selected properties of the bulk metallic glass-former Vit106. Transition temperatures represent onset values measured at the identified heating rates using DSC; where multiple transitions are visible, temperatures represent onset of the first transition. 75

5.1 Chemical composition of the iron spheres used in production of Mg-based syntactic AMF. Values are given in parts per million by mass (mppm). 147

7.1 Chemical composition of the Duocel® foams used in the dissolution method, along with the compositions of bulk specimens used for comparison, and the nominal composition of Al-6101 [18]. 184

7.2 Tomographic parameters calculated from three foam specimens, solutionized and then dissolved in room-temperature NaOH solution of pH 13. Error values represent standard deviations based on 5 measurements taken along the gauge length of each sample. 193
## List of Figures

1.1 Schematic representation of metallic foam production methods. 26

1.2 Optical micrographs showing foams from this work. (a) Low-density, open-cell aluminum foam. (b) Intermediate-density, open-cell amorphous Zr-based foam. (c) High-density, closed-cell amorphous Zr-based foam. Details are provided in later chapters. 29

1.3 Schematic representation of a metallic foam (in this case, an open-cell foam), attributed to Gibson and Ashby. Taken from Ref. [64]. 30

1.4 A representative compressive stress-strain curve for a metallic foam, in this case an aluminum foam with 8% relative density. From Chapter 3 of Ashby et al.[3] 33

2.1 Surface strains at failure for a series of Zr-based amorphous metal ribbons and wires, as a function of ribbon/wire thickness. From Conner et al. [37]. 61

2.2 Porous amorphous metals developed by other researchers, using liquid-state foaming methods. (a) Pd-based foam made using a gas-generating flux additive ($\rho/\rho_s = 24\%$) [168]. (b) Pd-based foam made by entrapping gas in the melt and then expanding it in the supercooled-liquid state ($\rho/\rho_s = 15\%$) [167]. (c) Pd-based foam made by casting into a bed of soluble NaCl particles ($\rho/\rho_s = 35\%$) [186]. (d) Pd-based foam made by precipitation of dissolved hydrogen gas during cooling. The relative density of this foam
was not listed, but is likely to lie in the range $\rho/\rho_s = 54$–$58\%$ \cite{187}. (e) Porous Zr-based BMG made by entrainment of inert gas in a rapidly-stirred melt ($\rho/\rho_s = 90\%$) \cite{167}. (f) Zr-based foam made by casting into a bed of leachable NaCl granules ($\rho/\rho_s = 64\%$) \cite{156}.

2.3 Porous amorphous metals developed by other researchers, using solid-state foaming methods. (a) Cu-based foam made by dissolution of crystalline Cu from a composite structure ($\rho/\rho_s = 25\%$) \cite{107}. (b) Porous Ni-based BMG made by dissolution of crystalline brass from a composite structure ($\rho/\rho_s = 58\%$) \cite{108}. (c) Isolated pore in a porous Zr-based BMG made by co-consolidation of BMG and aluminum nitride powders \cite{74}. (d) Porous Zr-based BMG made by partial electroconsolidation of compacted powders ($\rho/\rho_s = 66.5\%$) \cite{198}. Scale bars in these images were taken from the original texts, and estimated when scale bars were not provided explicitly. They should therefore be considered approximate.

3.1 Schematic representation of the melt infiltration process as implemented in this work.

3.2 Estimated corrosion penetration rates for amorphous Vit106 coupons in nitric acid baths at ambient temperature, containing dissolved BaF$_2$ in proportions chosen to simulate full dissolution of patterns from infiltrated samples (typical concentration: 5–8 mM). The hollow triangle demonstrates the potential benefits of corrosion inhibitors (in this case, fine alumina powder), which reduce the aggressiveness of fluoride ion liberated by the dissolving salt.
3.3 SEM micrographs showing: (a) morphology of unsintered 230 µm BaF₂ powders; (b) morphology of as-sintered 230 µm BaF₂ powders, showing slight rounding but no substantial reshaping; (c) macrostructure of a sintered 230 µm BaF₂ pattern before infiltration; (d) macrostructure of Vit106 foam (22% dense) replicated from a 230 µm pattern; (e) magnified view of the foam in panel (d), showing pore, strut and node structure; (f) view of the deformed foam in panels (d,e) after unloading from 79% engineering strain.

3.4 SEM micrographs of an amorphous Vit106 foam (diameter: 4.5 mm, relative density: 22%) after pattern removal in ultrasonically-agitated 2M nitric acid. (a) Uniform macrostructure of the foam. (b) Surface of the foam, showing sockets left behind by individual BaF₂ particles. (c) Individual foam strut, having high aspect ratio. The surface of this strut shows small indentations ('scalloping') produced by the corrosive leaching bath.

3.5 X-ray diffraction pattern taken from a section of replicated Vit106 foam following dissolution of its pattern in nitric acid.

3.6 DSC data (heating rate 0.33°C/s) from (a) monolithic amorphous Vit106; (b) amorphous Vit106 foam following pattern removal in ultrasonically-agitated nitric acid; and (c) amorphous Vit106 foam following pattern removal in stagnant nitric acid.

3.7 SEM micrographs illustrating mechanisms of compressive deformation in Vit106 foam (pore size 230 µm and relative density 23%, similar to the foam in Fig. 3.3d,e). Low-magnification images show foam structure following unloading from various applied macroscopic strains: (a) low strain (4%); (b) intermediate strain (24%); (c) high strain (43%). Also shown are deformed
struts within the sample following unloading from: (d) 4% strain; (e) 9% strain; (f) 14% strain; (g) 19% strain. Visible fractures are indicated by arrows in the panels where they first appear.

3.8 Engineering compressive stress-strain curves of Vit106 foams (a) as a function of relative density for constant pore size 230 µm; and (b) as a function of pore size for near-constant relative density (22.4–23.8%). Insets magnify the low-strain regions for better visualization of serrations. The stress-strain curve of a crystalline aluminum foam (relative density 28%, pore size ca. 500 µm) is shown for comparison.

3.9 Initial loading stiffness for Vit106 foams as a function of relative density and pore size. Also shown are best fits according to a power-law scaling relationship, Eq. 1.1, using \((C_1, n_1) = (0.30, 2.2)\) and \((0.24, 2)\). The point representing the damaged 14% dense sample was not used in regression and is denoted by an open symbol. The stiffness of the finest-pore specimen (red marker) was also not used, as this specimen was used for acoustic emissions experiments and its low-strain data were affected by the requiring coupling fluid.

3.10 Yield strength for Vit106 foams as a function of relative density and pore size. Also shown are best fits according to a power law scaling relationship, Eq. 1.2, using \((C_2, n_2) = (0.26, 1.9)\) and \((0.15, 1.5)\). The point representing the damaged 14% sample was not used in regression and is denoted by an open symbol.

3.11 Schematic illustration of an elastic-perfectly plastic amorphous metal strut (square cross-section of edge length \(h\)) in the fully plasticized condition.
The distance from the centerline to the neutral axis is given by \( y_n \), and the tensile and compressive strengths are given by \( \sigma_T \) and \( \sigma_C \), respectively, indicated by the shaded stress distributions.

### 3.12
Strain energy absorbed by Vit106 foams up to densification, per unit foam volume, as a function of flow stress at a nominal strain of 25%. The densest sample (28%) carried high stress but exhibited lower energy absorption than expected due to premature failure. Shown for comparison are the aluminum foam produced by replication of NaCl (open circle) and the approximate range for other aluminum foams, as compiled in Ashby et al. [3]. The dashed line is provided as a visual guide to represent the trend in Vit106 data.

### 3.13
Cumulative strain energy density lost during recovery from brittle fractures (serrations) during compression of replicated Vit106 foams. Strain energy density loss is estimated by subtracting the actual strain energy density during each serration from that of an idealized stress strain curve lacking serrations and having a linear change in flow stress over the same region.

### 3.14
Reloading stiffness for a foam with 230 \( \mu \text{m} \) pore size and 28% relative density as a function of plastic strain. Data were normalized by the stiffness immediately prior to yield (1.9% strain). Also shown for completeness are similar data from other foams of equal pore size but varying density, showing less precision but similar overall behavior.

### 3.15
X-ray diffraction patterns taken from deformed samples of (a) amorphous Vit106 foam; and (b) crystalline Vit106 foam prepared by devitrifying an amorphous specimen.
3.16 Scanning electron micrograph showing a representative salt-replicated foam structure (in this case, eutectic Al-Si). The pore size and relative density of this foam were 150-212 $\mu$m and 42%, respectively.

3.17 Schematic diagram illustrating the experimental setup for measurement of foam acoustic and mechanical data.

3.18 Compressive stress-strain curves for (a) amorphous Vit106 foam; (b) crystalline Vit106 foam; and (c) eutectic Al-Si foam. Also shown are cumulative AE events, normalized by the estimated number of pores in each sample.

3.19 Cumulative amplitude distributions for AE events studied in this work. (a) Full AE populations from the amorphous and crystalline Vit106 foams and the Al-Si foam. (b) Three subpopulations from the amorphous Vit106 foam, representing the strain intervals 10–15%, 30–35% and 70–75%. All distributions show linearity (i.e. power-law scaling) at lower amplitudes with deviation at high amplitudes. Dashed lines indicate fits using the GR relationship, Eqn. 3.9.

3.20 Evolution of acoustic activity in amorphous Vit106 foam with increasing applied strain, in 5% intervals. (a) Total events in each interval. (b) The GR parameter AE-$b$ characterizing each interval. Yield is indicated in both plots by vertical dashed lines.

3.21 Strain dependence of acoustic event amplitude (open circles, right scale) and stress (solid squares and line, left scale) in a region with two stress serrations, showing high-energy events initiating the serrations (indicated
by arrows; the horizontal dashed line shows the hardware saturation limit), followed by decreased acoustic activity during stress recovery.

4.1 Optical micrographs showing the structure of syntactic Vit106 foam: (a) low magnification image demonstrating foam uniformity; (b) magnified image of the polished surface, showing microscopic foam structure. Misshapen carbon microspheres are visible, as is a sphere wall fragment (indicated by arrow). Good wetting is inferred from the lack of interparticle porosity.

4.2 X-ray diffraction patterns collected from: (a) fully dense amorphous Vit106; (b) the surface of the Vit106 foam shown in Figure 4.1a. Crystalline reflections are indicated by markers.

4.3 DSC thermograms showing glass transitions and crystallization exotherms in: (a) fully dense amorphous Vit106 from the sample analyzed in Figure 4.2a; and (b) Vit106 foam from Figures 4.1, 4.2b.

5.1 Compilation of available data showing the relationship between fracture energy and the ratio of shear and bulk elastic moduli in amorphous metals. Also shown are toughness data for one Zr-based amorphous metal after various annealing treatments, whose times and temperatures are shown in the legend. Adapted from Lewandowski et al. [111]

5.2 X-ray diffraction pattern taken from an infiltrated Mg-based BMG/NaCl composite, showing that the alloy may be vitrified after infiltration of NaCl. The iron reflection dominating the pattern originates from the crucible.

5.3 Photograph of a syntactic Mg-based AMF produced by infiltration of molten Mg_{60}Cu_{21}Ag_{7}Gd_{12} into a bed of hollow iron spheres, after machining using
a diamond grinding wheel and diamond wafering saw. During grinding, portions of the ductile sphere walls were pushed over the exposed sphere cavities, forming burrs that suggest in this image an erroneously high sphere wall thickness.

5.4 Optical image of a polished cross-section of syntactic Mg-based AMF. The contrast visible in the matrix of the specimen is the result of corrosion during polishing, and possibly due to devitrification of the matrix during the hot-mounting process used in metallographic preparation.

5.5 X-ray diffraction pattern taken from an infiltrated syntactic Mg-based foam, showing that the alloy may be vitrified after infiltration of iron spheres. The iron reflection dominating the pattern originates from the walls of these spheres, and from the crucible wall. The phase appearing at 40.5° could not be identified.

5.6 Results of DSC measurements performed on specimens of Mg-based BMG, using a constant heating rate of 5°C/min. (a) DSC signature of the monolithic alloy, in the as-cast and devitrified states. (b) DSC signatures of foam specimens, both as-cast and after annealing at 200°C for 3 hours.

5.7 Compressive stress-strain behavior of syntactic amorphous Mg_{60}Cu_{21}Ag_{7}Gd_{12} foam. The inset shows a magnified view of the region shown in the blue box, for better visualization of the serrations in the curve.

5.8 Photographs taken during compression of the amorphous AMF specimen of Fig. 5.7. The images are identified by the average macroscopic strain at the time of the photograph.
5.9 Compressive stress-strain behavior of syntactic crystalline Mg$_{60}$Cu$_{21}$Ag$_7$Gd$_{12}$ foam, produced by devitrifying an amorphous foam by vacuum annealing at 200°C for 3 hours. The inset shows a magnified view of the region shown in the blue box, for better visualization of the (less-pronounced) serrations in the curve. The scales are the same as in Fig. 5.7, to facilitate comparison.

5.10 Photographs taken during compression of the crystalline AMF specimen of Fig. 5.9. The images are identified by the average macroscopic strain at the time of the photograph.

6.1 Schematic representation of the replication method for production of density-graded metallic foams.

6.2 Scanning electron micrographs illustrating the structure of the fine-pore polyurethane precursor foam used in the replication method: (a) low-magnification image showing pore structure and highlighting a partially-intact cell wall; (b) higher-magnification image illustrating the shape of the precursor struts.

6.3 Optical micrographs illustrating the macrostructure of a coarse-pore pure aluminum specimen (diameter ca. 14 mm, relative density 3.8%) processed by the replication method outlined in Figure 6.1. (a) side view, with the low-density face at the top of the panel and the high-density face at the bottom; (b) end view of the low-density face; (c) end view of the high-density face.

6.4 Scanning electron micrographs illustrating the mesostructure of the specimen shown in Figure 6.3a. (a) pore structure in the low-density region; (b) a typical nearly-straight strut in the low-density region; (c) pore structure in
the high-density region; (d) a heavily deformed strut in the high-density region; (e) example of replicated bubbles from imperfect investment settling; (f) example of major strut defect caused by incomplete infiltration.

6.5 Representative calibration data for the radiographic method of density profiling, measured using a layered aluminum foil standard (inset).

6.6 Radiographic images of the graded specimen of Figure 6.3a, with the low-density face at the top of the panel and the high-density face at the bottom. (a) radiograph of the stationary specimen; (b) radiograph of the rotating specimen. Radiographs have been contrast-enhanced for better visualization.

6.7 Relative density profile calculated from the radiograph in Figure 6.6b. Also shown for comparison is the predicted relative density profile estimated from precursor dimensions.

6.8 Tomographic renderings of selected volumes from the graded specimen of Fig. 6.3a, taken near: (a) the low-density face; and (b) the high-density face. The scale bar is approximate.

6.9 Relative density profiles calculated from full 3D tomographic data. (a) total relative density profile; (b) relative density profiles plotted separately for the innermost and outermost 50 vol.% of the structure; (c) magnified view of the boxed region in panel b. The predicted profile is shown as a smooth line in each panel for reference.

7.1 Schematic representation of the dissolution method for production of density-graded metallic foams.
Normalized rates of dissolution for commercial Al-6101 foams in aqueous solution. (a) NaOH solution; (b) KOH solution; (c) HCl solution. Data courtesy of Dr. Y. Matsumoto of the Oita National College of Technology (Oita, Japan).

Comparison between dissolution rates of foamed and bulk Al-6101 in aqueous NaOH solution of pH 13. Data courtesy of Dr. Y. Matsumoto of the Oita National College of Technology (Oita, Japan).

Dissolution rates as a function of NaOH concentration (molarity and pH) for Al-6101 foams and bulk specimens.

SEM micrographs of T6-treated foams after immersion in a pH 2 HCl solution at 23°C. Panels (a) and (c) show strut and node surfaces for foams with 7.5 and 5% relative densities, respectively; Panels (b) and (d) show individual strut of foams with 7.5 and 5% relative densities, respectively.

SEM micrographs of T6-treated foams after immersion in a pH 13 NaOH solution at 23°C. Panels (a) and (c) show strut and node surfaces for foams with 7.5 and 5% relative densities, respectively; Panels (b) and (d) show individual strut of foams with 7.5 and 5% relative densities, respectively.

SEM micrographs of ST-treated foams after immersion in a pH 13 NaOH solution at 23°C. Panels (a) and (c) show strut and node surfaces for foams with 7.5 and 5% relative densities, respectively; Panels (b) and (d) show individual strut of foams with 7.5 and 5% relative densities, respectively.

Representative compressive stress-strain curves for foams dissolved uniformly in room-temperature NaOH (pH 13). The highest-density specimen was in the as-received condition, while the two partially-dissolved specimens were
solution-treated prior to dissolution, and then aged to the T6 condition before mechanical testing.

7.9 Compressive mechanical properties of foams dissolved uniformly in NaOH (pH 13) and HCl (pH 1) solutions. (a) Strength; (b) Reloading stiffness. Also shown are best fits to a general power law relationship and to the Ashby-Gibson equations.

7.10 (a) Photograph of a commercial Al-6101 foam graded by nonuniform exposure to a room-temperature NaOH solution of pH 13. (b) Electron micrograph showing the undissolved, high-density region of the foam. (c) Electron micrograph showing the highly-dissolved, low-density region of the foam.

7.11 Relative density profile of the foam shown in Fig. 7.10, as determined by image analysis of polished cross sections. Data courtesy of Dr. Y. Matsumoto of the Oita National College of Technology (Oita, Japan).

7.12 Photograph of a commercial Al-6101 foam graded by nonuniform exposure to a heated (70°C) NaOH solution of pH 13.

8.1 Comparison between the compressive stress-strain curves of representative AMF specimens from this work and the work of the Inoue group in Japan [187]. The inset shows a magnified view of the low-strain region of each curve.

8.2 Comparison between the mechanical properties of replicated Vit106 foams in this work and hydrogen-blown Pd-based foams described in Ref. [187]. (a) Normalized compressive strength. (b) Normalized stiffness. Also shown
are least-squares regression fits to the empirical scaling equations [3] most
relevant to each structure.

8.3 Mechanical properties of porous amorphous metals reported in the
literature, including those in this work as well as salt-replicated Pd-
based [186], hydrogen-blown Pd-based [187, 188, 190, 189], spark-sintered
Zr-based [198], extruded Ni-based [108], and nitrided Zr-based [74]
specimens. (a) Normalized compressive strength. (b) Compressive failure
strain. For comparison purposes, a characteristic failure strain of 2% for
compression of monolithic amorphous metals is indicated with a dashed line.
Data from this work are distinguished by blue markers in both panels.

A.1 Schematic cross-sectional view of a strut of equilateral triangular shape,
subjected to bending in a plane oriented perpendicularly to the page. In
(a) the applied moment produces tension along the edge of the strut and
compression along the opposing face; in (b) it has the opposite sense,
producing compression along the edge and tension in the face.
CHAPTER 1

Introduction

In this chapter, the state of scientific and applied knowledge in the fields of porous materials and amorphous metals is reviewed. Within the greater context of materials science, both these fields must be considered young; however, both are already too broad to admit full discussion here. In the interest of brevity, therefore, only those aspects of porous materials and amorphous metals which have obvious bearing on the work in subsequent chapters will be reviewed here. Appropriate references are provided in the text for readers interested in a larger perspective.

1.1. Porous and Foam Materials

In the most general sense, porous materials may be defined as those that contain an appreciable fraction of void space or porosity [64, 194]. The meaning of “appreciable” in this context is broad, including levels of porosity ranging from a few volume percent (for example, in sintered materials) up to 99% or greater (for example, in aerogels). As such, it is common to distinguish the former cases, in which the material is best understood as a solid matrix with isolated pores, from the latter, in which it is better considered a set of distinct solid features arranged into a three-dimensional network. Although the exact level of porosity distinguishing these two cases is unclear, common practice (which is followed here) is to identify the latter group of materials, those with porosities exceeding ca. 50–70 vol.%, as a subgroup of porous materials known as cellular or foam materials [64, 3]. The density of a foam is usually not represented by its porosity, but rather its relative density $\rho/\rho_s$, where $\rho$ is the net density of the foam and $\rho_s$ is the density of the solid from which it is made.
According to the definition above, porous materials are ubiquitous, including both natural and artificial materials and those made from liquids (e.g., beer foam or soap froths), solid polymers (e.g., wood), ceramics (e.g., bone and brick), and metals (discussed below), while foam materials are more rare. Though all these materials (at least, those made from solids) share important similarities, their processing, properties, characterization methods, and final applications vary widely. In recognition of this fact, it is necessary to restrict the discussion here to the specific topic of cellular metals or metallic foams, and refer the reader elsewhere [64, 194] for more general discussion of the wider field of porous materials.

1.1.1. Processing of Metallic Foams

Crystalline metallic foams can be processed from a variety of base alloys and through a variety of processing approaches [10, 3], the most common of which are listed in Figure 1.1. Most of the methods listed in this figure have been applied primarily, if not exclusively, to aluminum and its alloys, which enjoy the widest commercial and research interest of any metallic foams (due mainly to their high specific strength, low processing temperatures and chemical and oxidation resistance) [3]. Some have also been applied to other low melting metals (e.g., Mg [200], Zn [204], Sn [179], Pb [204, 197], or to higher-melting metals (e.g., Ni [103, 112, 151, 17, 152], Fe [204, 17], or Ti [112, 17]), while a smaller number are appropriate to foaming of ceramic or polymeric materials in addition to metals [64].

As shown in the figure, metallic foams can be processed from the vapor, solid, and liquid states of their base alloys. Generally speaking, vapor and solid state methods are used for high-melting alloys whose melting points render liquid-state methods impractical; the one notable exception to this is the powder compact method developed by the Banhart group in Germany, in which gas-generating additives are blended into a metallic powder prior to consolidation and foaming in the semi-solid or liquid state [204, 12]. Liquid-state methods, naturally, are
used mostly for low-melting metals. The relative simplicity and cost-effectiveness of liquid-state methods have allowed them more thorough study than vapor and solid-state processes [3, 9].

Liquid-state foaming, in its simplest and most common form, involves entrapment of gas bubbles during solidification. This gas is most commonly introduced externally through pressurized nozzles, rotating impellers, or porous crucible surfaces [180], but can also be generated within the melt itself through decomposition of suspended chemical additives (e.g., metal hydrides[94] or hydrated ceramic powders[168]). In certain alloys (e.g., Cu–H), gas-filled pores can also be precipitated eutectically during solidification[170], while in others (e.g., Hg in Al, used to make the first metallic foams ca. 1948[178]) it may be generated explosively by pressure quenching a mixture of the molten alloy and a volatile immiscible fluid.
The pore structures of metallic foams processed by gas entrapment are usually the result of a balance between the mechanisms of pore generation (e.g., gas flow rate, or the rate of gas evolution from powder surfaces) and those of pore coarsening (merging of pores, due to diffusion of gas through the membranes separating those pores, or rupture of the membranes themselves) and collapse (merging of pores with the outside environment). The physics underlying both sets of mechanisms are fairly well understood for aqueous and polymer-based foams, but significantly less so for molten metal foams [194]. This gap is created by the absence of effective surfactants for molten metals, which instead rely on fine ceramic particulates for stabilization against coarsening and collapse [12, 3]. Despite substantial research into the physics of foamed dispersion-stabilized melts, it is still not clear whether these particles function via thermodynamic means (i.e., by altering effective surface energies in the melt, which are the driving force for coarsening and collapse) or kinetic means (i.e., by increasing the viscosity of the foamed melt and thereby inhibiting the gravitational drainage that leads to membrane rupture) [47, 197].

In addition to entrapment of physically- and chemically-blown gases, pore space can also be introduced into liquid metals using replication techniques. In these methods, pore structure is defined by casting around temporary placeholder materials of the appropriate size and morphology, for example leachable salts like NaCl [207] or combustible space-fillers like resin-coated polystyrene [124], followed by chemical, thermal, or mechanical removal of the placeholder. In a variant of this basic method, low-density placeholders such as hollow spheres are left within the alloy permanently, creating “syntactic” foams [157, 98, 8]. In a second variant, foams can be produced by casting the molten alloy into the channels of a negative pattern created by infiltration of a refractory ceramic slurry into the pores of a sacrificial polymer foam[199].

The advantage of replication methods, which figure prominently in this work, is the fact that the pore size and morphology of the final foam product is determined by that of the replication pattern material (that is, by the salt, hollow spheres, or the mold formed from
the polymer precursor foam), rather than by the less-predictable dynamic processes of bubble formation, coarsening, and collapse. As such, replicated foams often enjoy high reproducibility and uniformity of structure and properties, and can achieve wider ranges of pore size and fraction than these other processes \[163\]. On the other hand, they are often more complex, and more costly, than gas entrapment methods. The majority of industrialized liquid-state foaming methods, with the exception of replication by investment casting, are therefore still based on gas entrapment \[3\].

### 1.1.2. Structure of Metallic Foams

It is common to follow the work of Joseph Plateau (see Ref. \[194\]) in classifying the structural elements of which foam structures are built. According to Plateau’s system, a general foam structure consists of a network of three types of elements, whose arrangement in space follows simple topological laws. These elements include the *membranes* or *cell walls* (thin, nearly-flat regions created between two impinging pores, analogous to grain boundaries formed between pairs of neighboring grains), *struts* (slender, beam-like features formed at the mutual intersection of three membranes, analogous to triple points in grain structures), and *nodes* (where a set of struts created by impingement of several neighboring pores meet at a point). In some cases, all three elements are present in the final structure; such structures, consisting of non-percolating pores, are termed *closed-cell*. In other cases, and quite commonly in metallic foams, rupture of the cell walls leads to *open-cell* foams, having interconnected porosity. For certain applications (e.g. buoyant materials and some structural materials) closed-cell architectures are preferred, while in others (fluid filtration, catalysis, biomaterials) open-cell architectures are needed. Three micrographs of foams from this work, illustrating the wide variety of structures among foams processed by different routes, are shown in Fig. 1.2.
Figure 1.2. Optical micrographs showing foams from this work. (a) Low-density, open-cell aluminum foam. (b) Intermediate-density, open-cell amorphous Zr-based foam. (c) High-density, closed-cell amorphous Zr-based foam. Details are provided in later chapters.
The structures of real metallic foams (such as those shown in Fig. 1.2) are highly irregular, and a unified mathematical description would be untenable. Fortunately, it is generally adequate to represent a metallic foam using only a few simple parameters, most importantly relative density, pore size, anisotropy, and connectivity (and more rarely, pore size distribution and pore morphology) \cite{64,194,3}. Of these, the single most predictive is relative density, which is related to nearly all important properties of a foam by way of simple scaling relationships, and which is generally a far better predictor of these properties than any other parameter \cite{3}. The relationships between the properties and relative densities of foams are almost always empirically determined; however many relationships are also predictable using simple model representations of foam structure. The most common, and most successful, of these structures is called the Gibson-Ashby model (hereafter, the GA model) shown in Fig. 1.3 \cite{63,64,3}. In this model, from which important scaling relationships for properties ranging from strength and stiffness to thermal conductivity can be derived, foams are represented as periodic arrangements of slender solid beams, mutually interconnected at their midpoints.
In anticipation of later discussions, it is important to note two important features of the model. The first of these features is the lack of enlarged nodes in the GA model. Localization of mass at the intersections between struts is a necessary prediction of surface area minimization, as rounding of the corners at such intersections leads to reduced surface area relative to the GA model. Nonetheless, its omission from the GA structure does not invalidate the basic predictions of the GA model, even in foam structures with relatively pronounced nodes. The strongest evidence for this is given by the adherence of salt-replicated foams to the model, despite the prominent nodes characteristic of those structures [53, 65, 163]. The enlarged nodes in these foams manifest themselves through a slight additional “knock-down” in mechanical properties, reflecting the fact that material within the nodes of a foam is usually “dead mass” that contributes little to load-bearing capacity, but are otherwise well-represented by the GA model [163].

A more important feature of the GA model is its prediction that application of a uniaxial stress to the foam (e.g., along the vertical direction in Fig. 1.3) results in deformation of the struts through bending, rather than uniaxial, modes. Such is the case, at least, when the aspect ratios of those struts are large enough; in the case of shorter, stouter struts, resistance to bending is increased and thus so is the importance of axial deformation modes. It is not difficult to see that, for a fixed pore size (determined by $l$ in Fig. 1.3), low aspect ratio struts favoring axial deformation correspond to high values of $t$, or high-density foams. The change in mechanical properties that comes with the transition between these limits underlies the distinction made earlier between low-density foam materials, which are dominated by bending, and more general porous materials, in which axial deformation is appreciable. As stated at that time, the distinction is somewhat arbitrary but is usually placed in the range of 30–50% relative density [64, 3].
Along these lines, it is also important to note that the effective strength and stiffness of a beam loaded transversely (in bending) are lower than its uniaxial strength and Young’s modulus [90], and therefore that the bending modes characteristic of stochastic foam materials are mass-inefficient. In order to circumvent this limitation, researchers have devoted substantial efforts towards the development of highly-regular (i.e., not stochastic, as are conventional metallic foams) structures in which local deformation is mostly, or entirely, axial. It has been shown [45] that achievement of fully-axial deformation in these lattice-block materials (LBM) is possible when their structures consist of nodes at which 12 or more struts meet. Such connectivity is, for topological reasons, impossible in conventional liquid-state foaming [194], and thus LBM must be cast using carefully-designed molds of the desired architecture. In addition, it will be shown in Chapter 2 that bending deformation is essential for the achievement of ductility in amorphous metal foams. Thus, despite their potential advantages for crystalline alloys, LBM structures made with amorphous metals were not investigated in this work.

1.1.3. Properties of Metallic Foams

Metallic foams have a number of unique non-structural properties that are difficult to obtain using other materials, for example fluid permeability and tortuosity, large specific surface area, acoustic damping, and controllable thermal and electrical conductivity [3]. These properties, though important to the broader field of metallic foams, are not considered here in depth, as the emphasis of this work is rather the development of novel structural metallic foams. For a broader discussion of non-structural applications, the reader is referred to the comprehensive discussion in Ashby et al. [3]

The structural properties of metallic foams are related to the unique shape of their stress-strain response, particularly in compression. This response, of which an example is given in Fig. 1.4, consists of three distinct regions: an initial, quasilinear loading region, an extended
Plateau region of constant or slightly-increasing flow stress, and finally a densification region of rapidly-increasing stress at high values of strain. The transition between the loading and Plateau regions is generally the result of the collective collapse of a plane of pores oriented roughly perpendicularly to the loading axis, known as a crush banding. Destabilization in the structure caused by such a crush band causes neighboring pore layers to collapse at nearly the same stress, and in this way the crush band expands during the Plateau region of the stress-strain curve until the entire gauge length has been consumed. At this point the porosity has been largely crushed out of the specimen, and formation of new contacts between features in the crushed foam leads to steeply-rising stress, leading to a gradual transition into densification.

The primary properties of interest in a compressive foam stress-strain curve are the stiffness $E$ and compressive strength $\sigma$. As stated in the previous section, these properties are related to those of the parent alloy (denoted by the subscript $s$) through simple scaling relationships involving relative density $\rho/\rho_s$. In the case of open-cell metallic foams, these relationships take
the form:

\begin{align}
E &= C_1 \cdot \left( \frac{\rho}{\rho_s} \right)^{n_1} \cdot E_s \\
\sigma_y &= C_2 \cdot \left( \frac{\rho}{\rho_s} \right)^{n_2} \cdot \sigma_{y,s}
\end{align}

and are known as the Gibson-Ashby or GA equations, as they are derived directly from consideration of the GA model (Fig. 1.3). In these equations, the parameters \(C_1, C_2, n_1,\) and \(n_2\) are fitting parameters. The prefactors \(C_1\) and \(C_2\) are related to the mass efficiency of the foam structure, and to the concentrations and severity of flaws, and are often called *knockdown factors*. Typical values of \(C_1\) and \(C_2\) from literature data are 1.0 and 0.3, respectively, but these are subject to very large variations [64, 3]. The scaling exponents \(n_1\) and \(n_2\) are more consistent between foams, and typically take the values 2 and 1.5, respectively [64, 3]. The corresponding equations for closed-cell foams are more complex, but empirical data often show only small differences between open- and closed-cell foams of equal relative density, due mostly to the flaws (e.g., perforations and wrinkles) present in the membranes of most closed-cell foams [64, 3]. A more significant assumption in Eqn. 1.1 and 1.2 is the assumption of bending deformation, i.e. of low relative density [63]. Deviations from the predictions of the equation result, particularly in the case of strength, in higher-density structures [64, 3].

At this point it is necessary to clarify the meaning of the term *stiffness* as applied to a metallic foam. In contrast to convention in solid materials testing, the slope of the initial loading region of a foam stress-strain curve (Fig. 1.4) is generally not taken to be its stiffness. This is because initial loading in foam materials nearly always involves reorientation of struts, and local microplasticity, and thus these slopes are not strictly linear but rather sublinear [3]. True linearity is achieved by unloading and reloading near the point of macroscopic yield, and these
values (usually significantly higher than the slope of initial loading, and more reproducible) are the preferred source of stiffness data [64, 3]. In this work, it was sometimes possible to collect reliable stiffness data from unload/reload cycles, but (due to small sample sizes, and proportionally small elastic displacements) not in every case. Thus the origin of stiffness values is given within each individual discussion.

For the same reasons of local microplasticity during loading, the strength of a metallic foam is not generally taken to be the load at which energy is first plastically dissipated. Rather, the strength of a foam (here and elsewhere) is taken to be the point of macroscopic yield, as determined by a significant change in slope of the stress-strain curve [3]. This value, which represents the transition between the loading and Plateau regions of the stress-strain curve, is also often called the Plateau stress, and is determined by the intercept of tangents drawn from these two regions. In cases where the transition is accompanied by a drop in stress, the maximum stress preceding the drop is taken to be the foam strength.

The mechanical properties of foams in tension are, by comparison with those described above, rarely of interest. This is because the pores within foam materials tend to act like cracks in tension, such that even foams made from ductile metals show poor ductility in tension, with the result that tensile loading of foams is almost entirely avoided (for this reason, mechanical properties throughout the rest of this work should be taken to imply compressive loading, unless otherwise noted) [64, 3]. Nonetheless, local tensile loading always occurs on one face of a component subjected to bending, which is an important deformation mode for many foam applications. The poor properties of foams in tension are, in these circumstances, usually mitigated by their incorporation into sandwich structures, in which a foam layer is bonded between two dense metal face sheets. These face sheets play several roles, including providing substrates for bonding and joining operations, prevention of fluid flow through the foam, and confinement and strengthening of the foam surfaces, where plasticity and tensile damage often initiate during
use [3]. These added benefits often lead to substantial improvements in foam properties with only a small penalty in overall material density [3, 128], and are therefore extremely important for the future development of foam applications. However, desire to understand the fundamental properties of the new foam structures discussed in this work, free of the complications of sandwich processing and the convolution of foam with face sheet properties, indicated that investigation of sandwich structures in this work would be premature.

1.1.4. Applications of Metallic Foams

The GA equations demonstrate that metallic foams have very high values of several figures of merit, e.g. $E^{1/2}/\rho$ and $\sigma^{3/2}/\rho$ (beam bending) or $E^{1/2}/\rho$ and $\sigma^{3/2}/\rho$ (panel flexure), that are used to gauge performance in weight-limited structural design [3]. As a result, the main set of applications for metallic foams is in structural materials, such as lightweight beams and panels, rotating disks, drums, and flywheels [3]. The structural application in which metallic foams most excel, however, is energy absorption. The ability of foams to plastically absorb extreme amounts of energy while minimizing transfer of stress (Fig. 1.4) makes them extremely efficient in packaging, impact and blast mitigation applications. In this capacity their efficiency rivals that of hollow tube structures, but unlike those structures, most metallic foams can absorb impacts from any direction [3].

The other main set of applications for metallic foams is in fluid management, where permeability and controllable pore size, combined with high tortuosity, allow for high-efficiency filtration. In addition, large internal surface areas allow rapid heat transfer with flowing fluids, making metallic foams efficient heat exchangers and flash arrestors. These internal surfaces additionally provide large substrate areas for catalysis or electrode applications [64, 3, 9].

One application which combines both structural and non-structural properties of metallic foams is orthopaedic biomaterials, e.g. bone replacement materials [139, 67, 48]. In this role,
the porosity of a foam not only serves to improve its bonding to surrounding tissue (for example, by ingrowth of bone cells throughout the material), but allows for matching of mechanical properties (most importantly, stiffness) between the foam and remaining bone. Matching of these properties minimizes the damage done by the implant on the surrounding tissue during use (an effect known as stress shielding) and the resulting complications, which include buildup of scar tissue and progressive implant loosening and failure [146].

1.2. Amorphous Metals

Pioneering work by Duwez and colleagues in the 1950’s [100] demonstrated that under certain experimental conditions, metallic alloys could be induced to form glassy or amorphous microstructures during solidification, distinguishing them fundamentally from all metals known at that time. This discovery gave birth to the field of metallic glasses, or amorphous metals, and since that time researchers have made vast improvements in the processing, characterization, industrialization, and fundamental understanding of these unique materials and their equally-unique properties. In the following sections, these improvements will be detailed, to the extent that they are relevant to the work presented in later chapters. For a larger perspective on the history and future of the field, the reader is referred to excellent reviews by Inoue [84], Schneider [164], Wang [192], and Loffler [119].

1.2.1. Glass Forming Ability

Amorphous materials, or those which lack long-range atomic order, have been known to man for thousands of years in the form of vitreous rock (e.g., obsidian), and later in the forms of glassy silicates (e.g., window glass) and polymers (e.g, polystyrenes). In 1960, Duwez and colleagues proved that amorphous structures were also possible in metals, by producing small amorphous specimens of Au$_{75}$Si$_{25}$ using special splat quenching techniques capable of producing cooling
rates on the order of $10^5$–$10^6 \degree C/s$ [100]. Although such extreme processing conditions rendered the glassy alloys impractical, this work demonstrated that glass formation in metals was possible, and initiated a wave of theoretical and experimental interest.

In 1974 these efforts culminated in the milestone discovery of a Pd-Cu-Si alloy which could be vitrified with a dimension of 1 mm, corresponding to a critical cooling rate (that is, a cooling rate which is sufficient to bypass crystallization of the alloy during solidification) on the order of $10^3 \degree C/s$ [24]. Although an alloy with this critical casting thickness would not raise attention today, one millimeter is often (perhaps arbitrarily) used as a criterion for delimiting the best glass-forming alloys, known today as bulk metallic glasses (BMG) [192]. Eight years after the discovery of this first BMG, castable dimensions had reached 10 mm, another milestone that placed metallic glasses within the cooling rate limitations of conventional casting methods such as copper mold casting and water quenching (10–100 $\degree C/s$) [192]. A great number of modern alloys, including Zr[141], Pd[86], Fe[171], Cu[41], Mg[123], and rare-earth-based[114] compositions, can now boast centimeter dimensions, while the best modern BMGs can be cast with dimensions of approximately 10 cm [84].

Although critical cooling rates and maximum castable diameters are not simple to measure experimentally, they remain the most general way of quantifying the glass-forming ability (GFA) of an alloy; thus a “good” glass-former may be defined simply as one which has large castable dimensions. However a second, more easily measured parameter is also used in quantifying GFA: the width of the temperature interval over which the alloy remains in the metastable supercooled liquid (SCL) state during reheating from a glassy state (i.e., the temperature interval over which the glassy phase persists before devitrifying, or crystallizing). The size of this temperature interval, defined as $\Delta T_x = T_x - T_g$, where $T_x$ is the characteristic crystallization temperature and $T_g$ is the glass transition temperature, is known as the thermal stability of the alloy. Thermal
stability is easily measured by heating the alloy at a constant rate and determining the temperature $T_x$ at which it crystallizes, by detection of the accompanying exotherm. Typical modern alloy have values of $\Delta T_x$ in the range of 40–80°C, though the highest reported value is around 135°C [192].

The precise value of $\Delta T$ depends on heating rate (as crystallization in amorphous metals is primarily a kinetically-limited process), and as such it is not a true material constant; nonetheless, it is often used on account of the simplicity of the associated measurement. It is also of practical relevance, however, because it defines the temperature and/or time window during which forming, joining, and other low-temperature processing (including foaming, as discussed later) of a glassy alloy can be accomplished without crystallization. Although thermal stability and more rigorous measures of GFA like critical cooling rate are not entirely unrelated, there exist many alloys in which one or the other is favorable, while the other is poor, and it is therefore customary to describe BMG alloys using both parameters [172].

With the profusion of new BMG alloys over the last two decades, a number of empirical rules have been established to help identify glass-forming compositions. The most familiar of these is the fact that nearly all glass-forming compositions are found at or near low-lying eutectic features in phase space, since at such compositions the temperature interval during which the alloy is both thermodynamically prone to crystallization and kinetically able to do so (between $T_{liq}$ to $T_g$) is smallest [84]. Several other empirical guidelines have also been established more recently, the most important of which are: (1) compositional complexity (i.e., three or more alloy components); (2) small or negative enthalpies of mixing among primary components; and (3) large (12% or more) differences in atomic radii among those components [173]. Details are available in Ref. [173] and [84], but briefly, the second criterion reflects thermodynamic resistance to phase separation, and is therefore related to the criterion regarding eutectic compositions. The first criterion reflects the fact that adding components to a homogeneous melt is believed
to destabilize the crystalline phases ordinarily favored by that melt, decreasing the difference in free energy between those phases and the liquid phase, and also to decrease the probability that random density fluctuations will produce critical nuclei of a stable crystalline phase. Variability in atomic radius, the third criterion, pushes alloys towards more complex lattice types, which are correspondingly more difficult to nucleate (and less prone to heterogeneous nucleation by contaminants with simpler crystalline structures). Differences in atomic radius also improve atomic packing density in the melt, increasing melt viscosity and retarding the atomic transport required for growth of the complex crystals. Experimental evidence confirms the efficiency of packing in molten glass-formers, as well as their high viscosity: equilibrium melt viscosities at the liquidus are roughly 1000 times greater in glass-forming alloys than in non-glass-forming alloys \[126\].

1.2.2. Processing of Amorphous Metals

Once a glass-forming composition has been identified, maximizing the likelihood of its retaining an amorphous structure on solidification from the melt implies, firstly, ensuring rapid solidification, and secondly, minimizing the number of nucleation sites available during solidification. The first of these is readily secured using processing methods like splat quenching, melt spinning, chilled copper mold casting, or water quenching. Though critical to glass formation, such steps add little to the complexity and cost of processing (at least, when modern alloys with low critical cooling rates are used). By contrast, the need for controlling the concentration and effectiveness of nucleants in the melt substantially increases both complexity and cost, and therefore dictates the most important components of amorphous metals processing.

The first potential source of nucleants in glass-forming melts is solid phases formed by accidental deviation from the ideal glass-forming composition. These phases are particularly harmful for amorphous metals because glass-forming eutectics are usually surrounded by steep liquidus
surfaces, implying rapid increases in $T_{\text{liq}}$ with slight deviations in composition. Deviations to the bulk composition of an alloy are, naturally, fairly easy to avoid; local fluctuations within the alloy have equally harmful effects, however, and are more difficult to control. Conventionally, these fluctuations are avoided by massively superheating the melt during initial alloying, to ensure complete homogenization. This is done using high-temperature alloying via arc melting or induction melting, where temperatures typically far exceed the thermodynamic melting point of the alloy. To further ensure homogeneity, alloyed ingots are also inverted and remelted several times. Even with such precautions, however, alloys containing refractory components such as Nb, Mo, or Ta can be extremely difficult to homogenize, and it is often necessary to first alloy the highest-melting components, and then add less refractory components in a second melting step. All glass-forming alloys in this work were produced using arc melting processes.

The second source of nucleants is foreign or contaminant phases. Massive contamination is usually easily avoided (albeit not without added expense) by using high-purity stock metals during the alloying process; typical purities (including those used for all the alloys in this work) are in the range of 99.5% or better, on a metals basis. More problematic are less concentrated contaminants that form highly refractory phases which precipitate very early during solidification, such as oxygen, carbon, boron, and nitrogen. Of these, oxygen is by far the most harmful: the literature consistently reports severe losses in GFA with oxygen concentrations as low as 10–100 atomic parts per million [116, 135, 14, 16, 117, 106], and loss in alloy toughness has been reported [39, 95] even in systems in which oxygen fails to cause devitrification.

Although the mechanisms by which oxygen degrades GFA are not universally understood, several potential mechanisms have been identified. The first of these is formation of oxide nuclei from one of the constituent elements in the alloy, which is problematic simply because these inclusions remain in the solid state even when the remainder of the alloy has melted, serving as sites for heterogeneous nucleation of crystalline phases immediately upon passing below the alloy
liquidus temperature [106]. It has also been suggested that oxygen alters short-range ordering patterns in the melt even where stable oxide particles are absent[16]. However it is evident that not all oxide inclusions lead to degraded GFA; the stable oxide-forming metals Gd[52], Sc[106, 89, 142], and Y[72, 201], for example, have in fact led to pronounced increases in GFA in glass-forming alloys. Evidence suggests that the high stability of Gd_{2}O_{3}, ScO_{3} and Y_{2}O_{3} allows these metals to scavenge oxygen from other atomic species in the melt, minimizing the amount of free oxygen available for formation of more harmful oxides. Evidently these more stable oxides, unlike whatever oxides form naturally (presumably ZrO_{2} in the case of Zr-based alloys [155]), are far less efficient as heterogeneous nucleation sites than those native oxides themselves.

Whatever the cause, it remains the case that avoiding devitrification through oxygen contamination requires, in addition to high-purity stock components, cost-intensive use of high vacuum equipment during alloying and all subsequent remelting (rare but notable examples exist in the form of air-castable Fe-based[122] and Mg-based[140] alloys). In light of the difficulty of ensuring both adequate cooling rate and alloy purity during any post-processing steps, it is customary to verify the amorphous state of a BMG alloy wherever it is used, even when the GFA of that alloy has been established by others. Detection of crystallinity in an amorphous metal is approached using two experimental techniques: x-ray diffraction (XRD) and differential scanning calorimetry (DSC). As XRD is a common technique throughout materials science, it is not necessary to belabor the details here; it suffices to say that, in the case of amorphous metals, lack of long-range order implies a broad continuous range in interatomic spacing that manifests as a diffuse diffraction halo rather than a set of distinct reflections. Detection of crystalline phases, whose scattered intensity is condensed into these comparatively sharp and easily-identified reflections, is consequently the primary goal of XRD analysis in amorphous metals.
Although XRD is, in crystalline materials, often used for phase identification as well, it is rare that crystalline reflections originating from partially-crystalline glass-forming alloys are indexed to this end. Rather, when phase identification is required, it is achieved by methods with higher spatial resolution, such as selected-area electron diffraction (SAD). There are several reasons for this. Firstly, the primary phases to form during devitrification of a glass-former often have similar interatomic spacings to the amorphous phase (since crystals with vastly different structures are, except in cases of extreme slow cooling, unable to form in measurable quantities), and thus their reflections are tightly grouped into the same angular range as the amorphous halo and proportionally difficult to resolve. Since these phases are usually metastable, they are also usually non-reproducible. Along similar lines, they can be strongly influenced by low-level impurities which are not known a priori. Finally, in those cases where equilibrium phases do have sufficient time to grow, these phases usually have complex structures that are proportionally difficult to index.

X-ray diffraction analysis of amorphous metal samples in this work was performed using Ni-filtered Cu-Kα x-radiation using an accelerating voltage of 40 kV and source current of 20 mA. Scans were performed between scattering angles (2θ) of 20–55°, in discrete steps of 0.05–0.1°, depending on the alloy under investigation, and were chosen to include only the primary amorphous halos of these alloys. While secondary amorphous features always exist at higher scattering angles, the poor scattering power of an amorphous phase requires, in order to achieve adequate signal to noise ratio within reasonable collection times, restriction of the angular range of the scan. This restriction is more pronounced in foam specimens because only a fraction of the illuminated surface is scattering in these cases, and thus count rates are lower in proportion to the specimen porosity.

The second major experimental method used with amorphous metals is differential scanning calorimetry (DSC). In this method, small specimens are heated at a constant temperature rate,
and the heat flux required to effect this heating rate in the specimen is compared to the flux required to heat a standard of known heat capacity and with known phase transitions (in all cases, the standard used here was an empty aluminum pan of the sort used to contain the specimen itself). Any phase transformations in the specimen (in the case of amorphous metals, this includes an endothermic glass transition and one or more exothermic crystallization events) lead to departure between the fluxes into the specimen and standard at the corresponding transition temperature [70].

In this work, DSC was performed using specimens with masses of ca. 15 mg and heating rates not exceeding 0.33°C/s. In experiments with maximum temperatures above 400°C, specimens were sealed into aluminum pans under a cover of argon cover gas using a glove bag; lower-temperature experiments were performed on specimens sealed under ambient conditions. No significant chemical reactions (e.g., oxidation, vaporization, or interdiffusion with the aluminum specimen pans) were visible by eye in any specimen after testing. Transition temperatures were defined by the intercept of tangents drawn from the baseline and the leading edge of the transition feature; this is accepted practice, as the onset temperature is less sensitive to artifacts from heating rate and thermal lag than is the peak transition temperature [70]. Quantitative measurement of heats of transformation was achieved by subtraction of a sigmoidal baseline from the differential calorimetric signature (i.e. the flux representing the specimen alone, the aluminum pan being already compensated for by way of the standard), followed by integration of the baseline-subtracted data.

1.2.3. Properties of Amorphous Metals

The properties of amorphous metals which have sparked the greatest industrial interest fall into two classes: magnetic properties and mechanical properties. Exploitation of the former set of
properties far preceded the latter, with Fe-based amorphous metals finding use as magnetic materials as early as the late-1970’s, and with active development still ongoing [75]. Throughout most of this period, however, penetration of amorphous metals into broader, non-magnetic applications has been hindered by the dimensional limitations associated with high critical cooling rates. Only with the advent of bulk glass formers in the last two decades have amorphous metals found significant use as structural materials. The following subsections describe the properties of amorphous metals that recommend them for use as such.

1.2.3.1. Processing Temperatures. Among the principal advantages of amorphous metals are the low liquidus temperatures associated with their near-eutectic compositions, which help mitigate the costs associated with high-purity stocks and vacuum processing. Liquidus temperatures vary widely among different compositions, and often are not even explicitly measured (due, invariably, to greater experimental interest in the glass formation and characteristic crystallization temperatures); however, an informal survey of literature reveals liquidus temperatures in the range of 400–1000°C. In practice, however, the presence of refractory impurity components (e.g., oxides) increases effective liquidus temperatures for most alloys, requiring that processing temperatures as much as 100°C above the nominal alloy liquidus be used in order to avoid deterioration of GFA [134].

In addition to stable melt processing above the liquidus, amorphous metals may be processed over limited time intervals (as much as 30 minutes for the best glass formers [165]) in the SCL region between $T_g$ and $T_x$. Along with further reductions in processing temperatures and costs, processing in the SCL state effectively bypasses cooling rate limitations by maintaining processing temperatures close to the glass transition. SCL processing also allows techniques developed for shaping or blowing of viscous glassy silicates and polymers to be applied to metals.
Supercooled liquid forming of Ce-based BMG, for example, has already been demonstrated below 100°C [206].

On the other hand, low transition temperatures also limit the maximum operating temperatures of amorphous metals. At temperatures above the glass transition, amorphous metals undergo embrittling structural relaxations and devitrification. Devitrification, in particular, usually involves formation of brittle intermetallic phases that drastically reduce the strength and toughness of the alloy [109, 84, 164, 87, 192, 119], and consequently catastrophic failure of a load-bearing amorphous metal component would be the likely result of an accidental temperature excursion above the glass-transition.

1.2.3.2. Mechanical Properties. Lack of crystalline order in amorphous metals implies the absence of dislocation plasticity, and consequently the absence of any plastic flow mechanism active far below the theoretical strength. Without such a mechanism, amorphous metals enjoy extremely high compressive strengths, generally in the range of 800 to 5000 MPa, with lanthanide and Mg-based alloys falling in the lower portion of this range (800–1200 MPa), Zr- and Pd-based alloys in the middle (1500–2000 MPa), and Cu- and Co-based alloys achieving the highest strengths (as much as 5000 MPa or more) [84, 164, 87, 192, 119].

Lack of dislocation plasticity also applies, in principle, to tensile strength, although the difficulty of machining tensile specimens from most amorphous metals makes such measurements rare, and insufficient data exist to classify tensile strengths with the same certainty. What little data exist support the notion that tensile strengths in amorphous metals are lower than compressive strengths by approximately 20–30% [121]. The nature of this asymmetry is in need of further study, due to the fact that high ductility is possible in amorphous metals during bending deformation (discussed in the next chapter), a mode in which strength is limited by tensile, rather than compressive, uniaxial strength.
Because most glass-forming alloys are heavily alloyed with lighter elements such as metalloids or aluminum, their densities are usually modest in comparison with crystalline alloys of comparable strength \[84\]. This fact has been quantified by Loffler \[119\], who found an average specific strength around 350 MPa·cm\(^3\)/g for amorphous alloys, versus 150 MPa·cm\(^3\)/g for crystalline alloys. It should be noted, however, that the lack of strong glass formers based on aluminum, and the necessity to heavily alloy Mg-based amorphous metals, also implies that the range of densities offered by amorphous metals is more restricted than the range offered by crystalline alloys. The nominally-Mg-based alloy described in Chapter 5, to give one example, has a density roughly 2.5 times greater than that of pure magnesium.

The elastic moduli of amorphous metals, on the other hand, do not benefit from the absence of dislocations, but rather suffer (in comparison to crystalline alloys based on close-packed structures like FCC and HCP lattices) from the openness of amorphous atomic structures (see Ref. \[191\] and the references therein). Thus crystalline metals usually show \(E/\sigma_y = 500–10,000\), while amorphous metals show only \(E/\sigma_y = 50\) \[191\]. In absolute terms, commercial alloys in the Zr-Ti-Cu-Ni-Al and Zr-Nb-Cu-Ni-Al systems, representative of a large number of BMG alloys, have moduli in the range of 80–100 GPa \[193\]. The highest reported Young’s modulus appears to belong to a Co-based alloy, and takes the value 268 GPa \[87\]; the lowest reported modulus is 31 GPa, measured in a Ce-based alloy \[206\].

The unique combination of high strength with low modulus in amorphous metals leads to abnormally high elastic strains around 1.5–2.5%. Indeed, it was this combination of properties which led to the first significant commercial development of BMGs for use in golf club heads, where elastic energy storage dramatically improves club performance, as well as in springs and actuators \[4\]. While other such applications exist, for example biomedical applications where stiffness matching between implant materials and host tissue is needed \[67\], low stiffness may be considered a drawback for most structural applications.
In addition to imparting high strength, lack of dislocation plasticity affects amorphous metals in the same manner as crystalline ceramics and intermetallics; namely, through severe loss in ductility. The only known mechanism of plasticity in amorphous metals is adiabatic shear banding. The process of shear banding is not perfectly understood; however, it is believed that shear bands nucleate during loading at regions of excess free volume in the structure (of which there are usually many, due to the highly nonequilibrium processing of amorphous metals) [196]. Local shear strains within these bands may be on the order of unity, and sufficient energy can be dissipated during unrestricted propagation of a band that local temperatures may soften or even melt the alloy [110]. In unconstrained loading geometries, however, macroscopic failure results from motion of a single shear band across the entire specimen, such that macroscopic plastic strains remain very small (typically less than 0.5% in compression, and less in tension), and despite large local plasticity the alloys appear brittle on large scales [119].

To circumvent this characteristic brittleness, researchers have developed a small number of glass-forming alloys that do exhibit ductility in uniaxial compression. In 2004, Schroers and Johnson [165] reported a Pt-based composition with a large compressive plastic strain of 20% and a fracture toughness of 80 MPa√m. The physical basis of this ductility is not certain, as this alloy is unique in the literature, but the authors suggested that the high Poisson’s ratio of the alloy (0.42) favors extension of shear bands under applied stress rather than initiation of cracks from those bands. Most of the remaining “ductile glasses” are actually not completely amorphous. In 2005, for example, Das et al. demonstrated that 8% failure strain was possible in a binary Zr50Cu50 alloy consisting of a glassy phase with dispersed nanocrystals, and an impressive 18% in ternary Cu47.5Zr47.5Al5, which was nominally amorphous but showed evidence of nanometer-scale inhomogeneity [43].

In an attempt to address the lack of ductility in the remaining alloys (which constitute the vast majority), researchers have extensively investigated amorphous metal matrix composites
(AMMC). All composite approaches share a basic line of reasoning: if poor ductility in monolithic alloys is the result of free propagation of shear bands across macroscopic distances, then enhanced ductility must result from obstacles which impede the motion of shear bands, and thus induce branching or multiplication (analogously to precipitation and forest hardening in crystalline metals) [111]. The presence of obstacles such as second-phase inclusions also frustrates shear band motion by creating complex, multiaxial local stress states which favor bending of shear band paths [187], and which may even direct shear bands towards inclusions, by which they are interrupted [28].

Investigations of AMMC fall broadly into three categories: nano- and quasicrystalline reinforced amorphous metals, in-situ composites, and ex-situ composites. Briefly, it may be said that while the first method works very well in certain alloys[105], it is not universally applicable, and nanocrystallization of certain amorphous metals leads to catastrophic loss of strength and toughness. In-situ composites, by which is usually meant amorphous matrices containing large volume fractions (often 70 vol.% or more) of dendritic BCC metals precipitated directly from the uniform melt during alloying, show highly-increased failure strains, but are locally inhomogeneous and subject to large property variation as a result of the strong cooling-rate dependencies of the dendritic reinforcing phase[42]. In some cases (particularly Ta in Zr-based alloys[51, 77]) the precipitated reinforcement is not dendritic, but rather particulate in nature, which allows greater regularity in properties, but these alloys have not been extensively studied. The third approach, mimicking the methods of crystalline MMC processing, requires an extra processing step to introduce reinforcement, and is therefore more costly than the first two. However these methods offer the greatest flexibility in choice of reinforcement composition and structure, as well as the most reproducible properties.
1.2.3.3. Corrosion Resistance. Another property of amorphous metals that can be easily understood by comparison with their crystalline counterparts is high corrosion resistance. The corrosion resistance of amorphous metals arises primarily from their lack of such crystalline defects, such as grain boundaries, dislocation steps, or interphase boundaries, as are usually responsible for initiation of corrosion in crystalline materials [84]. In part, it also arises from the tendency of amorphous metal surfaces to form passivating amorphous oxides, which have low electrical conductivity, and to the disproportionate quantities of noble metals found in many glass formers [143, 130].

Despite these apparent advantages, several important points should be noted, especially in light of the prominence of BMG corrosion in subsequent discussions. The corrosion resistance attributed to BMG by virtue of their microstructural homogeneity is often overstated; in practice, amorphous alloys always contain some crystalline inclusions resulting from impurities. These inclusions increase the susceptibility of the BMG to pitting, and pits can often grow rapidly after initiation due to the highly-active nature of metastable amorphous phases [56, 132]. This situation grows worse when the fraction of crystalline inclusions is high, as in AMMC. In these materials, galvanic interactions can lead to catastrophic dissolution of the glassy matrix, attended by excavation of the reinforcing phase [57]. Finally, it must be remembered that a favorable comparison between corrosion resistance in amorphous metals and crystalline alloys of similar composition (which is often the topic of investigation [60, 59]) does not imply equally-favorable comparison against all relevant crystalline alloys. Comprehensive comparisons between amorphous alloys and competing corrosion-resistance engineering alloys have, for the most part, not yet been made.
1.3. Next-Generation Metallic Foams

The discussion in Section 1.1 illustrates both the advantages and disadvantages of current metallic foam technology. Examination of the GA equations clearly reveals one of these disadvantages; namely, that the strength and stiffness of metallic foams (and by extension, many of their key figures of merit) are limited fundamentally by the corresponding properties of the base alloys from which they are made. Given that the majority of metallic foam research has focused on aluminum foams, it follows that the majority of available metallic foams are subject to the limitations imposed by the relatively low strength and stiffness of aluminum alloys. This limitation is not unknown to the research community, and efforts to bypass those limitations using stronger, stiffer base alloys have already been described. However, these efforts are themselves limited by the fact that improved mechanical properties in these alloys are realized only at the cost of processing difficulties associated with the high melting points and, in many cases, high chemical reactivities of these more refractory metals. As a result, foam processing research has been consistently faced with compromises between maximizing mechanical performance (which favors high-melting alloys) and simplifying processing (which favors low-melting alloys).

The work presented in the next four chapters introduces a potential solution to this impasse, namely, substitution of amorphous alloys for the crystalline alloys to which this unfavorable compromise applies. The underlying motivation for such a substitution can be found in Section 1.2; amorphous alloys enjoy strengths superior to those of low-melting crystalline metals (indeed, superior to those of all crystalline metals, if the strongest amorphous metals are included) while retaining melting points well below those of the stronger, stiffer crystalline metals. The major difficulty in implementing this solution is uncertainty that, in light of the poor ductility of amorphous metals in uniaxial loading, an amorphous metal foam could ever take advantage of its high strength and low melting point without suffering from brittleness of the sort that would exclude it from many key applications. A detailed discussion of the issue of ductility
in amorphous metal foams is deferred until the next chapter, but it suffices here to state that there are several reasons to expect a favorable outcome when substituting amorphous alloys for conventional crystalline ones.

It must be emphasized from the outset that no claim is being made here that amorphous metal foams, in their current state, rival or surpass crystalline metallic foams as structural materials, or that they present an immediate solution to the processing-property tradeoff just described. Such claims would clearly be premature. Rather, the goal of this work is to demonstrate, at an introductory level, the potential for future amorphous metal foams to make such a claim. The substantial progress which would be required to make use of this potential is a topic deferred until all the relevant results have been presented.

In the shorter term, processing-property compromises in crystalline metal foams can also be addressed through optimization of the mechanical properties of currently available crystalline metal foams. There are, naturally, many different approaches that could be taken to this end, most of which lie outside the scope of this work. In the spirit of exploring novel ideas for next-generation metallic foams, however, one optimization method was considered here. The underlying motivation comes from natural cellular materials such as wood and bone, which differ from their artificial counterparts by virtue of having strong gradients in local density \[64, 175\]. Historically, the desire for improved control over structure, as a means of improving the reliability of foam materials in service, has driven research efforts towards minimizing local density gradients, rather than exploiting them [3]. Only recently, with the success of these efforts, has attention returned to the potential benefits of local density gradients like those appearing in optimized, naturally-evolved foam structures.

Close examination of the literature reveals several aspects of foam performance that could be improved through intelligent exploitation of structural gradients, and specifically of gradients in local density (as this is the parameter by which local foam properties are most easily varied).
Some of these areas are essentially non-structural, for example heat transfer [182] and electrode efficiency [177, 174]. Others are primarily structural in nature, such as ease of assembly (for example, during fabrication of sandwich components where foam materials must be bonded or fixed to solid materials with very dissimilar properties) and overall mass efficiency (i.e. the achievement of a design specification using a foam component of lowest possible mass) [44, 147, 34]. Using a finite element method to optimize the mechanical response of structural foam components under simple loading conditions, Daxner et al. [44] demonstrated the utility of density gradients in both these respects; optimized density distributions near features such as bolt-holes, and in simple structural environments such as central loading of panels, were found to be highly nonuniform. In a separate corroborating study, Conde et al.[34] predicted a 15% savings in the overall weight of a density-graded, yield-limited sandwich beam in bending, relative to a uniform-density sandwich capable of supporting the same load.

A number of processing approaches have already been created or modified to allow production of density-graded porous materials which may take advantage of this potential. Some of these methods were ostensibly developed for functionally-graded MMC, but include as intermediate steps the production of density-graded ceramic foams [40, 88]. Other methods were developed directly for processing of graded porous ceramics, without a metallic matrix [31, 97, 120, 113, 205]. These ceramics-oriented methods generally, however, include processing steps that are not easily extended to metals, and literature pertaining directly to density-graded metallic foams is therefore comparatively sparse.

Of the methods designed to introduce density gradients in porous metals, only a few are suited specifically to lower-density foam architectures; these latter have been demonstrated in Cu [182, 136], Ni [177], Mg [6], and Al-based [147] metallic foams. Of these, the only experimental study of the impact of density gradients on metallic foam mechanical properties
was performed by the Mortensen group using graded, salt-replicated Al foam sandwich structures [147, 34]. A notable feature of this method, and of graded metallic foaming methods in general, is the production of stepwise or discontinuous density gradients. Processing of such “layered” foam structures enjoys the advantage of simplicity, as each individual layer has uniform density and can therefore be processed using well-established foaming methods. However it is also likely that discontinuities in material density at the interfaces between layers will entail higher flaw densities and/or property incompatibilities. The problem of property discontinuity in layered structures is particularly acute in foam materials, since the mechanical properties of foams scale strongly with density (see Section 1.1.3). For these reasons, it is suggested here that optimal density-graded foam structures will have continuous, rather than stepwise, density gradients. The last two chapters describe methods for achieving such structures using aluminum.
CHAPTER 2

Amorphous Metal Foams

This chapter serves as an introduction to the newly-developed field of amorphous metallic foams (AMF), in which the two distinct material classes introduced in Chapter 1 are combined in a way that helps to mitigate the shortcomings of each individual class. The mechanisms by which these shortcomings are addressed through AMF will be made explicit in the discussion which follows, and the state of the art in the field, nascent as it is, will be reviewed here in its entirety to demonstrate the effectiveness of their synergy.

It is important to remember throughout the subsequent discussion that the work presented in later chapters was conducted currently with, and independently from, the work being discussed here; thus, the limitations and questions raised by the discussion below, clear as they may have become in retrospect, were not always so when the work in later chapters was actually being performed. Accordingly, some of those limitations will not be addressed, and some questions will go unanswered, throughout the remaining chapters. The most important of these, however, will be revisited in the discussion of future work in Chapter 8.

2.1. Motivation

The clearest motivation for study of amorphous metals in foam architectures is the possibility of expanding the range of mechanical properties available to materials engineers in applications favoring use of metallic foams. Of the mechanical properties of amorphous metals discussed in Section 1.2.3, the two that offer the greatest potential in this capacity are high specific strength and high strength/stiffness ratio.
Specific strength dictates performance in specific-strength-limited structural design, e.g., in static beams, columns or plates, rotating disks (flywheels), shells (pressure vessels) and rotating drums (centrifuges) [3]. Rearranging the empirical relationship between foam and solid strength (Eqn. 1.2) shows that the specific strength of a foam is directly proportional to that of the base alloy; thus, the high specific strength of amorphous metals (roughly twice that of crystalline alloys, as discussed in Section 1.2.3) recommends them strongly for use in these applications.

High strength/stiffness ratio (i.e. high elastic strain) dictates performance in a smaller, but not less important, set of applications such as elastic hinges and compression gaskets [3]. Combining the GA equations (Eqn. 1.1 and 1.2) shows that the strength/stiffness ratio of a foam material is proportional to \((\frac{\sigma_s}{E_s}) \cdot \left(\frac{\rho}{\rho_s}\right)^{-1/2}\). Thus, at a given relative density, the high strength to stiffness ratio of amorphous metals favors them for these applications as well; at a given absolute density, however, only AMF made from the lowest-density amorphous metals are likely to compete with available crystalline foams in this regard.

Perhaps the most exciting structural applications for AMF, however, are in mechanical energy absorption (e.g., packaging or armor materials). The mechanical energy absorbed prior to densification, per unit volume of foam, is given by the area under its stress strain curve, or approximately \(\sigma_y \cdot \epsilon_d\), where \(\epsilon_d\) is the densification strain (Fig. 1.4). Accordingly, the high specific strength of AMF would allow them, assuming stress-strain behavior similar to other foam materials, unprecedented potential for blast and impact mitigation. This potential would, however, apply mostly towards the protection of stronger objects, as higher strength (for a foam of prescribed area) implies higher load transfer; thus, AMF would be most appropriate for the protection of vehicles and structures, which can safely sustain higher loads, rather than the protection of more delicate objects such as human beings. For these applications, polymer and aluminum foams are usually needed.
Another application envisioned for AMF is in orthopaedic biomaterials, for example bone replacements, where open-cell AMF may compete with the Ti-based foams currently in use [139, 48]. Though the supporting literature is less complete for amorphous metals than for titanium and other well-established biomedical alloys, several reports show promising wear and corrosion properties for amorphous metals in simulated biological fluids, two of the key requirements of biocompatibility [81, 82, 130]. Also, most amorphous metals are nonmagnetic, facilitating post-operative imaging and evaluation as compared to modern Fe- and Co-based prosthetic implants. The high strength of AMF would allow smaller, less intrusive implants, while comparatively modest elastic moduli would allow porous implant stiffness to be more easily matched to that of the host bone tissues. Stiffness matching is considered an essential part of alleviating “stress-shielding” complications in bone replacements [146].

In all these applications, it must be reiterated that the benefits offered by amorphous metals are not purely mechanical in nature, but also (in principle, though reductions in material cost and contamination sensitivity are still required) processing related. The clearest advantages of AMF, in other words, should present themselves in applications whose requirements not only exceed the capacity of low-melting crystalline foams, but specifically those for which the complexity of solid- or vapor-state processing used with high-melting crystalline alloys (or the foam structures produced by such processes) is undesirable. Replacement of crystalline metal foams by AMF can also offer the additional benefits of amorphous metals described in Section 1.2.3, such as wear [66] and corrosion [84] resistance, or unique magnetic properties, which may be hard to achieve with current technology. These properties, in particular, might recommend AMF for multifunctional foam applications such as heat exchangers, catalyst supports, or fluid filters.

Realizing the potential of AMF in nearly all the applications proposed here, however, requires that the general shape of the AMF stress-strain curve be similar to that of ductile crystalline metals, i.e. it requires compressive ductility on par with ductile crystalline metal foams. That
such ductility could exist in AMF, in light of the characteristic brittleness of amorphous metals, was not obvious at the outset of this work. This crucial topic, which has since been given both theoretical and experimental investigation, is the subject of the next section.

2.2. Origins of Compressive Ductility in Amorphous Metal Foams

Compressive ductility is a critical property of metallic foams in nearly every application, particularly those requiring energy absorption. Tensile ductility, though clearly advantageous as well, is less critical because pores in a foam material tend to act as cracks, and thus the tensile ductility of foams (even those made from ductile crystalline metals) is usually poor [3]. Outside of applications involving bending, where limited tensile ductility is easily mitigated by the presence of a solid facesheet with high tensile ductility, foams are rarely subjected to tensile loads.

Were amorphous metal foams to show as poor compressive ductility as their monolithic counterparts, their high processing cost would therefore render them inferior to crystalline foams; consequently, investigation into foaming of amorphous metals is ill-founded unless one or more mechanisms can be identified which might impart improved compressive ductility for amorphous metals in foam architectures. Review of the extensive literature treating ductility in amorphous metals supports the existence of at least two such mechanisms.

The first of these mechanisms arises from the structural similarities between AMF and particulate-reinforced AMMC, the compressive ductility of which has been firmly established in the literature (see Section 1.2.3). The toughening mechanisms active in AMMC should, for the most part, also be active in “gas-reinforced” composites, i.e. foams; stress concentrations still exist at the surfaces of pores, and shear bands cannot propagate directly through a pore. The only expected difference is the lack of favorable thermal mismatch stresses surrounding pores, as these stresses are only produced when a reinforcing particle has a different coefficient of thermal
expansion than the matrix and can induce a residual stress field around itself [28]. Nonetheless, in certain cases (for example, solidification of the alloy around solid pore formers, which forms the basis of Chapters 3, 4, and 5), even this mechanism may remain active in foam architectures.

The effectiveness of composite-type toughening in amorphous metals has been dramatically demonstrated by Wada et al. [188]. In this work, the authors prepared Pd-based amorphous metals with up to 4 vol.% of finely-dispersed 20–30 µm pores, and showed that even this small amount of porosity was sufficient to induce 18% plastic strain to failure in uniaxial compression (compared to 0% plastic strain in the monolithic alloy). Composite-type toughening is also believed responsible for the plasticity seen in high-density porous amorphous metals produced by the same researchers, where compressive failure strains were still higher [187, 190, 189]. These materials will be described in detail below.

Not all results support the proposition that small levels of porosity generate ductility, however. For instance, an amorphous Zr-based BMG of comparable porosity (4.7%) produced by spark-plasma sintering of powder compacts showed <2% plastic strain to failure in compression [198]. Porous powder-consolidated Zr-based BMG containing ZrN particles and 2% residual porosity also failed to exhibit composite toughening [74], enjoying less than a 1% improvement in ductility (at comparable porosity the Pd-based alloy in the previous study [188] showed about 10% plastic strain).

These reports certainly indicate that low levels of porosity do not automatically result in plasticity. Nonetheless, they share an important feature which distinguishes them from the materials studied by the Inoue group; specifically, they were powder processed rather than cast. It could be suggested, therefore, that the ductility that should have resulted from composite effects was offset in these powder-processed alloys by brittleness associated with retained oxide at the original powder interfaces, which has proven problematic in other studies of powder-processed BMG [92].
In addition to composite toughening, there exists a second mechanism by which porosity could induce plasticity in an amorphous metal foam. Though this mechanism was not well understood until recently, its effects were reflected in studies throughout the mid-1990’s (for a comprehensive list of examples, see the references in Conner et al. [37] and Ravichandran and Molinari [154]). In these studies, amorphous wires and ribbons (the largest amorphous metal components readily available at the time) were shown to be highly ductile in bending. Many of these studies reported that amorphous metal wires and ribbons could be pinched back onto themselves without fracture.

As the focus of research at that time was on increasing the thickness of these components, the loss of this bending ductility in thicker sections (e.g., plates or rods) was not carefully considered until recently. In 2003, Conner et al. compiled data for bending ductility in Zr-based BMG wires and ribbons and quantified its relationship to sample thickness [37]. As shown in Fig. 2.1, reproduced from this work, surface strains at failure can exceed 100% in sub-millimeter specimens of Zr-based BMG. By combining simple beam bending theory and fracture mechanics arguments, the authors rationalized this relationship and reproduced the effect in numerical simulations [37, 38].

The essential arguments involved in their explanation are as follows. For a beam made of an elastic-perfectly plastic material (an appropriate model for BMG containing stable shear bands [203, 202, 37]) deformed in simple bending, balance of moments within the beam cross-section requires that the ratio of the depth of the plastic zone (the region in which local strain exceeds the elastic limit) to the total beam thickness is constant, at any particular curvature. Consequently, for a given curvature a thinner beam has, in absolute terms, a smaller plastic depth. Treating shear bands spanning this plastic depth as cracks, fracture mechanics arguments show that the shear offsets produced at the specimen surface by shorter cracks are smaller, and thus that the likelihood of fracture initiation at the shear offsets in a thinner specimen is also
smaller. This leads, naturally, to increased bending ductility. In addition, the strain energy relaxed by propagation of shorter shear bands is lower, and thus the size of the nearby region which is unloaded by each shear band is also smaller. Consequently, additional shear bands can initiate and propagate closer to the first, and in this way the density of shear bands, and the resulting ductility, are increased as well.

The relevance of stable shear banding to ductility in AMF arises from the close structural similarity of the long, slender struts within many foams (see, for example, Gibson and Ashby’s model foam in Fig. 1.3) and wires of the sort studied by Conner et al. It has already been stated that, given sufficiently low relative density, the struts in such a structure can be made sufficiently slender that they deform locally by bending, even when the applied stress is uniaxial and compressive. The clear implication of this, namely that the struts in a low-density AMF should benefit from stable shear banding processes in addition to composite toughening, was not lost on those who studied the mechanism. It was they who first suggested that this mechanism
should prove effective in ductilizing amorphous metal struts in foams [37], although by that point the study of AMF processing was already underway, both here and elsewhere.

### 2.3. The State of the Art

Before either mechanism of plasticity in AMF had been envisioned, the search for AMF processing methods had already been initiated by Apfel and Qiu, who proposed foaming amorphous metals using an approach they developed and demonstrated with glassy polymers [150]. In their method, porosity is generated by explosive vaporization during pressure-quenching of glass-forming polymer melts mixed with insoluble, nonreactive, volatile foaming agents. The rapid cooling needed to suppress crystallization of the melt was accomplished naturally as the latent heat of evaporation of the volatile agent was extracted from the melt.

Unfortunately, the method proposed by Apfel and Qiu was never demonstrated in a metallic glass-former, most likely because it is unclear that suitable nonreactive and volatile agents exist for contamination-sensitive amorphous metals. The first successful method was reported in 2003 by the Johnson group in California [168], nearly a decade after the proposal of Apfel and Qiu and almost simultaneously with the work of Conner et al. [37] This method is based on expansion of water vapor bubbles formed during decomposition of hydrated B$_2$O$_3$ flux particles in a Pd$_{45}$Cu$_{27}$Ni$_{10}$P$_{20}$ melt [168]. Reported densities were as low as 1.4 g/cm$^3$ ($\rho/\rho_s = 16\%$), with closed pores sizes of 200–1,000 µm size. This process was modified a year later, such that only a small fraction (15 vol.%) of small pores (75 µm) was introduced at high temperature, while expansion to pore sizes and fractions comparable to the simpler method was accomplished in a second step at lower temperature [167].

A similar alloy, Pd$_{42.5}$Cu$_{30}$Ni$_{7.5}$P$_{20}$, was also foamed in 2003 by the Inoue group in Japan, who quenched mixtures of the glass-forming melt and NaCl granules, and then dissolved the NaCl placeholder in water [186]. Using this latter method, densities as low as 3.3 g/cm$^3$ ($\rho/\rho_s$
were produced, with open cells about 125–250 µm in size. In 2004, the same group reported an additional method for foaming Pd-based amorphous alloys, in which hydrogen gas is dissolved into the melt at high pressure and then precipitated and trapped as bubbles during simultaneous pressure and temperature quenching [187], an approach reminiscent of hydrogen-metal eutectic methods used to produce “gasar” or “lotus-type” foam structures in crystalline metals [170]. Using this new method, densities of 3.4 g/cm³ (ρ/ρₘ = 36%) were achieved, with closed pores averaging 200 µm in size. In later studies, this method was extended to lower relative densities (ρ/ρₘ = 29%) and pore sizes (80 µm and below) [190, 189]. Images illustrating the structure of all these foams are shown in Fig. 2.2a-d.

All of these reports utilized Pd-based compositions with superior GFA and high resistance to contamination (due to nonreactive, noble components), but also high density (9.4 g/cm³ [188]) and extremely high cost. However, AMF have also been produced from commercial Zr-based amorphous metals with greater applications potential. The majority of published work in Zr-based AMF comes from the research described in subsequent chapters, which was published between 2004 and 2006. However, at least two other groups have since reported AMF processing using similar alloys (it is notable that, given the standard definition of a foam material given in Chapter 1, both these materials are more properly defined as porous amorphous metals; however for completeness, and to facilitate later analysis, all porous amorphous metals are included in this discussion). In the first of these reports, published in 2004, pores with 250 µm mean size were dispersed into Zr₅₈.₅Nb₂₈Cu₁₄.₆Ni₁₂.₈Al₁₀.₃ by entrainment of gas into the melt during rapid convection. No evidence was provided of porosities exceeding 10% (ρ/ρₘ = 90%) [167], however. In a later study from 2006, molten Zr₄₁.₂₅Ti₁₃.₇₅Cu₁₂.₅Ni₁₀Be₂₂.₅ was pressure infiltrated into NaCl particles using a two-zone U-turn infiltration design [156]. The density of the resulting AMF was much lower than in the previous case, 3.6 g/cm³ (ρ/ρₘ = 64%), but pore sizes were
Figure 2.2. Porous amorphous metals developed by other researchers, using liquid-state foaming methods. (a) Pd-based foam made using a gas-generating flux additive ($\rho/\rho_s = 24\%$) [168]. (b) Pd-based foam made by entrapping gas in the melt and then expanding it in the supercooled-liquid state ($\rho/\rho_s = 15\%$) [167]. (c) Pd-based foam made by casting into a bed of soluble NaCl particles ($\rho/\rho_s = 35\%$) [186]. (d) Pd-based foam made by precipitation of dissolved hydrogen gas during cooling. The relative density of this foam was not listed, but is likely to lie in the range $\rho/\rho_s = 54$–$58\%$ [187]. (e) Porous Zr-based BMG made by entrainment of inert gas in a rapidly-stirred melt ($\rho/\rho_s = 90\%$) [167]. (f) Zr-based foam made by casting into a bed of leachable NaCl granules ($\rho/\rho_s = 64\%$) [156].
much larger (pore size was reported to be 500–800 µm, though the published image, Fig. 2.2f suggest a larger size). Images of these two structures are provided in Fig. 2.2e,f.

The AMF described above were produced, in part or entirely, using liquid-state foaming methods. More recently, solid-state processing of AMF has also been achieved. The basic approach underlying these methods was first proposed by Gebert et al. in 2004 [58], and consists of selective chemical dissolution of one phase from a two-phase composite (in the original proposal, dissolution of La-rich phases from a matrix of amorphous Zr-based matrix). This approach is essentially an extension to amorphous metals of processes pioneered by the Roesler group in production of Ni and nickel aluminide foams from Ni-based superalloys [158, 159], or of the more general approach of selective dealloying used in processing of nanoporous metals [49]. It has already been implemented twice in 2006 by Lee and Sordelet at Ames Laboratories, once in the production of porous Cu-based BMG ($\rho = 3.4$ g/cm$^3$ or 25%, pore sizes from <100 nm to about 2 µm) through dissolution of elemental Cu from warm-extruded powder blends [107], and once in production of Ni-based BMG ($\rho = 4.6$ g/cm$^3$ or 58%, with elongated pores about 200 µm in length) by removal of brass from similar blends [108]. Images showing the structure of these foams are shown in Fig. 2.3a,b.

Two additional reports of porous powder-processed BMG have been made in 2006 by the Inoue group. In one report, Hasegawa et al. [74] studied the effects of small amounts of porosity (ca. 2%) retained in melt-spun ribbons made from powder compacts of Zr-based BMG and aluminum nitride, the results of which were already described above. In the second, powders of Zr$_{55}$Cu$_{30}$Al$_{10}$Ni$_5$ are partially consolidated by spark plasma sintering, leaving residual porosity between 5 and 67 vol.% [198]. Images showing the structure of these porous BMG are also included in Fig. 2.3c,d.
Figure 2.3. Porous amorphous metals developed by other researchers, using solid-state foaming methods. (a) Cu-based foam made by dissolution of crystalline Cu from a composite structure ($\rho/\rho_s = 25\%$) [107]. (b) Porous Ni-based BMG made by dissolution of crystalline brass from a composite structure ($\rho/\rho_s = 58\%$) [108]. (c) Isolated pore in a porous Zr-based BMG made by co-consolidation of BMG and aluminum nitride powders [74]. (d) Porous Zr-based BMG made by partial electroconsolidation of compacted powders ($\rho/\rho_s = 66.5\%$) [198]. Scale bars in these images were taken from the original texts, and estimated when scale bars were not provided explicitly. They should therefore be considered approximate.

The porous amorphous metals shown in Fig. 2.2 and 2.3 represent the state of the art in porous amorphous metals and AMF, as of the time of this writing (September, 2006). Examination and comparison of these structures illustrate the substantial advances that have been made in the field (not including the results described in this work) since 2003. Methods now exist for production of foams with both isolated (Fig. 2.2a) and fully-interconnected (Fig. 2.2b) pore structures, allowing access to both corresponding application sets. These processing methods have been extended to both spherical and angular pores, isotropic (Fig. 2.3b) and anisotropic
(Fig. 2.3a) in character. Pore sizes ranging from the nanoscale (Fig. 2.3a) to the millimeter-scale (Fig. 2.2b) have been reported. Finally, relative densities ranging from roughly 15% (in this work) to more than 90% (Fig. 2.2e, and several others) can now be studied.

In the following three chapters, the approaches to AMF processing studied here will be described in detail, and the properties of the resulting foams will be studied. This study begins in the next chapter with the processing and characterization of low-density salt-replicated Zr-based AMF, and is followed by consideration of two forms of syntactic AMF, processed from Zr- and Mg-based amorphous metals. After review of the properties of these foams, and comparison to the reported properties of those shown in Fig. 2.2 and 2.3, new directions for study will be proposed in Chapter 8.
CHAPTER 3

Replicated Amorphous Metal Foams

As discussed in Section 1.3, one of the factors limiting industrial uptake of metallic foams is the gap between foaming technology, developed largely for low-temperature liquid-state processing of aluminum, and the requirements of advanced applications demanding mechanical properties of the sort which aluminum alloys cannot deliver. Although this gap has been partially filled through processing of foams made from stronger, higher-melting alloys, these efforts have necessarily left behind a great deal of the simplicity and control gained through research with aluminum foams. The stated purpose of the work presented in this and the following two chapters is to offer a compromise by which the gap might be further filled using strong, low-melting amorphous metals.

3.1. Processing

3.1.1. General Methodology

The first step in exploring such a compromise is development of processing techniques appropriate to foaming of amorphous metals. As described in the Introduction, many basic foaming approaches have been developed for metals, including those based on the vapor, solid, and liquid states of the base alloy; thus the discussion should begin with exploration of the relative merits of these techniques, within the context of amorphous metals. The arguments put forth below are general, and thus will not need to be repeated in subsequent chapters.

Vapor-state processing through chemical or physical vapor deposition onto sacrificial substrates, used mainly in the production of crystalline nickel-based foams [3], could in principle
be extended to amorphous metals as well. Vapor-state methods would be most appropriate, however, for simple binary glass-formers having critical cooling rates too high for liquid-state processing, as the effective cooling rates associated with vapor processes are substantially higher than those possible in the bulk. For more sophisticated, higher-order amorphous alloy systems (such as those used in this work), ensuring adequate compositional accuracy and uniformity during deposition would be essentially impossible; in any case, vapor-state processing would be unnecessary for these alloys, as their critical cooling rates are low enough to allow simpler and cheaper methods to be applied. For these reasons, vapor-state processing will not be investigated here.

Solid-state processing methods, which in the context of amorphous metals would refer to methods whose working temperatures remain always below the glass transition temperature, can also be considered. Though it would be natural to suggest the use of powder metallurgical techniques in this context as well, no literature seems to exist documenting successful consolidation of amorphous powders below the glass transition, probably due to the very high flow stresses of amorphous metals at low temperature and, possibly, the presence of bond-inhibiting oxide films on the powder surfaces [92]. Though newly-developed techniques for electrochemical removal of oxygen from amorphous metals may minimize the latter effect[15, 21], it is still likely that most powder methods will rather fall into the category of supercooled liquid-state processing, described below.

Nonetheless, two true solid-state methods are conceivable: firstly, honeycomb structures fabricated from amorphous metal ribbons by mechanical bonding (e.g. stamping); and second, textile structures woven from amorphous metal wires. Both methods would enjoy the advantage of completely decoupling the vitrification and “foaming” steps, eliminating dimensional and alloy limitations, but would also be limited in terms of available architecture and properties.
Due to lack of suitable processing equipment, and the inconclusiveness of the relevant literature data, solid state methods were also not investigated here.

Many crystalline metals are foamed in the semi-solid state, i.e. between the solidus and liquidus temperatures of the base alloy, or above the melting point of the matrix of a particulate composite [3]. Corresponding methods (referred to as supercooled-liquid-state or SCL-state methods) exist for amorphous metals, in which foaming is achieved between the glass transition and characteristic crystallization temperatures [168]. The width of the supercooled-liquid region between these temperatures is typically 20–135°C [192]. For the best glass formers, sluggish kinetics (associated with high melt viscosities in the range of $10^7$–$10^{12}$ Pa·s [167]) allows processing windows of up to 30 minutes in the SCL state, during which foaming can be achieved [165]. Rapid cooling from the SCL state, even with substantial porosity, is made trivial by the proximity of the glass transition, such that dimensional limitations are all but eliminated when foaming in the SCL state.

It is, furthermore, possible to combine SCL-state foaming with a preliminary high-temperature step, during which a small amount of pore-formers (e.g., pressurized gas or gas-generating powders) is introduced into the melt. After introduction of the pore-former and quenching of the melt, the resulting “prefoam” material may be foamed by reheating into the SCL state [167, 188, 189]. Reheating prefoam materials sealed inside net-shaped molds would allow net-shape processing, an approach used by the Banhart group in Germany for Al-based foams [204].

On account of such natural advantages, SCL-state foaming methods hold great promise for the future of AMF, and will accordingly be revisited in the final chapter. Supercooled-liquid methods are not, however, the simplest experimental approaches to foaming, as illustrated by the processes introduced by the Johnson [168, 167] and Inoue groups [187, 190, 189] and
described in the previous chapter. For this reason, the work here focuses, instead, on simpler foaming methods involving only the liquid state.

Liquid-state processing is by far the most common approach to foaming of crystalline metals, avoiding as it does the expense of vapor deposition or powder production and consolidation [3], and indeed most of the AMF processing methods of Chapter 2 make use of the liquid state in at least one stage. This is a natural reflection of the fact that the high viscosity of glass-forming melts improves foam stability by slowing deleterious drainage, coarsening, and sedimentation processes [194]; the equilibrium viscosity of a typical bulk glass-forming melt at its liquidus, though lower than in the SCL state, is still three orders of magnitude higher than that of a typical pure metallic melt [126]. Such high viscosity should allow glass-forming alloys to be foamed in the liquid state without the ceramic thickening additives used with crystalline metals [3], simplifying processing. Foaming above the liquidus temperature, where crystallization is thermodynamically forbidden, also affords nearly unlimited (i.e., only contamination-limited) processing windows.

Extension of liquid-state foaming methodologies to amorphous metals entails two considerable difficulties. The first of these is the high risk of melt contamination during introduction of external phases, such as blowing agents or solid placeholders, during foaming. Most foaming methods favor small, uniform pore sizes in order to ensure isotropic and statistically-reliable foam properties [3]). As a result, finely-dispersed blowing agents and placeholders will be desirable, at the cost of high contact areas with the alloy and proportionally more severe potential for contamination. A compromise must thus be drawn between desired AMF property uniformity and degraded glass-forming ability.

Cooling rate requirements, the second difficulty incurred by use of the liquid state, exacerbate the need for fine porosity by placing limits on maximum achievable foam dimensions, and thereby on maximum allowable pore size. The severity of these limitations can be estimated using
data compiled by Ashby et al.\cite{3} from crystalline metallic foam literature. These data suggest that thermal conductivity $\lambda$ for metallic foams scales roughly as $(\rho/\rho_s)^{1.7}$, while specific heat $c_p$ is independent of density. Thus thermal diffusivity $\alpha = \lambda/\rho \cdot c_p$ scales as $(\rho/\rho_s)^{0.7}$. The characteristic thermal diffusion distance, which is proportional to $(\alpha t)^\frac{1}{2}$ (where $t$ is the duration of the quench), then scales as $(\rho/\rho_s)^{0.35}$ because $t$ is defined by the temperature interval of the quench and critical cooling rate of the alloy, both being constants for any particular alloy in the absence of contamination. This characteristic distance defines the thickness of material through which a thermal wave-front may pass during a quench from the molten state, and is thereby directly related to the maximum castable dimension of the amorphous material; this dimension should then scale roughly as $(\rho/\rho_s)^{0.35}$.

According to this reasoning, an AMF of relative density 30% could be cast from the liquid state with dimensions roughly 66% those of the monolithic alloy (although limited alloy supplies prevented a decisive verification of this prediction, the maximum dimensions of foams in this chapter were at least 44% that of the alloy; see Table 3.1). Modern bulk amorphous alloys are regularly vitrified in dimensions of 10–100 mm, suggesting maximum foam dimensions in the range of 6.6–66 mm. Applying the criterion that foam dimensions should exceed pore sizes by at least a factor of 7 in order to achieve reliable properties \cite{3}, maximum pore sizes must in turn fall in the range of 0.66–9.4 mm, well within the capabilities of existing foaming processes. This analysis, though far from exact, motivates the important conclusion that limitations incurred by rapid solidification are not stringent enough to prevent the practical development of AMF, even in methods where the alloy is fully-foamed before quenching from a molten state. It also, however, highlights the fact that successful processes for low-density AMF must simultaneously ensure fine porosity, a restriction unique to AMF and in conflict with the need to avoid alloy contamination caused by incorporating high volume fractions of fine pore-forming phases.
It remains only to determine which of the liquid-state methods summarized in Chapter 1 are most suitable for amorphous metals. Early investigations were conducted using several of these methods. Introduction of an inert gas through a porous crucible wall (a process referred to as sparging [194], and enjoying the benefit of requiring no contact between the melt and any external pore-forming phases) was found to be difficult to control, despite high melt viscosity. Pores were found to be large in size (up to several millimeters) and prone to both coarsening and collapse, and vitrification was difficult due to the need for supplying an inert gas atmosphere to the exterior of the crucible. Melting of alloy charges with a blowing agent (zirconium hydride) was unsuccessful due to the difficulty of dispersing this agent in the viscous melt prior to decomposition and gas release. The technique conventionally used to delay hydride decomposition, involving oxidation of the blowing agent [127], could not be used in this case due to the oxygen sensitivity of the glass-formers. Casting of Vit106 in the interstices of packed patterns of thin-walled titanium tubes, which had been stabilized against dissolution in the Vit106 by pack carburization, was not successful because the carburization process could not be made to produce surfaces sufficiently uniform to prevent attack by the melt. Infiltration of yttria investment molds, produced by slurry casting around polymer precursors, yielded acceptable foam structures but did not allow sufficient thermal conductivity for vitrification.

Though some of these methods would undoubtedly be successful with continued study, they were discontinued in light of the success of replication experiments, which form the basis of this and subsequent chapters. The basic outline of replication methods, and the advantages and disadvantages of replicated foam structures, have already been laid out in Chapter 1. In the following sections, details of the specific application of this method to Vit106 will be discussed.
3.1.2. Alloy Selection

The next step in development of liquid-state processing methodologies for AMF is identification of those amorphous alloys most suitable for liquid-state foam processing. Based on the discussion of the previous section, such alloys may be identified using the following criteria:

1. High glass forming ability, as determined by low critical cooling rate and high thermal stability;

2. Commercial relevance and research safety, as determined by absence of precious and toxic components.

3. High resistance to crystallization induced by external phases, such as might be introduced during a foaming process; and

4. Substantial published research establishing criteria (1–3) and presenting relevant mechanical, thermal, and processing data for the monolithic and reinforced alloy

The first criterion suggests alloys with critical casting diameters of several millimeters or more. Although many alloys now meet this criterion (see the Introduction), the alloys with the largest critical casting diameters available at the inception of the project were those of the Zr and Pd families. Among these alloys, Pd-based compositions (most importantly, Pd_{43}Cu_{27}Ni_{10}P_{20} and Pd_{42.5}Cu_{30}Ni_{7.5}P_{20}) have clearly superior GFA [84]; however these alloys fail the second criterion due to the excessive cost of high-purity Pd. The best glass-forming alloy in the Zr family, Zr_{41}Ti_{14}Cu_{12}Ni_{10}Be_{23} [141] (referred to by the trade name \textit{Vitralloy I} or \textit{Vit1}) also fails this criterion, due to the high toxicity of beryllium.

The third criterion is fulfilled by many of the remaining members of the Zr alloy family, which have been used extensively as matrices for composite materials [29, 193, 27, 26]. However the composition which enjoyed the most complete early study, in terms of processing and characterization, is Zr_{57}Nb_{5}Cu_{15.4}Ni_{12.6}Al_{10} (hereafter referred to by its trade name, \textit{Vitralloy}...
<table>
<thead>
<tr>
<th>Property Description</th>
<th>Value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquidus Temperature $T_{liq}$</td>
<td>842°C</td>
<td>DSC 0.33°C/s; Ref. [35]</td>
</tr>
<tr>
<td>Crystallization Temperature $T_x$</td>
<td>469°C</td>
<td>DSC 0.33°C/s; Ref. [35]</td>
</tr>
<tr>
<td>Glass Transition Temperature $T_g$</td>
<td>409°C</td>
<td>DSC 0.33°C/s; Ref. [35]</td>
</tr>
<tr>
<td>Reduced Glass Transition Temperature $T_{rg}$</td>
<td>0.61</td>
<td>$T_g/T_{liq}$</td>
</tr>
<tr>
<td>Thermal Stability of the SCL State $\Delta T_x$</td>
<td>60°C</td>
<td>$T_x - T_g$</td>
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<tr>
<td>Critical Casting Diameter $D_c$</td>
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<td>Ref. [119]</td>
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<tr>
<td>Heat of Crystallization $\Delta H_x$</td>
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<td>Ref. [30]</td>
</tr>
<tr>
<td>Density $\rho$</td>
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<td>Ref. [28]</td>
</tr>
<tr>
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<td>Ref. [28]</td>
</tr>
<tr>
<td>Shear Modulus G</td>
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<td>Ref. [28]</td>
</tr>
<tr>
<td>Bulk Modulus K</td>
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<td>Ref. [28]</td>
</tr>
<tr>
<td>Poisson Ratio $\nu$</td>
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<td>Ref. [36]</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion $\alpha$</td>
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<td>Ref. [36]</td>
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<tr>
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<td>Ref. [26]</td>
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<td>Ref. [36]</td>
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<tr>
<td>Tensile Fracture Strength $\sigma_T$</td>
<td>1200 MPa</td>
<td>Ref. [36]</td>
</tr>
</tbody>
</table>

Table 3.1. Selected properties of the bulk metallic glass-former Vit106. Transition temperatures represent onset values measured at the identified heating rates using DSC; where multiple transitions are visible, temperatures represent onset of the first transition.

Vit106). Accordingly, Vit106 was chosen as the base alloy for development of AMF processing. A list of the most important properties of Vit106 is provided in Table 3.1.

All base alloy samples used in this work were produced by arc melting of high-purity elemental metals, the technique used for alloying of essentially all amorphous metals. The stock metals used for arc melting included Zr crystal bar turnings (99.5%), Nb plates (99.97%), Cu shot (99.999%), Ni pellets (99.995%), and Al pellets (99.999%). Prior to melting, stock metals were cleaned ultrasonically in acetone and methanol and placed on a water-cooled copper hearth inside the arc melting chamber. After evacuation to high vacuum (typically $10^{-4}$–$10^{-3}$ Pa) and flushing with high-purity argon, a Ti getter button was melted for three minutes to dissolve and entrap any remaining oxygen. The stock metals were then melted for three minutes,
then flipped and remelted two more times to ensure homogeneity. After arc melting, irregularly-shaped buttons were recovered. These buttons were mostly amorphous, but contained crystalline skull material in regions near their contact with the hearth. To achieve completely amorphous charges for foaming experiments, buttons were sectioned and remelted at 975°C under high vacuum (typical pressures given above) in uncoated stainless steel crucibles with inner and outer diameters of 8.1 and 12.7 mm, respectively, followed by brine quenching (see below). Remelted ingots were machined out of the crucibles and subjected to XRD; only those buttons which could be cast in this fashion without detectable crystallinity were used for foam specimens.

3.1.3. Infiltration

Selection of a particular amorphous alloy also requires selection of a crucible material in which the alloy can be processed without inducing harmful chemical reactions. The true extent and effect of crucible reactions on glass formation in the alloy is generally not known in advance, but gross predictions can nonetheless be made based on binary interactions between alloy and crucible components.

In the case of Vit106, the high affinity of Zr for oxygen, carbon, boron, and nitrogen [155] was expected to prohibit use of common ceramic crucible materials like quartz, alumina, zirconia, graphite, and boron nitride. Indeed, early experiments revealed visible reaction between Vit106 and all these materials. In all but one case (formation of ZrC between Vit106 and graphite), these reactions caused catastrophic devitrification of the alloy, forbidding their use in future experiments. Although formation of ZrC did not preclude use of graphite crucibles, it was found that formation of ZrC corresponds to reactive wetting of the two phases, such that Vit106 infiltrates the open porosity of commercial graphites, interfering with infiltration of the desired pattern material. For this reason, graphite also was excluded as a crucible material.
Consequently, metallic crucibles were necessary for processing experiments. The alloy offering the best combination of cost, machinability, and stability in contact with molten Vit106 was stainless steel. Although processing in stainless steel crucibles did not lead to noticeable deterioration of GFA in any case, detectable levels of iron were found in Vit106 (using energy-dispersive x-ray spectroscopy or EDX) within 500 \( \mu \)m of Vit106/steel interfaces, after typical melting and infiltration times of 7–10 minutes; as such, it was necessary to remove this amount of material from the surfaces of all remelted ingots and foam specimens.

Crucibles took the form of long uniform-diameter tubes (inner and outer diameters 8.1 and 12.7 mm, respectively) welded to custom-machined tips. The overall length of these crucibles was approximately 60 cm, sufficient to allow the tip of the crucible to be inserted in the hot zone of a vertical tube furnace, while the majority of the crucible length was maintained outside the hot zone, where it was coupled into the vacuum and pressurization manifold. The tips themselves were cylindrical in shape, with inner diameters varying from 5–7 mm and outer diameters of 6.5–8.5 mm. The inner diameter of each crucible was smaller by exactly 1.5 mm than the outer diameter, giving a constant wall thickness, in the region where the foam resides at quenching, of 0.75 mm. In order to ensure radial cooling (cooling must be radial to ensure that specimens exceeding the maximum castable dimensions do not contain misleading regions of amorphous material caused by conduction through the bottom of the crucible), the bottom portion of each tip consisted of solid stainless steel with a thickness of at least 5 mm. Prior to use, all crucibles were thoroughly cleaned using a commercial oxide-stripping stainless steel cleaner (Bradford Derustit SS-3, Clifton Park, NY) and rinsed several times with water, acetone, and methanol, to prevent introduction of contamination in the form of extrusion lubricants, machining oils, and oxide scales formed during welding of tips onto tubes in construction of the crucibles.

Specimens were prepared using the process of melt infiltration, used primarily for the production of polymer- and metal-matrix composites (see Ref. [32, 23, 131, 54] for more complete
discussion). This process begins with a preform or pattern prepared by packing, pressing, and/or sintering of the reinforcing phase of the composite. This preform is placed in a crucible and a charge of the solid matrix material is loaded onto it; often a spacer material (usually a nonreactive cloth or felt, powder, or porous disk) is used to separate the preform and charge. The entire crucible is then evacuated while still at a temperature below the melting point of the matrix material, and then the temperature is raised above the melting point, causing the charge to melt and collapse under its own weight onto the preform or spacer. During this melting stage, the molten matrix pools on top of the preform and creates a gas-tight liquid seal with the interior crucible wall, thereby isolating the preform from the volume above the melt. After a seal has been thus established, gas is admitted to the top of the crucible, generating a pressure gradient across the pooled melt which drives it into the interstices of the preform, creating a composite which is then solidified.

The key parameters in an infiltration process include the temperature, applied gas pressure, and the hold time over which this pressure must be applied to ensure adequate infiltration [54]. Other key parameters include the preform porosity and particle size, and the wetting relationships among the molten matrix, crucible wall, and preform material. Generally speaking, infiltration is facilitated by increased temperature (through diminished melt viscosity), pressure (increased driving force for melt penetration), and hold time, as well as high preform porosity and coarse particle size (to minimize the effects of capillary drag forces [131]). Other factors, such as particle shape and surface roughness and any particle/melt interfacial reactions, also influence infiltration.

Infiltration of all Vit106-based specimens was performed as shown in Fig. 3.1. Pattern materials were carefully lowered into the crucible tip, along with a charge of ultrasonically-cleaned Vit106. This charge was initially suspended in the upper region of the crucible (outside the hot zone) using a high-purity tungsten wire basket and a small piece of magnetic steel wire.
Figure 3.1. Schematic representation of the melt infiltration process as implemented in this work.

Tungsten was chosen as a basket material based on the availability and ductility of wires, and its known chemical stability in contact with molten Vit106 [29, 27, 30]. After several cycles of evacuation and flushing with high-purity argon gas (99.9996%), patterns were preheated to 975°C under high vacuum ($10^{-3}$–$5 \times 10^{-3}$ Pa) to remove adsorbed atmospheric moisture. After equilibration of the pressure inside the crucible (typically 3–5 minutes), the Vit106 charges were lowered magnetically to the crucible tip and allowed to melt for a period of 5–10 minutes. After the melting period, argon was readmitted to the crucible at a pressure of 153 kPa. After a varying holding time of several minutes under pressure, the crucibles were removed from the hot zone and immediately quenched in order to vitrify the Vit106 phase.

In all infiltrations, the quench media (or quenchant) used was NaCl brine at a concentration of 8.5 wt.%, strongly agitated and chilled to within 0–3°C. This medium was selected to maximize overall cooling rates, based on literature study of cooling rates during quenching of steels [184]. Higher cooling rates should be possible using aqueous NaOH, and by replacing simple agitation with ultrasonic agitation. However these approaches are less practical and were not studied here.
Following quenching, infiltrated specimens were machined into uniform right cylinders using a diamond grinding wheel and diamond wafering saw. This was necessary because simple machining (e.g., lathing) of specimens usually caused excessive damage, and electric discharge machining was not generally possible on account of large fractions of non-conducting pattern material. In certain cases, electric discharge machining was used later to remove regions of handling and corrosion damage from specimens prior to mechanical testing.

3.1.4. Pattern Selection and Removal

There are many potential pattern materials for use in foaming by replication. In the production of aluminum foams, NaCl is the pattern material of choice due to its high melting point (relative to aluminum) and high solubility in water [53]. The melting point of NaCl (801°C [115]) is not, however, sufficiently high to allow its use as a pattern for Vit106, which requires processing temperatures about 130°C [116] above its liquidus (842°C) in order to preserve its full glass-forming ability. Such temperatures, given the stringent purity requirements of glass-forming metallic melts and the high contact area between infiltrated melt and salt pattern, effectively preclude the use of bromide, iodide, and chloride salts, as well as many fluoride salts. There are several fluorides, nonetheless, with melting points well in excess of 975°C, including the highly-stable alkaline earth fluorides MF\textsubscript{2} (M = Mg, Ca, Sr, or Ba) [115]. Among these, SrF\textsubscript{2} and BaF\textsubscript{2} were selected for study based on their high melting points of 1477°C and 1368°C, respectively [115].

Packing and sintering of these pattern materials were studied using SrF\textsubscript{2} (180–355 μm) and BaF\textsubscript{2} powders (212–250 μm) prepared by crushing monocrystalline pieces of optical-grade (99.999+% 99.999+%) material with a mortar and pestle. Sieved powders were packed in graphite crucibles and sintered for 10 hours at temperatures of 1400–1440°C (for SrF\textsubscript{2}) and 1200–1350°C (for BaF\textsubscript{2}) in three different atmospheres: high vacuum (10^{-4}–10^{-3} Pa), low vacuum (0.1–1 Pa), and argon
cover gas. Among these, high vacuum conditions gave for both salts the best overall balance among pattern mechanical integrity, contamination by/reaction with graphite, and evaporation losses.

Accessible sintering temperatures for BaF$_2$ in high-vacuum conditions were limited to 1250–1275°C (homologous temperature 0.93–0.94) by evaporation losses; the equilibrium vapor pressures of BaF$_2$ in this temperature range are 5–12 Pa [73], well above the working pressure maintained by the vacuum furnace. Conversely, SrF$_2$ was effectively sintered under the same conditions at temperatures as high as 1400–1440°C (homologous temperature 0.96–0.98), in which range it has comparable vapor pressure (5-10 Pa) [13]. It is noteworthy that early attempts to use water-soluble NaF (melting point: 996°C) [115] as a pattern material for Vit106 led to attack of Vit106 charges by salt vapor during melting, preventing pooling of the alloy as required for melt infiltration. Equilibrium vapor pressures for SrF$_2$ and BaF$_2$ at the infiltration temperature of 975°C are $2\cdot10^{-4}$ Pa and $6\cdot10^{-3}$ Pa, respectively [13], posing little threat to the alloy.

No densification was observed for either salt under any sintering conditions, even with BaF$_2$ powders as fine as 100–150 µm. Lack of densification during sintering is well established for NaCl, a result of the fact that the dominant mechanism of sintering in NaCl is evaporation-condensation, as opposed to bulk or grain boundary diffusion [181]. Densification in NaCl is observed only when particle size is sufficiently small, around 100–150 µm [181]. It is possible that the corresponding critical particle sizes for SrF$_2$ and BaF$_2$ fall below that of NaCl; however, powders finer than 100 µm were not investigated in the present work, in order to minimize infiltration times and pressures, contact area with the molten alloy and leaching times.

For this reason, the final packing density of sintered SrF$_2$ and BaF$_2$ patterns reported here was equal to the tap-dense packing fraction, 50±2% (errors represent one standard deviation). This may also be taken as the maximum initial volume fraction of Vit106 in infiltrated samples,
i.e. the maximum initial relative density of all foams. In practice, however, the relative density of Vit106 foams was found to be lower. One explanation for this discrepancy is incomplete infiltration, though in general little or no uninfiltrated porosity was visible in polished composite cross sections (after infiltration but before leaching; it is noted, however, that the transparency of the polished salt in such sections could make small levels of porosity difficult to see). As discussed previously, improved infiltration is possible using higher pressures, temperatures, and hold times. Higher infiltration pressure was generally not possible because equipment that may be used safely at high temperature and high pressure could not also be rapidly quenched. Higher temperatures and hold times were avoided in order to minimize the time available for contaminating reactions to occur between the molten alloy and neighboring preform and crucible phases. Thus incomplete infiltration, if a factor in causing low composite densities, could not be readily eliminated. The second explanation for the discrepancy is the fact that foam specimens were always ground from the interior portions of the infiltrated composites. In this region, more distant from the crucible wall and its attending disruption in packing efficiency [61], it is likely that the local salt fraction was increased, and therefore that the Vit106 fraction was decreased. Though independent confirmation of this effect was not feasible, calculations show that the salt packing fractions required to explain these discrepancies, even in the absence of residual uninfiltrated porosity, would be plausible [61], in the range of 60–65%. Some combination of the two effects is the most likely explanation for low composite density.

Dissolution of each pattern material was studied in several media. Although both BaF$_2$ and SrF$_2$ have measurable solubilities in water [115], early experiments confirmed that leaching patterns in water alone, particularly from infiltrated samples, was not feasible. By contrast, both salts were susceptible to dissolution in strong acids. Although the exact mechanism for this dissolution is unclear, it has been suggested [176] that BaF$_2$ dissolves in HNO$_3$ through the formation of Ba(NO$_3$)$_2$ and HF. Similar exchange reactions likely describe the dissolution
of BaF$_2$ in HCl and SrF$_2$ in HCl and HNO$_3$. The capacity of these acids to dissolve SrF$_2$ and BaF$_2$ may then be attributed to the high aqueous solubilities of acidified HF, (Sr,Ba)(NO$_3$)$_2$, and (Sr,Ba)Cl$_2$ [115].

The effects of these strong acidic leaching media on Vit106 were studied using quadrilateral test coupons (mass: 0.75–1.0 g) cut from plates of amorphous Vit106, polished with 1200 grit SiC paper, and thoroughly cleaned before immersion in each medium. Mass losses were measured after 24–48 hours immersion, and corrosion penetration rates estimated based on the measured coupon surface areas, under the assumption of uniform corrosion. Evidence of localized corrosion (pitting) on these coupons was seen after 24 hour immersion in stagnant 2–4M HCl, while at concentrations of 8M and above, massive macroscopic damage was observed. Attempts to leach infiltrated samples using even lower (<2M) HCl concentrations led to low dissolution rates with visible discoloration of the alloy, such that HCl was not further investigated.

Figure 3.2 shows corrosion penetration rates using various HNO$_3$ baths. For acid concentrations between 1M and 8M, no mass losses were measured after 24-hour immersion in stagnant pure acid. Addition of 5–8 mM BaF$_2$ (simulating the mean fluoride concentration present during dissolution of infiltrated BaF$_2$ patterns) to HNO$_3$ baths led to measurable mass losses over the same series of concentrations, with comparable penetration rate for all concentrations tested. Comparison of the data in Fig. 3.2 with literature data [176] for dissolution of BaF$_2$ in nitric acid shows that the maximum ratio of salt dissolution rate to alloy corrosion rate is achieved with 2M HNO$_3$, which was selected on this basis as the optimal bath concentration for salt removal with minimal alloy loss.

Agitation (using a magnetic stir bar) of fluoride-bearing HNO$_3$ solutions led to 4–5 fold increases in coupon mass loss (Fig. 3.2), presumably due to the higher concentration and mobility of dissolved atmospheric oxygen in the stirred baths. Ultrasonic agitation did not significantly alter corrosion rates relative to magnetic stirring; however, infiltrated Vit106/BaF$_2$ samples
Figure 3.2. Estimated corrosion penetration rates for amorphous Vit106 coupons in nitric acid baths at ambient temperature, containing dissolved BaF$_2$ in proportions chosen to simulate full dissolution of patterns from infiltrated samples (typical concentration: 5–8 mM). The hollow triangle demonstrates the potential benefits of corrosion inhibitors (in this case, fine alumina powder), which reduce the aggressiveness of fluoride ion liberated by the dissolving salt.

showed initial rates of mass loss (measured after 4 hrs immersion) eight times higher for ultrasonic agitation compared to stirring in 2M HNO$_3$, after normalizing for sample surface area. This may have resulted from breakup or debonding of the BaF$_2$ particles in ultrasonic baths, increased acid convection within the foam cells, or enhanced removal of Ba(NO$_3$)$_2$ or other dissolution intermediates formed on the surface of BaF$_2$ exposed to nitric acid, with attendant increases in overall salt dissolution rate. In any case, ultrasonic agitation undoubtedly lowers the immersion time required for pattern removal, and thereby lowers the overall loss of alloy during leaching. Corresponding measurements using HNO$_3$ containing dissolved SrF$_2$ were not made, after early observations showed that dissolution rates for Vit106/SrF$_2$ samples, in acid concentration ranges where Vit106 coupons corroded uniformly, were impractically low.
As discussed in the following sections, corrosive attack of Vit106 by HNO$_3$ was noticeable but generally not problematic. It is nonetheless worth noting that protection against corrosive attack might be accomplished through impressed current polarization, sacrificial anodes, or the use of inhibitors. Though no information is currently available regarding the corrosion chemistry of Vit106 in the aggressive media used here, the high zirconium content of Vit106 may prove useful by allowing methods for corrosion mitigation in Zr alloys to be applied to Vit106. For example Zr alloys are known [169, 144] to be passive in HNO$_3$ but highly susceptible to passive film disruption by fluoride, in qualitative agreement with observations presented here. Accordingly, inhibiting additives such as alumina, silica, Al(NO$_3$)$_3$, and P$_2$O$_5$ have been developed to lower the aggressiveness of fluoride towards Zr, e.g. by binding it into inert complexes [169, 144]. A preliminary example of this effect is shown in Fig. 3.2, where the rate of corrosion of a Vit106 coupon in stirred fluoride-bearing 2M nitric acid containing 75 g/L of fine (6–23 µm) Al$_2$O$_3$ powder is shown. Compared to the same solution without Al$_2$O$_3$, the corrosion rate has been more than halved.

3.2. Structure

In this section, the structure of both BaF$_2$ patterns and the corresponding replicated foam structures are illustrated using a representative specimen processed from salt particles sieved to a size of 212–250 µm. In the interest of brevity, pore sizes throughout this chapter will be given as the median of the as-sieved particle size range (in this example, 230 µm). It is freely acknowledged that actual pore sizes in the resulting foams will span the entire as-sieved range, and within this range will not be uniformly distributed. It is likewise acknowledged that final pore sizes may be slightly higher than initial salt particle size due to alloy dissolution. Such simplifications should be borne in mind, but will not fundamentally alter any of the following conclusions.
Scanning electron micrographs showing the size and shape of unsintered and as-sintered 230 µm BaF₂ particles are shown in Figs. 3.3a and 3.3b, respectively. Unsintered BaF₂ particles were elongated and angular; though sharp particle edges showed some rounding, sintering did not substantially alter either aspect ratio or overall angularity, and faceting of the particles was not observed. Analysis of visible necks within the sintered pattern indicated neck widths primarily in the range of 20–60 µm. After infiltration of sintered patterns (Fig. 3.3c) with molten Vit106, no significant porosity was observed using optical microscopy, suggesting that replication of the topological features of the salt was near-complete.

As expected, foam structures recovered after dissolution of the salt contained angular pores, and many non-equiaxed pores (though due to the randomness of particle packing, this was not expected to lead to macroscopic anisotropy), as illustrated in Fig. 3.3d,e. No clear evidence was found that this angularity was mitigated through the leaching process, despite the expectation that highly-convex surfaces, such as sharp edges and corners, should be more susceptible to corrosion. After compression to high (ca. 80%) strain, the foam structure was uniform and visibly dense, with the exception of the sample edges; no sign of macroscopic sample cracking was visible after unloading (Fig. 3.3f).

Figures 3.4a-c show representative SEM images from a Vit106 foam of nominal pore size 230 µm and relative density 22% following removal of its BaF₂ pattern by 16 hrs immersion in ultrasonically-agitated 2M nitric acid. Pattern removal was likely completed after only 4 hrs immersion, based on an inflection in a plot of mass loss vs. time, which occurred at a mass loss equal to that predicted based on initial sample mass and volume fractions. The foam was, however, replaced into a fresh bath for an additional 12 hours in order to continue lowering its relative density by alloy dissolution to a target value of 20–25% (using this process, a similar foam was reduced to about 14% density, as described below), chosen to demonstrate that foam density can be tailored through dissolution without incurring excessive damage to the foam.
Figure 3.3. SEM micrographs showing: (a) morphology of unsintered 230 µm BaF$_2$ powders; (b) morphology of as-sintered 230 µm BaF$_2$ powders, showing slight rounding but no substantial reshaping; (c) macrostructure of a sintered 230 µm BaF$_2$ pattern before infiltration; (d) macrostructure of Vit106 foam (22% dense) replicated from a 230 µm pattern; (e) magnified view of the foam in panel (d), showing pore, strut and node structure; (f) view of the deformed foam in panels (d,e) after unloading from 79% engineering strain.
Figure 3.4. SEM micrographs of an amorphous Vit106 foam (diameter: 4.5 mm, relative density: 22%) after pattern removal in ultrasonically-agitated 2M nitric acid. (a) Uniform macrostructure of the foam. (b) Surface of the foam, showing sockets left behind by individual BaF$_2$ particles. (c) Individual foam strut, having high aspect ratio. The surface of this strut shows small indentations (‘scalloping’) produced by the corrosive leaching bath.

This immersion treatment was broadly representative of those used for all samples, though total necessary immersion times varied between about 5 hours and about 36 hours; generally speaking, immersion time increased with decreasing target density, decreasing pore size, and increasing specimen diameter.

The structure of this foam is highly uniform and has a high proportion of mass localized at the nodes where struts meet. Such localization has been observed previously in aluminum foams made by the salt replication method, and is a result of the geometry of the salt particles and the resulting interstices within the sintered salt patterns [162]. It is conventionally assumed to be mechanically inefficient, as it leads to higher foam density for a given strut thickness (and hence load-bearing capacity); recent data, however, do not support this interpretation, suggesting instead that redistribution of mass towards the nodes places it more efficiently into regions of the strut subjected to the greatest bending moments [65]. In any case, mechanical inefficiency would usually be accepted in light of the exceptional uniformity and fine control over pore size and morphology achievable in replicated foams.

Figure 3.4c shows an individual strut within the foam. The surface of this strut exhibits a “scalloped” texture (characterized by the presence of shallow circular pits or craters) that is
common to all the Vit106 surfaces within the foams following acid leaching. This texture is not seen on foam surfaces prior to leaching, and is therefore believed to result from corrosive attack of the alloy during pattern removal, perhaps localized attack occurring at small crystalline surface inclusions [56, 132].

3.2.1. Glass Formation

As shown in Fig. 3.5, the XRD pattern of foams (all gave similar patterns, though only one representative pattern is shown in the figure) showed no evidence of devitrification (a pattern taken from heavily-crystallized Vit106 is provided later, in Fig. 3.15b), or of residual salt. Such was the case for specimens having diameters up to 7 mm; in order to conserve alloy, and to facilitate non-destructive leaching of salt preforms, larger specimens were not produced.

The results of differential scanning calorimetry (heating rate 0.33°C/s) for unprocessed monolithic Vit106 are shown in Fig. 3.6a. The onset temperatures of the glass transition and
crystallization exotherms are 399 and 474°C, respectively. For a foam specimen whose preform was leached in an ultrasonically-agitated acid bath (Fig. 3.6b), an additional broad exothermic feature beginning at about 450°C is superimposed onto this bulk signal, while in a foam specimen whose bath was not agitated (Fig. 3.6c) the additional exotherm dominates the trace. The same feature was found to be present in monolithic (not foamed) specimens of Vit106 subjected to a simulated leaching bath of fluoride-bearing 2M nitric acid, albeit with lesser magnitude, and even in monolithic specimens exposed to fluoride-free acid, with still smaller magnitude. Accordingly, it is believed that the feature originates in a surface corrosion product of Vit106, induced by exposure to nitric acid and exacerbated by the presence of fluoride, and further exacerbated when high local fluoride concentrations are produced during dissolution of the salt within the small confined pores of a foam structure. Supporting this conclusion was the fact that the total heat release associated with the exothermic feature did not scale with sample mass or volume, and hence most likely reflected a surface reaction (though without an accurate measure of the surface areas of small foam DSC samples, this cannot be quantified).

Although this exotherm obscured the small endothermic glass transition in foam samples, the onset of crystallization in foam specimens was essentially unchanged from the unprocessed monolithic alloy, suggesting that contact between the molten alloy and the salt pattern only minimally affected the crystallization pathway of the Vit106. Due to the small magnitude of the feature in ultrasonically-leached specimens (Fig. 3.6b), which constitute all the specimens discussed hereafter, the effects of corrosion products on foam properties were not considered further.
3.3. Mechanical Properties

A series of SEM images depicting the deformation of a sample of pore size 230 μm and relative density 23%, after unloading at regular intervals up to a strain of 43%, is shown in Fig. 3.7a-c. Except for some minor shearing (Fig. 3.7b-c), deformation was uniform to the naked eye with no evidence of crush bands commonly found in other foam materials [3, 22]. Though the comparatively high density of this sample, and the existence of large nodes connecting struts, prevented line of sight through the sample and may have obscured any visible evidence, it is notable that uniform deformation was also reported in comparable Al-based crystalline foams made using NaCl [161].
Images illustrating local deformation in a pair of adjacent slender struts near the surface of this sample are shown in Fig. 3.7d-g. One of these struts (left in Fig. 3.7d-g) underwent pronounced plastic deformation near its junctions with adjoining nodes (i.e., plastic hinging) before fracturing when the foam reached an average uniaxial strain between 14 and 19%. By contrast, the neighboring strut (right in Fig. 3.7d-g) showed little or no visible plasticity, succumbing to fracture at lower applied strain (one crack appeared between 4 and 9% strain, a second between 9 and 14%). Many further instances of both deformation modes were observed, indicating that both occurred frequently and were distributed with high uniformity inside the foam.

Engineering compressive stress-strain curves are shown as a function of density for samples of constant pore size (230 µm) in Fig. 3.8a, and as a function of pore size for samples of near-constant relative density (22.4–23.8%) in Fig. 3.8b. The densest sample examined (28%) exhibited ductile foam behavior up to ca. 50% strain, at which point a portion of the densified foam fractured from the sample, and the test was terminated. Though minor spalling of material was apparent from the side surfaces of all Vit106 samples at high strain, the remaining samples were compressed to strains in the vicinity of 80% without macroscopic fracture, and exhibited behavior typical of ductile metallic foam in compression: an initial linear, pre-yield region followed by a second post-yield region of slowly rising flow stress (Section 1.1.3). Denser samples showed smaller relative increases in flow stress after yield (about three-fold by 50% strain, compared to more than six-fold for the least-dense sample over the same interval). No dependence on pore size, other than variations in the intensity of serrations (discussed in detail in a later section), was observed up to a strain of 25%; thereafter, a somewhat faster increase in flow stress was recorded as the pore size decreased, Fig. 3.8b. The relative increase in flow stress following yield in a pure aluminum foam (relative density 28%, replicated from NaCl with an approximate size of 500 µm) was approximately ten-fold over the same range of strain, significantly higher than in any Vit106 sample.
Figure 3.7. SEM micrographs illustrating mechanisms of compressive deformation in Vit106 foam (pore size 230 µm and relative density 23%, similar to the foam in Fig. 3.3d,e). Low-magnification images show foam structure following unloading from various applied macroscopic strains: (a) low strain (4%); (b) intermediate strain (24%); (c) high strain (43%). Also shown are deformed struts within the sample following unloading from: (d) 4% strain; (e) 9% strain; (f) 14% strain; (g) 19% strain. Visible fractures are indicated by arrows in the panels where they first appear.
The necessary use of aggressive leaching media in removing the BaF$_2$ placeholders implied that relative density decreases were largely affected through corrosive attack of the alloy, a process proceeding more rapidly on high-surface-area features like struts and less rapidly on the nodes connecting the struts. The effect of this nonuniform mass loss was most pronounced at the lowest relative densities (14–15%), where foam surface damage was visible in the form of uneven sample surfaces, preventing full contact with the compression platens at low strains. As a result, this sample showed (Fig. 3.8a, inset) an unrealistically high yield strain ca. 4% and proportionally erroneous stiffness, as a result of early yield representing only the contacted portion of the sample. This sample was included for completeness, and also because its high-strain properties (e.g., those related to serrations and densification) were still believed valid; however, its low-strain data, assumed to contain contributions from damage and surface unevenness, were not included in analysis involving stiffness or strength.

Additionally, the sample of relative density 24% and 180 $\mu$m pore size was used to investigate the possibility of acoustic emissions measurements, the results of which will be discussed in a later section. For present purposes, it is noted that the use of silicone coupling fluid on the sample faces during compression led to a similar result (Fig. 3.8b, inset) as for the low-density sample above, reducing accuracy of the lowest-strain data. It is believed that the yield stress of this sample was accurate but, due to the layer of coupling fluid, the loading stiffness and yield strain were inaccurate, being too low and too high, respectively.

In each sample, abrupt losses in flow stress occurred throughout the post-yield linear region of the stress-strain curve (Fig. 3.8, insets), where they were visible as serrations followed by gradual recoveries. These serrations were accompanied by emission of sparks from the foam interiors, and sparks were also observed during uniaxial failure of large specimens of monolithic Vit106. Such emissions can be attributed to high elastic energy release (due to high strength
Figure 3.8. Engineering compressive stress-strain curves of Vit106 foams (a) as a function of relative density for constant pore size 230 µm; and (b) as a function of pore size for near-constant relative density (22.4–23.8%). Insets magnify the low-strain regions for better visualization of serrations. The stress-strain curve of a crystalline aluminum foam (relative density 28%, pore size ca. 500 µm) is shown for comparison.
and low modulus) combined with the exothermic oxidation of Zr-based particulates expelled
during fracture.

Increasing flow stress in the post-yield linear region (Fig. 3.8) has been previously observed
in crystalline metallic foams, and arises from two primary factors: strain-hardening in deformed
struts, and contact forces developed between nodes connecting these struts [162, 93]. Since
amorphous metals show perfectly-plastic behavior in geometries where plasticity is allowed [38],
the first explanation is unlikely to apply to Vit106 foams; the latter, however, is expected to
influence flow stresses. Contact forces are likely to develop in the compressed Vit106 foams
due to their prominent nodes (Fig. 3.3d,e), and increases in reloading stiffness observed at low
strains (Fig. 3.14b, discussed below) further indicate their presence early in the stress-strain
curve. It is notable that in pure aluminum foams of similar relative densities and structures,
processed by replication of NaCl patterns, steeply rising flow stresses were also observed, and
this was confirmed by the aluminum foam studied here [162]. The increases in those aluminum
foams were attributed to both intrinsic strain hardening and contact forces.

In this context, the observed increase in relative slope in the post-yield linear region with
decreasing Vit106 foam density reflects the fact that yield strength (governed by strut size)
decreased more rapidly with density than the contact forces (governed by node size), because
of the preferential action of the acid bath on the struts. It may also represent the faster accu-
mulation of damage in the denser samples, as discussed below; the minor pore size dependence
corroborates this latter explanation, since the more damage-prone coarse foams showed smaller
relative increases in flow stress. The fact that all Vit106 samples showed smaller relative stress
increases than the aluminum foam may therefore reflect higher rates of damage in the Vit106.

All curves (except for the foam that fractured) were also terminated at high strains by
rapidly-increasing flow stress (i.e., densification). Final densification was gradual, as for all
ductile foams, and difficult to identify exactly due to the gradually changing slopes of the stress-strain curves. Thus densification strains were assigned systematically using the intersection of two lines, the first drawn along the post-yield linear region between 10 and 30% strain and the other tangent to the stress-strain curve at a strain of 70%, which visibly exceeded the onset of densification in all samples. Densification strains using this method ranged from 60 to 66%; for the purposes of strain energy calculations, densification strain for the prematurely-fractured sample (28% relative density) was taken to be 50%. Using this same method, the densification strain of the aluminum foam was 61%, within the range of the Vit106 foams.

Densification strain is known to be sensitive to relative density and pore architecture [22]. According to Ashby et al. [3] densification strain is primarily a function of relative density and takes the form:

\[
\epsilon_d = \alpha_1 \cdot \left( 1 - 1.4 \cdot \left( \frac{\rho}{\rho_s} \right) + 0.4 \cdot \left( \frac{\rho}{\rho_s} \right)^3 \right)
\]

where \( \alpha_1 \) is a constant equal to 0.9–1.0. Another equation is proposed by Chan and Lie [16]:

\[
\epsilon_d = 1 - \alpha_2 \cdot \left( \frac{\rho}{\rho_s} \right)^{\frac{1}{2}}
\]

where \( \alpha_2 \) is a constant with a best-fit value \( \alpha_2 = 0.85 \) for the present Vit106 foams. For the range of densities investigated here, densification strains predicted by Eqs. 3.1 and 3.2 are 62–80% and 55–68%, respectively. Both models give acceptable fits to the data (which ranges between 60 and 66%), though Eq. 3.1 generally slightly overestimates densification strains for Vit106 foam. It is, however, emphasized that the numerical value of densification strain is sensitive to the particular procedure used to calculate it; thus a comparison of this sort is valuable less for its numerical accuracy as for demonstrating that final densification occurs approximately at the same strains in Vit106 foams as in conventional ductile metal foams. This was additionally
confirmed by using the same procedure on the highly-ductile pure aluminum foam of comparable relative density, and achieving a value of 61%, within the range measured for Vit106 foams, and between the predictions of Eqs. 3.1 and 3.2, which range from 55–62%.

3.3.1. Stiffness and Strength

The stiffness of Vit106 foams, as measured during initial loading, increased with relative density as shown in Fig. 3.9. Despite the fact that unload/reload stiffness data are preferred over initial loading values (Section 1.1.3), stiffness was nevertheless measured here during initial loading, where the full extent of the data could be used, rather than from reload data, for which less than half the linear stress-strain region could be used due to sample resettling. Nevertheless, for some specimens (those having higher yield stresses or longer gauge lengths) reload stiffness data could be calculated. These data are provided in the discussion of damage in the next section.

Compressive yield strength was defined by the intercept of tangents in the immediate pre- and post-yield portions of the stress-strain curve; the existence of pronounced serrations post-yield, and the resulting difficulty in accurately defining a tangent there, introduced some error into yield stress values. Within this uncertainty, no difference was detected between the strength (or indeed between the whole stress-strain curves) of two foams of 230 μm pore size and similar relative densities (23.2 and 22.4%), but with different diameters (3.0 and 4.5 mm, respectively). Because all other sample diameters lay between these limits, it was concluded that sample size effects were not appreciable within the samples tested. It is further noted that no significant change in strength was observed as a function of pore size for samples of similar relative density (23.2–23.8%), as shown in Fig. 3.8b. The early portions of the stress-strain curves (Fig. 3.8a, inset), however, clearly show that yield strength increased with density, with values ranging between about 6 and 34 MPa. Yield stress data for all samples are shown in Fig. 3.10 as a function of relative density and pore size.
Figure 3.9. Initial loading stiffness for Vit106 foams as a function of relative density and pore size. Also shown are best fits according to a power-law scaling relationship, Eq. 1.1, using \((C_1, n_1) = (0.30, 2.2)\) and \((0.24, 2)\). The point representing the damaged 14% dense sample was not used in regression and is denoted by an open symbol. The stiffness of the finest-pore specimen (red marker) was also not used, as this specimen was used for acoustic emissions experiments and its low-strain data were affected by the requiring coupling fluid.

In the absence of processing-related microstructural variations, most data show no distinct variation of foam stiffness with pore size for either ductile [137] or brittle [19] foams; an increase in stiffness at low pore size, however, has been reported in Mg-based foams [195]. Due to the effect of acoustic coupling fluid on the 180 \(\mu m\) sample, it is not possible to verify here the presence or absence of a similar trend in Vit106; the two larger pore sizes (230 and 330 \(\mu m\)), however, did indeed show very similar loading stiffness. On the other hand, an inverse dependence of compressive strength on pore size has been reported for brittle ceramic foams, e.g., silicate glass [129] and glassy carbon [19], even in the absence of microstructural variations. This dependence may be rationalized using Weibull statistical approaches and arises from
Figure 3.10. Yield strength for Vit106 foams as a function of relative density and pore size. Also shown are best fits according to a power law scaling relationship, Eq. 1.2, using \((C_2, n_2) = (0.26, 1.9)\) and \((0.15, 1.5)\). The point representing the damaged 14% sample was not used in regression and is denoted by an open symbol.

decreasing strut volume and surface area with decreasing pore size, and consequent increases in effective strut strength [129, 19, 83]. The absence of significant pore size dependence in Vit106 compressive strength supports the view that Vit106 foams more closely resemble ductile crystalline metal foams than brittle ceramic foams. It is notable, however, that size effects in high-strain compressive flow stress [53] and tensile strength [46] have been reported in some replicated aluminum foams, perhaps associated with differences in the density of geometrically-necessary dislocations and oxide scale thickness, and that a small effect was found in replicated magnesium foam [195]. More complete investigation of this conclusion would be possible using foams with finer porosity, but this was not pursued here due to processing difficulties associated with infiltrating and leaching finer salt particles.
3.3.2. Scaling Behavior

As discussed in Section 1.1.3, the stiffness $E$ and strength $\sigma_y$ of crystalline metallic foams are known, on the basis of dimensional arguments and empirical data, to exhibit power-law scaling behavior according to the GA Equations [64, 3], reproduced below:

\[ E = C_1 \cdot \left( \frac{\rho}{\rho_s} \right)^{n_1} \cdot E_s \]

\[ \sigma_y = C_2 \cdot \left( \frac{\rho}{\rho_s} \right)^{n_2} \cdot \sigma_{y,s} \]

where the subscripts $y$ denote yield strength, subscripts $s$ denote the properties of the solid phase, and $C_1$, $C_2$, $n_1$, and $n_2$ are fitting parameters.

Least-squares regression of initial loading stiffness data from Vit106 foams of 230 µm pore size (Fig. 4a; using $E_s$ from Table 3.1) provide $C_1 = 0.30$ and $n_1 = 2.2$, within the range of 1.8–2.2 found in crystalline metal foams but slightly above the most common value $n_1 = 2$ [3]. Although this may suggest a slightly more rapid stiffness loss with decreasing density, as might be expected given the nonuniform dissolution process underlying density decreases in Vit106 foam, use of the commonly-accepted value $n_1 = 2$ also gives an acceptable fit to the data, considering the limited number of data points. A similar analysis of strength data from foams of 230 µm pore size (Fig. 3.10) gave a scaling exponent of $n_2 = 1.9$, also within the empirical range of $n_2 = 1.5$–2.0 for crystalline metal foams, and above the commonly-accepted value of 1.5 [3]. Once again, use of the conventional scaling exponent of 1.5 gave an adequate fit to Vit106 data. Consequently, both stiffness and strength may be said to scale with relative density in approximately the same way for Vit106 as for crystalline metal foams, within the density range examined here (18–28%). Slightly more rapid loss in both stiffness and strength may have occurred in Vit106 foams, which would be in accordance with expectations related to their processing, but the difference
was not significant. The best-fit curves for stiffness and strength are shown in Fig. 3.9 and 3.10, respectively, along with those representing “conventional” behavior (i.e., $n_1 = 2$ and $n_2 = 1.5$).

The coefficients $C_1$ and $C_2$ in Eqns. 1.1 and 1.2 are related to strut geometry (e.g. cross-sectional shape and uniformity) and the concentration and severity of defects; as such, they are often referred to as knockdown factors representative of the overall mechanical efficiency of the foam architecture, as described in the Introduction. Empirical data for conventional metal foams are best fit by the values $C_1 \approx 1$ and $C_2 \approx 0.3$ [64, 3]. The lower best-fit value of $C_1 = 0.30$ found for Vit106 was in part due to the non-optimal mass distribution in the replicated structure, but also reflects the fact that initial loading stiffness is typically markedly smaller than unloading/reloading stiffness [3]. Quantitative evaluation of this statement is impossible without full reloading stiffness data, but the high reloading stiffness measured for the highest-density foam (70% larger than initial loading stiffness) indicates that the coefficient $C_1$ is not as small as suggested by the initial loading data.

Interpretation of the coefficient $C_2$ is rendered difficult in the case of Vit106 (and other amorphous metals) due to ambiguity in the definition of the solid yield strength $\sigma_{y,s}$ used to normalize foam strength data. Equating this factor to the compressive strength of Vit106 (1800 MPa; Table 3.1) gave the best-fit value $C_2 = 0.20$, while use of the tensile strength (1200 MPa; Table 3.1) gave a higher value of $C_2 = 0.31$. While the latter is comparable to the accepted value for other low-density, open-cell metallic foams, the former suggests a significant additional knockdown, and would place Vit106 foams nearer the bottom of the empirical range for $C_2$. Clarification regarding the definition of $\sigma_{y,s}$ is needed to determine ideal or optimal foam strength and also, therefore, to assess the efficiency of different architectures.

Such clarification can be made by reexamining the geometrical arguments giving rise to Eq. 1.2. Using a simple but predictive model architecture, Gibson and Ashby show that metallic foam yield stress is directly related to the fully plastic moment $M_p$ of a characteristic strut
within their model foam (Fig. 1.3) [63, 64]. This quantity, representing the maximum bending moment that can be sustained by a beam, is equal to the applied moment that causes full plasticization of the beam cross-section (a condition known as \textit{plastic hinging}). For a beam of uniform prescribed cross-section, $M_p$ can be calculated by solving the equations of force and moment equilibrium within a cross-sectional plane of the beam, given the uniaxial constitutive behavior of the beam material [90].

Although methods exist for solving this problem for many beam and loading geometries, the idealizations inherent in foam structure modeling do not justify a full analysis. Thus the problem is typically solved for uniform doubly-symmetric struts assuming elastic-perfectly plastic or power-law strain-hardening constitutive relations [62, 162]. Since amorphous metals are known to exhibit perfectly-plastic behavior in confined loading [38], it suffices for present purposes to compute the proper normalization factor for elastic-perfectly plastic Vit106 struts with uniaxial tensile and compressive yield strengths of magnitude $\sigma_T$ and $\sigma_C$, respectively; though the method is general, a strut of square cross-section (edge length $h$) is used to illustrate.

One such strut, in the fully-plasticized condition, is shown schematically in Fig. 3.11. The distance between the neutral axis and the midplane of the strut, $y_n$, in this condition is determined by equilibrium of normal forces in the tensile and compressive regions:

\begin{equation}
F_T - F_C = A_T \cdot \sigma_T - A_C \cdot \sigma_C = 0
\end{equation}

where $F_T$ and $F_C$ are the magnitudes of the tensile and compressive forces associated with each region. Introducing the tensile and compressive cross-sectional areas, $A_T = h \cdot (h/2 + y_n)$ and $A_C = h \cdot (h/2 - y_n)$, into Eq. 3.3 and solving for $y_n$ yields:

\begin{equation}
y_n = \frac{h}{2} \cdot \left( \frac{\sigma_C - \sigma_T}{\sigma_C + \sigma_T} \right)
\end{equation}
Figure 3.11. Schematic illustration of an elastic-perfectly plastic amorphous metal strut (square cross-section of edge length $h$) in the fully plasticized condition. The distance from the centerline to the neutral axis is given by $y_n$, and the tensile and compressive strengths are given by $\sigma_T$ and $\sigma_C$, respectively, indicated by the shaded stress distributions.

As expected, $y_n = 0$ when there is no tension-compression asymmetry ($\sigma_C = \sigma_T$).

With the tensile and compressive regions thus delineated, the internal moments exerted on the cross-section by these stress distributions can be calculated by reducing them to point loads, acting through the centroids (at $y_T$ and $y_C$, respectively) of the corresponding regions, and in opposition to the applied moment. At the point of collapse the internal moments just balance the fully plastic moment $M_p$:

\[ M_p = F_T \cdot y_T + F_C \cdot y_C \]  

Introducing Eqs. 3.3 and 3.4, as well as $y_T = \frac{1}{2}(\frac{h}{2} + y_n)$ and $y_C = \frac{1}{2}(\frac{h}{2} - y_n)$ into Eq. 3.5 and simplifying provides a compact expression for $M_p$:

\[ M_p = \frac{h^3}{2} \cdot \left( \frac{\sigma_C \cdot \sigma_T}{\sigma_C + \sigma_T} \right) \]  

In the absence of tensile/compressive asymmetry, $\sigma_T = \sigma_C = \sigma_y$ and Eq. 3.6 simplifies to:

\[ M_{p0} = \frac{h^3}{4} \cdot \sigma_y \]
We retrieve here the relationship used to derive Eq. 1.2. In the case of tensile/compressive asymmetry, $\sigma_y$ may be replaced by an effective yield strength $\sigma_{y,e}$ in Eq. 3.7, so that the conventional form of Eq. 1.2 may still be used. For a square strut this effective yield stress is found by equating Eqs. 3.6 and 3.7:

$$\sigma_{y,e} = \frac{2\sigma_T \cdot \sigma_C}{\sigma_T + \sigma_C}$$

(3.8)

Thus the appropriate strength normalization factor for foams with square struts is the harmonic mean of tensile and compressive strengths, a quantity which always lies closer to the tensile strength, i.e., is below the geometric mean $\hat{\sigma}_y = \frac{1}{2}(\sigma_T + \sigma_C)$; for Vit106 with $\sigma_T = 1200$ MPa and $\sigma_C = 1800$ MPa, the harmonic mean is $\sigma_{y,e} = 1440$ MPa, and the geometric mean is $\hat{\sigma}_y = 1500$ MPa.

Both square and triangular struts are common and reasonable idealizations for metal foams, and conform to microscopic observations from Vit106 foams. Repeating the analysis for an equilateral triangular strut of equal cross-sectional area (see Appendix A) gives a more complicated result due to the singly-symmetric nature of the cross section. The predicted values of effective yield strength depend on the sign of strut curvature (Eqs. A.5 and A.6) but take an average value of 1486 MPa for Vit106, slightly below $\hat{\sigma}_y = 1500$ MPa. Thus, in the absence of detailed knowledge regarding foam architecture, a reasonable approximation is to normalize amorphous metal foam strength data by a geometric mean value of the tensile and compressive yield strengths of the monolithic alloy. In light of the more precise calculations presented here, a mean of the effective yield strength for square and triangular struts (giving $\sigma_{y,e} = 1463$ MPa) is considered the most appropriate normalization factor for Vit106 foams. This value results in a best-fit coefficient $C_2 = 0.25$ for the Vit106 foams, within the range reported for crystalline metal foams [3].
3.3.3. Energy Absorption

Absorption or dissipation of mechanical energy through large strain accumulation at low and relatively constant stress is one of the most unique and important properties of foam materials, making them well suited for packaging and other energy management applications. While there are many ways of quantifying energy absorption capacity, depending on application requirements (e.g. maximum stress transfer or deflection, or minimum foam volume or weight), calculation of strain energy density (per unit volume or mass) dissipated up to densification, as a function of flow stress at 25% strain, allows direct comparison with aluminum foam data compiled by Ashby et al. [3]

As shown in Fig. 3.12, values of energy density up to densification were in the range of 16–44 MJ/m$^3$ or 16–28 MJ/Mg for Vit106 foams studied here, as compared to 3–20 MJ/m$^3$ and 6–30 MJ/Mg for aluminum foams of the same flow stress range, as indicated by the shaded region approximately representing aluminum foam data compiled by Ashby et al. [3] Therefore, as compared to aluminum foams, Vit106 foams absorbed considerably more energy per unit volume, but due to higher density, only moderately more energy per unit mass. It is notable that strain energy scales essentially, but not perfectly, linearly with relative density, on account of the varying post-yield slopes, and has no apparent dependence on pore size, despite the substantial differences in serration activity.

Although comparisons of this form are accurate, it should be remembered that high energy absorption in Vit106 foams was partly achieved through large flow stress increases past 25% strain, while many aluminum foams have smaller increases, which are often preferred in energy absorption applications to minimize stress transfer [3]. The replicated aluminum foam tested here offered a more direct comparison, since its structure and behavior closely resembled those of Vit106 foams; indeed, this foam showed an even larger relative flow stress increase than the
Figure 3.12. Strain energy absorbed by Vit106 foams up to densification, per unit foam volume, as a function of flow stress at a nominal strain of 25%. The densest sample (28%) carried high stress but exhibited lower energy absorption than expected due to premature failure. Shown for comparison are the aluminum foam produced by replication of NaCl (open circle) and the approximate range for other aluminum foams, as compiled in Ashby et al. [3]. The dashed line is provided as a visual guide to represent the trend in Vit106 data.

Vit106 foams (probably due to slower accumulation of internal damage, a topic discussed in the following section), rendering its strain energy density subject to the same increase due to high stresses beyond 25% strain. The energy absorption of this foam was 5 MJ/m$^3$ (7 MJ/Mg), substantially below that of any Vit106 foam, but close to the value that would be expected from a Vit106 foam of equal flow stress (Fig. 3.12). Due to the coincidence of the Vit106 trend with the aluminum foam envelope at low stresses, however, this is perhaps fortuitous.
3.4. Damage Evolution

Accumulation of microfracture damage during compression of Vit106 foams is evident through at least three separate observations. The most straightforward evidence comes in the form of visual observation of brittle strut fracture during compression of a nominally-ductile foam specimen, shown earlier in Fig. 3.7. Such fractures are to be expected, given that the ductility of Vit106 struts depends not only on strut morphology (in the sense that struts must be slender enough to favor bending), but also on local loading conditions (in a random structure, some struts will be subjected to axial forces even when their morphology would allow for bending).

The second indication of damage is the serrated appearance of the stress-strain curves themselves (Fig. 3.8), along with visual observation of sparks coinciding with the larger of these serrations. Given the small number of significant serrations in the foam stress-strain curves (ranging from 12 to 66) relative to the number of struts or nodes per sample (estimated to be on the order of $10^4$ for a typical sample), visible serrations represented only the most energetic fractures, most likely of struts and nodes (or small groups of struts and nodes) whose sizes, shapes or orientation relative to the load did not permit ductile deformation by stable shear band formation in bending, such as the one in Fig. 3.7.

Since flow stress within these serrations was lower than would be expected based on smooth and continuous extrapolation of the Plateau stress, the actual foams absorbed a smaller amount of strain energy than would hypothetical foams with identical flow characteristics except lacking the brittle failures responsible for serrations. This energy loss was calculated for each serration, using the difference in strain energy density between the actual serrated curve and a curve showing a linear flow stress change over the same strain range. This quantity represents a damage parameter capturing both the magnitude of the instantaneous stress drop (itself corresponding to irreversible strain in the foam due to damage) and the strain needed to recover the original stress-strain path. It is shown in Fig. 3.13 as a cumulative function of macroscopic sample...
Figure 3.13. Cumulative strain energy density lost during recovery from brittle fractures (serrations) during compression of replicated Vit106 foams. Strain energy density loss is estimated by subtracting the actual strain energy density during each serration from that of an idealized stress strain curve lacking serrations and having a linear change in flow stress over the same region.

As shown in Fig. 3.13, total strain energy lost due to foam damage increased with both relative density (with the exception of the densest sample, for which data extend only to 50% strain due to sample failure) and pore size, indicating that the fewest brittle features were present in low-density foams with fine porosity. This can be understood in terms of foam structure and the size effect that governs ductility in the struts. In these foams, decreased relative density
at constant pore size was achieved by thinning of struts at constant length; this should clearly improve ductility in Vit106 struts by making them more prone to ductile bending and buckling modes, by improving failure strains in those that already deform in this fashion, and possibly by increasing (for example, in a foam with tapered struts) the proportion of each strut having high bending ductility. A similar size effect led to changes in serration activity with pore size; for a given strut shape and arrangement (i.e., a given relative density), decreased strut dimensions associated with decreased pore size result in higher ultimate bending strains for struts, and thus in reduced serration number and severity. This rationalization of serration behavior supports the likely interpretation, given above, that serrations indeed reflect microfracture damage events.

The third piece of evidence is loss in foam stiffness with plastic deformation. Reloading stiffness was measured for several specimens as a function of strain and is shown in Fig. 3.14 after normalization by initial stiffness, i.e. by the stiffness measured closest to yield. Reloading stiffness for the densest sample (28%) immediately prior to macroscopic yield (nominal strain 1.9%, with estimated yield at 2.0%) was 2.8 GPa, ca. 70% greater than initial loading stiffness, such increases being also observed in other metallic foams [3]. Stiffness in this sample initially decreased with increasing plastic strain, reaching after a total strain of ca. 5% a minimum of about 70% of its value at yield. Thereafter the sample stiffness increased, surpassing its initial value at a total strain of about 9–10%. Though other samples showed high scatter, as stated previously and as shown in Fig. 3.14, similar trends were observed, with stiffness achieving a minimum in the range of 5–7% total strain.

In an effort to further understand the nature and severity of this internal damage, damage in Vit106 foams was studied using acoustic emissions (AE) analysis, which has proven useful in the study of similar fracture processes in monolithic and composite materials [32] as well as porous rocks [76], cellular ceramics [102], and more recently low-density crystalline metallic foams [91]. Through analysis of AE activity generated by internal microfracture, it will be shown...
Figure 3.14. Reloading stiffness for a foam with 230 µm pore size and 28% relative density as a function of plastic strain. Data were normalized by the stiffness immediately prior to yield (1.9% strain). Also shown for completeness are similar data from other foams of equal pore size but varying density, showing less precision but similar overall behavior.

that deformation in amorphous metal foams involves substantial damage (relative to ductile Al-Si foam), and that this damage resembles, in its AE signature, microfracture damage within brittle ceramic foams (including devitrified amorphous metal foam). Nonetheless, stabilizing mechanisms are active in the amorphous metal foam which allow high average compressive strains (ca. 80%) without final failure, so that macroscopically their compressive behavior is hardly distinguishable from that of ductile crystalline metal foams.
3.4.1. Experimental Methods

A Vit106 foam sample processed using a BaF$_2$ pattern of 150–212 µm particle size with final relative density 24%, machined to a diameter 3.5 mm and height of 7.6 mm, was selected for AE analysis; its fully amorphous state was verified by XRD before and after testing (Fig. 3.15a). A second amorphous Vit106 sample, processed from a BaF$_2$ pattern of 300–355 µm particle size with final density 17%, diameter 3.9 mm, and height 5.7 mm, was vacuum annealed at 450°C for 3 hours to induce devitrification, in accordance with the Vit106 TTT diagram [134]. The sample dimensions were remeasured after annealing to ascertain that no dimensional changes associated with viscous flow occurred during annealing in the supercooled liquid region. The foam was also examined after compression by XRD confirm crystallization (Fig. 3.15b).

In addition, a pure aluminum foam of comparable dimensions to the other specimens (3.9 mm diameter, 7.9 mm height, relative density 28%) was made by infiltration and dissolution of NaCl patterns prepared from ca. 500 µm NaCl powders. Finally, eutectic Al-Si (approx.
Figure 3.16. Scanning electron micrograph showing a representative salt-replicated foam structure (in this case, eutectic Al-Si). The pore size and relative density of this foam were 150-212 µm and 42%, respectively.

Al–12.6 wt.% Si) foam (3.5 mm diameter, 7.7 mm height, relative density 42%) was produced by replication of 150–212 µm NaCl powders. A scanning electron micrograph of this Al-Si foam is shown in Fig. 3.16; the structure of this sample was very similar to the structure of the other (i.e., pure aluminum and Vit106) samples and is broadly representative of replicated foams, showing high uniformity in density and pore size and pronounced nodes.

Quasistatic uniaxial compression was performed on all samples using a displacement-controlled screw-driven load frame (Fig. 3.17). A nominal strain rate of 5·10^{-4} s^{-1} was used everywhere, except that higher anticipated acoustic event rates motivated the choice of a lower strain rate of 10^{-4} s^{-1} for crystalline Vit106. To account for this difference, acoustic data are presented as events per unit strain, rather than per unit time. Compression was applied using hardened tool steel pistons with a lubricated steel sleeve ensuring parallelism, and average foam strain was determined from crosshead displacement after correction for load-train compliance using calibration data taken prior to and after each test. Due to the presence of coupling fluid between the
Figure 3.17. Schematic diagram illustrating the experimental setup for measurement of foam acoustic and mechanical data.

Sample faces and pistons, foam samples were subject to some realignment during initial loading, causing the lowest strain data to be inaccurate.

Acoustic activity was measured during compression by three broadband piezoelectric transducers (Deci Model SE9125-M) and recorded after pre-amplification (34 dB) using a Vallen AMS3 acoustic emissions test system (Fig. 3.17). One transducer (transducer number 2) was fixed to the upper piston using a rubber o-ring, while the remaining two (numbers 1 and 3) were magnetically fixed to the machine platens. All transducers were coupled using silicone grease. The amplitude detection range was 33.7–99.9 dB relative to a 1 μV transducer output before pre-amplification, with all events greater than 99.9 dB in amplitude recorded as 99.9 dB. Time resolution and rearm time for all transducers were 0.1 μs and 3.2 ms, respectively. At each detected event, crosshead displacement and load were simultaneously recorded from the load frame. In order to estimate noise generated by friction in the gauge region (for example, between the aligning sleeve and pistons), acoustic activity was also recorded during motion of the crosshead without the samples, giving a negligible average event rate of 24 (expressed as events per unit macroscopic sample strain, using the gauge length of the amorphous specimen as a reference). Frictional noise between foam struts and piston surfaces was estimated using the
pure aluminum foam, for which the average event rate was again negligible, 10 per unit strain. Following these tests, it was concluded that extraneous events (i.e., those not originating from inside the foam samples) during compression were negligible relative to the observed event rates, which were on the order of 20,000 in both Vit106 foam samples and 800 in the Al-Si sample.

3.4.2. Mechanical Properties

Compressive stress-strain curves for the amorphous Vit106, crystalline Vit106, and Al-Si foams are shown in Fig. 3.18a-c. The amorphous sample (Fig. 3.18a) exhibited a linear loading region, followed by yield near 27 MPa and a slowly-rising Plateau region punctuated by sharp serrations and terminated at high strains by densification, consistent with the general compressive characteristics of other amorphous Vit106 foams of various porosities and pore sizes, presented above. Deformation was macroscopically uniform throughout the test without visible crush bands, and the sample was found to be intact (except for minor spalling of material from the edges) after unloading from a final average compressive strain near 80%.

By contrast, no quasi-elastic loading region was evident for the crystalline sample (Fig. 3.18b), and accordingly a yield stress could not be accurately defined. Flow stress was highly uneven throughout the whole strain range and oscillated around a mean value of about 2 MPa, taking a maximum value of 5.5 MPa, well below even the initial yield stress of the amorphous sample. Deformation proceeded by unstable fracture and crushing near the pistons, as indicated by continuous release of numerous sub-millimeter foam fragments from these portions of the sample. Thus, the use of a macroscopic or average strain to describe deformation in this foam is not strictly appropriate, but the term has been retained for purposes of comparison in Fig. 3.18.

The eutectic Al-Si foam (Fig. 3.18c) showed linear loading and gradual yielding at stresses in the range of 5–10 MPa, followed by a smoothly increasing Plateau region and gradual densification. Deformation of both pure aluminum and eutectic Al-Si foams was stable and visibly
uniform, consistent with prior observations (above, and in Ref. [161]), with little noticeable spalling and no evidence of serrations or final fracture in either case.

The total acoustic events generated by the amorphous and crystalline Vit106 foam samples during compression to near 80% nominal strain were approximately 24,800 and 19,200, respectively, while the eutectic Al-Si foam generated only about 650 events over a comparable strain interval and the pure aluminum foam generated negligible acoustic activity, as mentioned previously. Estimating the number of pores in each sample (noting that the pores are generally angular in shape rather than spherical) as the total pore volume $V \cdot p$ (where $V$ is the total sample volume and $p$ the volume fraction of porosity) divided by the pore volume $d^3$, where $d$ is the median pore size (180 $\mu$m for the amorphous Vit106 and the Al-Si foams and 320 $\mu$m for the crystalline Vit106 foam), the total events per pore are estimated as 2.0 for the amorphous and 9.7 for the crystalline Vit106 sample, as shown in Fig. 3.18a,b. The corresponding value for the Al-Si foam was again much lower, about 0.1 (Fig. 3.18c). While the exact number of struts per pore depends on foam architecture, it can be stated that a 3D array of cubic cells, each defined by struts comprising its twelve edges and with each such strut shared between four adjacent coplanar cells, has three struts per pore. Thus, it is estimated roughly that during compression to 80% nominal strain the amorphous Vit106 foam exhibited a number of fracture events comparable to, or below, its total number of struts; by contrast, the crystalline Vit106 sample appeared to sustain multiple fractures per strut under the same conditions, and the Al-Si foam showed significant fracture in only a small proportion of its struts. In interpreting such a result, it is important to recall, however, that direct comparison of event numbers between Vit106 and Al-Si foams may be complicated by differences in internal damping coefficient and transmission properties at the foam/piston interface. The same limitations also apply to direct comparisons of event amplitudes between samples.
Figure 3.18. Compressive stress-strain curves for (a) amorphous Vit106 foam; (b) crystalline Vit106 foam; and (c) eutectic Al-Si foam. Also shown are cumulative AE events, normalized by the estimated number of pores in each sample.
3.4.3. Quantitative Acoustic Emission Analysis

Evolution of acoustic activity caused by microfracture within porous solids is often quantified using the concise framework originated by Gutenberg and Richter [69] in their analysis of earthquake magnitudes, a reflection of the view that large-scale (i.e., geological) and small-scale (i.e. microfracture) acoustic events share a common origin in cascades of strain energy release events within self-organized critical (SOC) systems [76, 145, 55, 5]. The cumulative amplitude distribution of the individual events comprising the cascades of a SOC system takes the form of a power law; in the case of earthquakes, this is expressed through the Gutenberg-Richter (GR) relationship:

\[ \log(N(W)) = a - b \cdot W \]  

where \( N(W) \) is the cumulative number of events having magnitude greater than or equal to \( W \) and \( a \) and \( b \) are the seismic GR parameters. Equation 3.9 can be applied directly to the analysis of AE data provided that the seismic \( b \) parameter is multiplied by twenty to account for the fact that the amplitude of AE events is recorded in decibels rather than logarithmic peak amplitude; this modified value is referred to as the AE-\( b \) parameter [5].

Application of the GR relationship to AE data is widespread in the study of microfracture in rocks [76] and model brittle materials like plaster [145, 55] and fiberglass [55], and has been extended successfully to porous brittle solids such as silicate glasses [5, 125] and alumina [5]. Its usefulness in these contexts rests on correlation of the GR parameters to internal microfracture mechanisms, and efforts have been directed towards quantitative prediction of the GR parameters in porous brittle solids using material constants influencing microfracture [5]. While quantitative analysis of this sort depends on data that remain unavailable for Vit106, evolution of the GR parameters during foam compression still provides useful insight into the evolution
of internal microfracture mechanisms. The GR parameter $a$ in Eqn. 3.9 essentially gives (logarithmically) the total number of AE events in the population. It must be noted, however, that the $a$ parameter represents a hypothetical zero-amplitude intercept for the distribution, while real AE data are truncated by detection thresholds; thus the relationship of $a$ to measured event rate is non-quantitative and in practice may be influenced by the fitted value of AE-$b$, rendering the latter parameter more reliable. The AE-$b$ parameter quantifies the exponent of decay of the amplitude distribution with increasing amplitude; thus, large values of AE-$b$ reflect AE activity with few high-amplitude fractures, while smaller values of AE-$b$ reflect activity with comparatively more highly-energetic fractures. Values of $a$ vary widely depending on the size of the population being considered and hence are not generally comparable across experiments, but values of AE-$b$ are far more general, with typical values in the range 0.4–2 [5].

Analysis of AE data according to the GR relationship, Eqn. 3.9, was performed for both the amorphous and crystalline Vit106 foam samples as well as the Al-Si foam. In all cases, as well as in the subpopulations discussed later, the distributions showed deviations from Eqn. 3.9 indicative of lower numbers of high-amplitude events than would be predicted by a power-law relationship, as shown in Fig. 3.19. Deviation at high energies has been noted in other AE studies [25, 145, 55, 5] and can occur for several reasons.

At a fundamental level, it results from the correlation between fracture event energy and the underlying length scale of the associated fracture [25, 76]. Power-law behavior in SOC systems is a reflection of self-similarity, and therefore may be expected to persist only to the extent that self-similarity also persists; if an upper limit on fracture length scale (and thus energy) is fixed, for example by the physical dimension of the sample or proximity to sample surfaces, then a similar limit is imposed on the extent of power-law behavior. Thus deviation of the GR distribution in the region of high event energy may reflect the fact that some events were generated by damage processes having spatial dimensions comparable to those of the sample,
Figure 3.19. Cumulative amplitude distributions for AE events studied in this work. (a) Full AE populations from the amorphous and crystalline Vit106 foams and the Al-Si foam. (b) Three subpopulations from the amorphous Vit106 foam, representing the strain intervals 10–15%, 30–35% and 70–75%. All distributions show linearity (i.e. power-law scaling) at lower amplitudes with deviation at high amplitudes. Dashed lines indicate fits using the GR relationship, Eqn. 3.9.
or taking place at locations sufficiently close to the sample boundaries that the events become interrupted, in the same way that seismic activity is affected by the finite thickness of the seismogenic crust of the earth [76] or model earthquake results deviate due to finite model sizes [25].

Similar power-law deviations may also result if damaged regions begin to impinge and interact, or through saturation effects associated with event counting at high amplitudes and rates [5, 138]. The likelihood of significant high-amplitude events being lost due to hardware saturation effects was low in the present case, however, in light of the fact that high-amplitude deviation was apparent (if less pronounced) in the Al-Si foam despite much lower event rates and a lack of any events approaching the saturation amplitude (99.9 dB). To avoid finite sample size effects and lost events at all values of strain, and to facilitate comparison between Vit106 and Al-Si foams, GR parameters were fitted using data of amplitude <65 dB.

3.4.4. General Microfracture Mechanisms

The value of AE-\textit{b} obtained by analysis of the entire population of AE events from the amorphous Vit106 foam (whose amplitude distribution appears in Fig. 3.19a) was 0.42±0.01, near the lower bound of commonly-observed AE-\textit{b} values [5]. Low values of AE-\textit{b} indicate a slow decay of the amplitude distribution, i.e. a broad underlying distribution of fracture energies. That such a broad distribution should exist in the Vit106 foam is not immediately apparent, in light of the fact that amorphous metals typically show little strength variation in monolithic form. However, it has been noted above that Vit106 struts within a foam fail both uniaxially and in bending, allowing (due to tensile-compressive asymmetry) for strut strengths anywhere between the tensile and compressive uniaxial strengths. This natural distribution, combined with the inherent distribution of strut dimensions in any foam architecture, contributed to the low measured value of AE-\textit{b} in the amorphous foam.
The value of AE-\(b\) measured in the crystalline Vit106 foam (Fig. 3.19a) was nearly identical, 0.44±0.03, indicating an equally broad strength distribution (though, as noted above, the absolute amplitudes or strut strengths are not generally comparable between samples). The source of strength distribution in the crystalline sample is the large fraction of brittle intermetallics phases resulting from the devitrification treatment, which, unlike the pure amorphous phase, are subject to natural strength statistics as well as substantial tensile-compressive asymmetry. A similar interpretation applies to the relationship between AE-\(b\) values in amorphous Vit106 foam and those measured in other highly-porous brittle ceramics expected to show strength-scaling or Weibull behavior. In glassy SiO\(_2\) having relative density 28–32%, AE-\(b\) values were found to lie in the range 0.38–0.63, while in Al\(_2\)O\(_3\) of relative density 29–31% the range was 0.34–0.52, both comparable to the measured values in Vit106 [5].

According to such an explanation, the narrower strength distribution among more ductile Al-Si struts (which show little or no tensile-compressive asymmetry) should lead to a narrower distribution in amplitude distribution, i.e. to a higher value of AE-\(b\). Indeed, the value of AE-\(b\) for the Al-Si foam, 1.44±0.08, was significantly above the values characterizing the Vit106 and ceramic foams (Fig. 3.19a) [5]. This higher degree of uniformity should allow for more gradual and diffuse damage accumulation by allowing fractures to nucleate more uniformly within the structure and by diminishing the number of anomalously-strong struts whose failure might initiate a localized damage cascade in the surrounding material. Consequently, it is suggested that high AE-\(b\) values (i.e., damage dominated by these weaker failures, such as in the Al-Si) represent diffuse damage accumulation, while lower AE-\(b\) values reflect degrees of damage localization. Such a conclusion is in line with observations from the brittle ceramic foams described above; in these systems, higher values of AE-\(b\) were found in weaker samples that showed some gradual damage accumulation, while stronger samples with lower AE-\(b\) failed more catastrophically [5]. From this standpoint the difference in AE-\(b\) between ductile Al-Si
foam and the more brittle Vit106 and ceramic foams reflects a greater tendency towards damage localization in the latter, a process that in many cases foreshadows final failure.

### 3.4.5. Damage Evolution

In order to quantify evolution of the internal damage process during compression of the amorphous Vit106 foam, and thereby identify the strains at which the predicted damage localization may be occurring, AE data were separated into subpopulations representing 5% intervals of applied strain and the cumulative amplitude distribution of each subpopulation was fitted to the GR relationship, Eqn. 3.9. Three such distributions, corresponding to three different 5% strain intervals, are shown in Fig. 3.19b to highlight variations in AE-\(b\), i.e. in the slope of the low-amplitude region of the distributions. Similar analysis using the Al-Si foam was, unfortunately, not possible because the low event rate in this sample did not permit statistically-reliable conclusions to be made using comparable subpopulations.

Evolution of the total events in each interval and the AE-\(b\) parameter for amorphous Vit106 foam are shown in Fig. 3.20 as functions of applied strain, with macroscopic yield indicated by the dashed lines. As shown in Fig. 3.20a, the measured events in each 5% strain interval decreased from a maximum just after yield through the densification region, albeit with large variations in the early Plateau region. This behavior is generally consistent with a damage accumulation mechanism in which fracture occurs first in the (large) population of features having low or average strength, and tending at higher strain towards sampling of the (smaller) high-strength tail of the strength distribution, with large variations likely resulting from the occasional generation of intense localized damage (as described below). A similar but more stable trend was evident for AE-\(b\) at low and intermediate strains, but whereas event rates continued falling within the densification region, the amplitude distribution of these events reverted towards higher AE-\(b\) (Fig. 3.20b) at the highest strains.
Figure 3.20. Evolution of acoustic activity in amorphous Vit106 foam with increasing applied strain, in 5% intervals. (a) Total events in each interval. (b) The GR parameter $AE-b$ characterizing each interval. Yield is indicated in both plots by vertical dashed lines.

Progression of the fracture mechanism from high $AE-b$ values in the quasilastic loading region towards lower $AE-b$ after significant deformation indicates an underlying evolution of the microfracture process from one consisting of primarily low-energy fractures towards one consisting of a greater proportion of energetic fractures. In keeping with the interpretation of the previous paragraph, this corresponds to sampling primarily of the (large) population of weaker struts at low strain, with a gradual evolution towards sampling of the (smaller) population of strong struts as well (note that power-law scaling ensures that the total events, Fig. 3.20a, are always dominated by low-energy fractures and hence do not reflect this trend as
clearly). Similarly, reversal of the trend at the highest strains (60–75%) indicates evolution back towards fewer (Fig. 3.20a) and less energetic (Fig. 3.20b) strut fractures, probably reflecting both exhaustion of the strongest portion of the strut population and the increasing effects of confinement associated with densification. Geometric confinement is known to increase ductility in amorphous metals, and might therefore have imparted improved fracture resistance to any struts surviving intact to such high strains [202, 37]. It is also possible, although experimental verification was not attempted, that large deformations and stresses led to friction welding among struts in the foam at large compressive strains.

For the reasons given in the previous section, it is further concluded that intervals of strain characterized by high AE-\(b\) values (i.e., dominated by these weaker failures) represent diffuse damage accumulation, while those intervals showing higher AE-\(b\) reflect instances of damage localization. Thus the early progression of damage was from diffuse to localized damage, a familiar progression in materials or systems failing by a damage accumulation mechanism in which the weakest regions fail first, followed by the stronger regions; however, unlike most such systems, the Vit106 foam did not fail upon failure of its strongest components, but rather reversed course towards diffuse damage again. The mechanism of this reversal is rationalized easily through the effects of confinement, but it remains noteworthy that the foam maintained integrity long enough for confinement effects to come into play. Its ability to do so (where, by comparison, comparable SiO\(_2\) and Al\(_2\)O\(_3\) foams failed at much lower strains despite having nearly identical AE signatures [5]) indicates that even severe and relatively localized damage events could be accommodated by the structure without overall failure, an ability that derives not only from the presence of a restraining network of ductile struts but also from a stabilizing mechanism associated with the foam structure itself.

Accommodation of the fracture of brittle struts in amorphous Vit106 foam by the surrounding networks of ductile struts was facilitated by the formation of point contacts between the
enlarged nodes that connect struts within the replicated foam structure (Fig. 3.16). These
large nodes, which are characteristic of replicated foam structures due to the irregularity of
salt particle packing [162], were brought into contact with struts and neighboring nodes at
relatively low local strains and thereby limited the severity of local pore collapse that would
normally accompany energetic strut failures. In doing so, they also minimized the destabilizing
effects that collapse of a pore would exert on neighboring struts, damping the propagation of
large spatially-limited cascades of pore failure that are often manifested in cellular materials as
 crush bands or macrocracking. Additional evidence of the importance of such contact forces
within replicated amorphous Vit106 foam takes the form of early increases in reloading stiffness
(which in the absence of such forces should decrease rapidly until final densification in response
to microfracture damage) after low strains of only 5–10% after yield, by the rapid increase of
flow stress throughout the Plateau region, and by a lack of visual evidence for large-scale crush
bands during deformation, all of which were also observed to some degree in replicated alu-
minum foam [162, 161]. The existence of such mechanisms is believed to explain the ability
of the amorphous Vit106 foam to undergo periods of localized fracture similar in every way
to those seen in brittle crystalline Vit106 and ceramic foams, without the macroscopic failure
observed in those cases. The details of how such localized damage was nucleated and damped
in the amorphous Vit106 foam is considered in the following section.

3.4.6. Stress Serrations

A distinguishing feature of amorphous Vit106 foam deformation is the presence of visible ser-
rations in the Plateau region of the stress-stress curve, which were described earlier. These
serrations, which were present in neither the pure aluminum nor Al-Si foam, clearly represent
large damage events of the sort discussed previously, but it is unclear from stress-strain data
alone whether the underlying process involved a single (or few) highly energetic fractures or the
cooperative fracture of many struts involved in a diffuse cascade, and to what extent (if any) these serrations are indicative of crush band nucleation. Both issues may be approached through GR analysis, as described below.

To isolate fracture processes preceding major serrations (i.e., serrations involving a relative loss in flow stress of 5% or more, of which there were twelve in the amorphous foam; no distinct serrations could be identified in the crystalline foam due to highly irregular flow stresses everywhere), the population consisting of the last 100 AE events preceding each serration was analyzed. The average event rate during these periods was elevated, ca. 33,000 per unit strain compared to an average of 25,000 for the entire test, and the parameter AE-b for the pre-serration population took the value 0.53±0.05. Since serrations were quite uniformly distributed within the region of low AE-b shown in Fig. 3.20b (the first and last serrations occurred around 7.5 and 32.1% strain, Fig. 3.18a), and since this value of AE-b was significantly higher than any of the values in that region (the highest of which was 0.46±0.01), this result is not simply an artifact of the larger evolution of behavior described in the previous section. The results indicate instead that immediately prior to the major serrations, the microfracture process consisted of a large number of relatively low-energy fractures. Such behavior can be interpreted as the accumulation of diffuse damage, in which the concentration of small damaged sites increases with strain until several such sites suddenly link, causing a macroscopic damage event, visible as a serration on the stress-strain curve. As described above, the constraining network of ductile struts and the formation of contact forces during such events prevented immediate sample failure at the serrations, though flow stress recovery was not immediate.

The last event recorded before each serration stress drop was typically of very high-amplitude: of the twelve serrations considered, eleven were immediately preceded by a saturating event of 99.9 dB (Fig. 3.21). Over the full course of the compression test, however, there were 62 additional saturating events that did not precede any visible serrations. This suggests the observable
serrations may have had actual amplitudes well in excess of that required to cause saturation in the acquisition hardware, and is in keeping with visual evidence of sparks accompanying serrations. Still, the average of the five events preceding each of the serrations was only 48.7 dB, so that the immediate source of serrations was the highly energetic fracture of a single strut or small number of struts, as compared to the collective fracture of a large number of weaker struts such as characterized the pre-serration periods. Therefore, linking of the smaller damage sites produced during the pre-serration periods into a single macroscopic flaw was ultimately restricted by the persistence of a single (or small number of) strong ligaments, and serrations resulted from the sudden failure of these ligaments and corresponding collapse of the surrounding regions of diffuse damage. Collapse produced sudden deflections that become manifested as stress drops during displacement-controlled compression tests.

Interpretation of stress serrations as indicative of damage localization is consistent with AE observations in Bentheim sandstone (porosity 22.8%), which showed similar behavior defined by short bursts of AE activity concurrent with stress serrations in an otherwise increasing stress-strain curve [11]. Micrographic analysis of these sandstones clearly showed formation of discrete and large-scale compaction bands resembling the crush bands common to metallic foams. Whether the localized damage regions in amorphous Vit106 foam followed conventional crush banding behavior, in the sense of radiating uniformly into the gauge length from a single source band, or whether serrations corresponded to formation of distinct bands in separate regions of the gauge length, is unclear from the AE data. Clarification could be offered by spatial localization of AE events using triangulation techniques or by microtomographic reconstruction of the foam at various stages of deformation.

Events recorded during the periods of stress recovery following each stress drop were generally low in magnitude and were characterized by an AE-$b$ value of 0.47±0.01. This value was higher than the overall values characterizing the early Plateau region where the serrations occurred
Figure 3.21. Strain dependence of acoustic event amplitude (open circles, right scale) and stress (solid squares and line, left scale) in a region with two stress serrations, showing high-energy events initiating the serrations (indicated by arrows; the horizontal dashed line shows the hardware saturation limit), followed by decreased acoustic activity during stress recovery.

(Fig. 3.20b), indicating a fairly low-energy fracture process during recovery. Event rates during recovery were less than the overall average event rate by a factor of three, as exemplified by plotting AE events alongside a small serrated portion of the stress-strain curve (Fig. 3.21). However, these rates were still well above any of the noise levels observed in other tests, and more than a factor of three higher than event rates measured during deliberate unloading/reloading cycles not following serrations.

Since the Kaiser effect, i.e. the cessation of acoustic activity during unloading and reloading at stresses below that from which the material was unloaded, has been near-perfectly represented in monolithic amorphous metals \([7, 185]\), this AE activity during recovery was likely the combined result of small numbers of strut fractures resulting from redistribution of internal stresses, as well as frictional noise generated between recently broken foam features. Frictional
events may have been especially numerous during recovery due to the large number of contacts formed during localized collapse at the serration, and the relatively large strut reorientations that likely accompanied stress redistribution. Accordingly, it is concluded that some accommodation certainly took place in the foam during recovery from large fracture events; these accommodation events were independent, however, of the immediate mechanism by which the initial high-energy fracture cascade was terminated, since AE events during recovery occurred only after comparatively large intervals of time and strain following the stress drop. This result is consistent with the view that additional mechanisms besides fracture (e.g. plasticity in nearby ductile struts, and the formation of new internal contacts) were responsible for preventing final failure in the amorphous foam.

A larger perspective on the place of these results within the larger field of AMF is deferred until the final chapter; however, it is worth reiterating here the essential, and perhaps surprising, conclusion that replicated Zr-based AMF can be capable of compressive plastic strains on par with foams made from ductile crystalline metals (despite the accumulation of internal damage during compression). This conclusion is the most important of those made in this work, and to the author’s knowledge it has not yet been demonstrated or reproduced by any other researchers; in most of these other results, the materials in question were of a relative density that gave qualitatively very different mechanical behavior. While these other forms of behavior are of interest in their own right, they are not “foam-like” and thus they most likely pertain to a different set of eventual applications. For applications requiring mechanical behavior of the sort associated with crystalline metallic foams (most notably, energy absorption materials), the highly-ductile Vit106-based materials described in this chapter remain the only available option.
CHAPTER 4

Syntactic Amorphous Metal Foams

Foam materials produced by the replication method described in Chapter 3 are necessarily open-cell, due to the need for removal of the pattern material after solidification, and are therefore targeted for applications in which open-cell structures are desired. The method described in this chapter for production of closed-cell AMF closely parallels this first method, but is targeted for roles where isolated, closed porosity is needed. The only major difference between this and the former method is that the infiltration pattern material in this discussion has sufficiently low density and reactivity that it may safely be left inside the material during and after solidification.

The pattern material used in this chapter consisted of a loosely-packed bed of small hollow spheres (often referred to as cenospheres), and the resulting foams are conventionally referred to as syntactic foams. The majority of syntactic foams in the literature consist of glass cenospheres in polymer matrices [33, 68, 99]; syntactic foams consisting of alumina [98], silica/mullite [8], and steel [153] cenospheres in Al-alloy matrices, as well as carbon cenospheres in magnesium matrices [71], have also been reported in the literature, however. While polymer-matrix syntactic foams are mostly used as flotation materials [33], syntactic metallic foams are targeted for structural applications, mostly related to their extraordinary energy absorption [78, 71, 98, 8, 153].

4.1. Processing

Hollow carbon microspheres (Carbospheres, Inc., Fredericksburg, VA) with diameter 25–50 µm and wall thickness 1–10 µm were used in the production of syntactic Vit106-based AMF
specimens. In the as-received condition, the majority of these spheres were found to be either broken, or sufficiently porous that their walls could be easily infiltrated by Vit106. Accordingly, as-received spheres were suspended in acetone and centrifugally sedimented for 2–3 minutes several times to isolate intact spheres. Isolated intact spheres were cleaned ultrasonically in acetone and methanol, and then vacuum dried at the processing temperature (975°C) for one hour to remove volatile components. A bed of dried spheres (ca. 5 mm diameter and 8 mm height) was then placed into the tip of a stainless steel infiltration crucible (with dimensions like those described in Chapter 3), and a thin perforated graphite spacer disk (ca. 2 mm thickness) was placed above the bed. The tube was given a light slurry coating of high-purity Y$_2$O$_3$ to minimize dissolution of the carbon microspheres into the steel, and the whole crucible (tube, Y$_2$O$_3$ coating, sphere bed, and spacer) was then preheated to 975°C under high vacuum (4·10$^{-3}$ Pa). After 30 minutes of equilibration, a prealloyed charge of amorphous Vit106 was magnetically lowered into the hot zone and allowed to melt for three minutes. This melt was then infiltrated into the microsphere bed using 153 kPa of 99.9996% pure Ar gas. After a 45-second infiltration period, the infiltrated sample was brine quenched.

4.2. Structure

Infiltration was generally found to be uniform only in the lowest 3 mm of the sphere bed, with spheres above this region tending to segregate towards the crucible walls. Although the uniform region was sufficient for the results described below, it was nonetheless problematic because it forbade machining of a compression specimen for measurement of ductility and other properties.

The reason for this nonuniformity is not entirely clear; however several likely explanations can be proposed. The first of these is that during evacuation and/or drying of the sphere bed just before infiltration, desorbing atmospheric moisture caused disruption of the powder bed.
Although evacuation and heating steps were done very slowly to minimize this disruption (a
case observed throughout this work during infiltration of fine, low-density or hygroscopic
reinforcements and referred to as fluidization), experimentation showed that some redistribution
of the spheres was nearly inevitable. In all infiltration tests, a small amount of spheres were
recovered from the infiltration tube walls above the sample after infiltration, confirming that
fluidized spheres can redistribute over lengths of several millimeters or more.

A second explanation is that the low-density spheres were redistributed by convection during
the infiltration process itself. Given the “bowl–shaped” distribution of spheres at the top of the
pattern, where infiltration begins, it is possible that motion of the melt pushed spheres at the
top of the pattern away, only infiltrating them where confinement of the bed at the bottom of
the crucible held the spheres in place. This phenomenon, also encountered several times and
related to the general phenomenon of viscous fingering, was observed in infiltration beds that
were not sufficiently well-packed (or sintered) to prevent preferential intrusion of the melt into
packing flaws rather than into the interstices of the pattern.

A third explanation is that the spheres floated upwards through the melt under the influ-
ence of gravity, after being initially infiltrated in a uniform manner. The plausibility of this
explanation, unlike the previous two, can be estimated quantitatively as follows. Density-driven
motion of an isolated circular particle through a viscous liquid under the influence of gravity is
described by Stokes’ Law [168]:

\[
\begin{align*}
(4.1) \quad v &= \frac{2gr^2(\rho_l - \rho_s)}{9\eta} \\
\end{align*}
\]

where \(v\) is the velocity of the particle, \(r\) is the particle radius, \(\rho_l\) and \(\rho_s\) are the densities of the
liquid and the solid particle, respectively, \(g\) is the gravitational constant, and \(\eta\) is the viscosity
of the liquid. The largest velocity corresponds to the largest particles, so \(r\) is taken to be 25 \(\mu\)m.
Because the spheres used for infiltration were those which were buoyant in acetone \((\rho = 0.79\)
\( \rho_s \) can be approximated as 0.79 g/cm\(^3\) (this is consistent with calculations based on mean sphere diameter and wall thickness, but these are less accurate). The density of a glass-forming melt is approximately the same as that of the solid amorphous phase, such that \( \rho_l = 6.8 \text{ g/cm}^3 \) (Table 3.1). The viscosity of the Vit106 melt at 975°C may be calculated from literature data as 54.5 mPa·s \([133]\). The expected particle velocity, according to Eqn. 4.1 is therefore ca. 150 \( \mu \text{m/s} \). For a set of interacting spheres with a packing density of 0.6 (approximately the packing density of the spheres; see below), however, this velocity is reduced according to the empirical relationship of Richardson and Zaki \([168]\), to \( v \cdot (1 - 0.6)^5 = 1.7 \mu \text{m/s} \). At this velocity the spheres should be able to travel approximately 50 \( \mu \text{m} \) during the lapse between infiltration and solidification. Although this calculation is only approximate, it clearly shows that gravitational effects cannot explain redistribution of spheres over millimeter scales, such that fluidization and fingering are the most likely explanations.

Figure 4.1a shows an optical micrograph of the lower region of a syntactic Vit106 foam produced by this method. The figure demonstrates that the foam structure within this lower region is uniform across the entire cross-section, with no evidence of sphere agglomeration, porosity due to poor wetting, or other macroscopic defects. Figure 4.1b shows a higher-magnification image of the same sample and highlights some of the features visible in the foam microstructure, which include irregularly-shaped spheres, infiltrated spheres, and sphere fragments, found among a majority of hollow, uninfiltreted spheres. Infiltrated necks as narrow as 1 \( \mu \text{m} \) were found between particles, indicating excellent wetting, though occasional uninfiltreted necks were also present. Analysis of several hundred particles reveals that the proportion of broken and infiltrated spheres is ca. 1\%, and consequently these flaws only marginally impact overall density; the proportion of misshapen spheres is much higher, ca. 18\%, with the remainder (81\%) being roughly spherical (in the plane of the image, at least) and intact.
Figure 4.1. Optical micrographs showing the structure of syntactic Vit106 foam: (a) low magnification image demonstrating foam uniformity; (b) magnified image of the polished surface, showing microscopic foam structure. Misshapen carbon microspheres are visible, as is a sphere wall fragment (indicated by arrow). Good wetting is inferred from the lack of interparticle porosity.

The net density of the foam, measured by helium pycnometry, is 3.4±0.2 g/cm³, corresponding to a relative density of 50±3%. Assuming an average density (see above) of 0.79 g/cm³ for the spheres, the calculated Vit106 volume fraction of Vit106 is 43%; this is in agreement with the results of image analysis, which showed a Vit106 fraction of 41±2%. The net relative density is, of course, higher than the Vit106 volume fraction due to the additional mass of carbon. While the relative density is required for engineering design, the BMG fraction is expected to be more relevant to the mechanical properties of the foam, since the highly irregular thickness of the microsphere walls makes them unlikely to contribute appreciable strengthening.

4.3. Glass Formation

Figure 4.2 shows XRD data verifying the amorphous structure of the foam and demonstrating the presence of ZrC, which was not visible using either optical or backscattered scanning
electron microscopy. Submicron interfacial ZrC has been observed in studies of similar Zr-based alloys with carbon fibers and carbide particulates, where it was concluded that the formation of ZrC does not significantly affect the glass-forming ability of the host alloy\cite{26, 96}. In a separate study, it was shown that interfacial ZrC allows for the reactive wetting of the BMG alloy Zr$_{41.2}$Ti$_{13.8}$Cu$_{12.5}$Ni$_{10.0}$Be$_{22.5}$ (Vit1) onto carbon substrates above 925°C \cite{166}. The present low-pressure infiltration of a viscous Vit106 melt around small carbon microspheres likely relies on the reactive wetting resulting from the presence of ZrC.

A much less pronounced peak is also visible in Fig. 4.1b, which does not correspond to ZrC. This peak corresponds to a major reflection of Nb$_2$C, which is only slightly less stable than ZrC and may therefore have formed in small amounts \cite{155}. However, the small peak size and lack of higher-order reflections (i.e., low volume fraction of the originating phase) makes it impossible to identify conclusively.

Results of differential scanning calorimetry (DSC), performed with a heating rate 0.33 K/s under argon on a small section of foam and an amorphous Vit106 sample taken from the same ingot used to make this foam, are shown in Figure 4.3. The thermogram for dense Vit106 exhibits a glass transition endotherm and two-stage crystallization exotherm appearing at 418°C and 473°C, respectively. These values are in accordance with those reported elsewhere for bulk Vit106 \cite{26}. The Vit106 foam shows the same two-stage crystallization behavior as the unprocessed Vit106, at nearly the same temperature (T$_x$ = 477°C). The heat of crystallization of the dense alloy is estimated at 48 J/g, which matches within 7% that of the foam (45 J/g) after adjusting for its lower Vit106 content. From these facts, it is concluded that the fundamental crystallization pathway of the Vit106 matrix is unchanged in the presence of carbon microspheres and that the foam is processable as a supercooled liquid at temperatures below ca. 473°C, similar to bulk Vit106.
The AMF glass transition, however, is obscured by a slow exothermic feature beginning near 440°C and continuing past the maximum temperature of the scan. It is unlikely that this feature reflects decomposition or crystallization of the glassy matrix, since the position and shape of the later exotherms (some 35°C higher) are the same as those of the dense alloy, and since the majority of this exothermic reaction takes place after crystallization of the Vit106 matrix. It is likely instead that it represents slow growth of the preexisting ZrC at the microsphere interface; this statement can be evaluated as follows.

The standard heat of formation of ZrC at ambient temperature is 202 kJ/mol [104]. Inserting handbook values of $a$, $b$, $c$, and $d$ for Zr, C, and ZrC [104, 101] into the standard fitting equation for heat capacity, $C_p = a + bT + cT^{-2} + dT^2$, it is also possible to calculate the the quantity $\Delta C_p = C_{p,ZrC} - C_{p,Zr} - C_{p,C}$ for temperatures more relevant to the experiment. Integrating
these values to a characteristic temperature of 500°C, chosen to represent the approximate
temperature of the carburization reaction, the standard heat of formation of ZrC is found to be
\[ \Delta H = 203 \text{ kJ/mol} \], close to that at room temperature.

Assuming a volume fraction of 0.4 for Vit106 in the DSC specimen, and assuming the
nominal atomic fraction of 0.57 for Zr within Vit106, it is estimated that the conversion of
the entire $5 \times 10^{-5}$ moles of Zr in the DSC specimen into ZrC would release ca. 10 J of heat.
The integrated area of the background feature, up to a temperature of 550°C, is about 0.93 J,
such that carburization of less than 10% of the Zr in the alloy would be sufficient to explain
the feature. The feature area appearing prior to the onset of crystallization is <0.1 J, so that
<1% of the Zr in the sample (beyond the initial amount reacted during infiltration) would have
reacted during the DSC test prior to crystallization; this explains how the crystallization process
and thermal stability may be largely unchanged despite the formation of ZrC, and the attendant
loss of Zr from the matrix, during the scan.
Based on the foregoing results, it was concluded that processing of syntactic Vit106 foams by infiltration of beds of carbon cenospheres was possible, and that this foaming process would not be attended by deterioration in the GFA of the alloy. On account of the difficulty in achieving macroscopic homogeneity along the direction of gravity, however, a specimen of syntactic foam having dimensions suitable for mechanical testing was never produced. Thus, despite the obvious benefit of testing the ductility of a foam having higher relative density than those produced by replication, and particularly one whose pore morphology was spherical rather than angular, nothing is known about the compressive properties of the AMF described in this chapter.
CHAPTER 5

Magnesium-Based Amorphous Metal Foams

In the two preceding chapters, a well-studied and robust commercial Zr-based amorphous metal was used to explore the fundamental properties of AMF. Although this alloy is, by general metallurgical standards, extremely brittle, recent experience with other alloy systems shows it to be among the toughest available amorphous metals (as, indeed, are the other Zr- and Pd-based alloys used by other AMF researchers in Section 2.3). This fact raises the question of what role, if any, intrinsic alloy toughness plays in the ductility of the AMF reported to date. This chapter begins to address the question by examining ductility in foams processed from a magnesium-based alloy falling near the lower limit of the intrinsic toughness range for amorphous metals.

5.1. Alloy Selection

Fundamental scientific understanding of the origins of toughness in amorphous alloys is still lacking. What understanding does exist arises from the strong negative correlation between the fracture energy $G$ and the ratio of the shear and bulk elastic moduli $\mu/B$ in amorphous metals, as shown in Fig. 5.1 [111]. This relationship, which also pertains to crystalline metals, has been rationalized by noting that shear modulus $\mu$ measures a metal’s resistance to plastic deformation, while bulk modulus $B$ relates to the severity of dilatation near a crack tip, such that a low value of $\mu/B$ can be associated with increased toughness by means of a favorable combination of low resistance to plastic deformation and high resistance to crack tip dilatation, i.e. a favorable balance of flow vs. fracture [111].
Figure 5.1. Compilation of available data showing the relationship between fracture energy and the ratio of shear and bulk elastic moduli in amorphous metals. Also shown are toughness data for one Zr-based amorphous metal after various annealing treatments, whose times and temperatures are shown in the legend. Adapted from Lewandowski et al. [111]

Toughness data for amorphous metals show that as-cast Zr-based alloys such as Vit1 and Vit105 (both closely related, in composition and properties, to the Vit106 used in the previous two chapters) have fracture energies in the range of 70–100 kJ/m$^2$, whereas compositions based on magnesium have lower fracture energies by about three orders of magnitude, roughly 0.1 kJ/m$^2$ and comparable to those of silicate glasses. Consequently, comparison of ductility in Mg-based AMF with that of the tougher AMF already available offers an efficient means for exploring the relationship between intrinsic alloy toughness (as measured by $G$) and foam ductility.

There are several Mg-based BMG described in the literature. The first of these was reported in the late 1980’s [85]. Since then, approximately half a dozen Mg-based amorphous metals have been developed, nearly all of which take the form Mg-(Cu,Ni,Ag,Zn)-(Y,Nd,Gd) [148,
Their development has been motivated mostly by a desire to reduce the cost of existing amorphous metals, the best of which are based on relatively uncommon or precious metals, but improvements in GFA have been carefully researched as well.

The highest critical casting diameter achieved by any of these alloys is 25 mm and was discovered in 2005 for the composition Mg$_{56}$Cu$_{26.5}$Ag$_{8.5}$Gd$_{11}$ [123]. It was intended that this alloy should be used for the experiments described below; however a miscommunication with the authors who provided the alloys revealed afterwards that the material actually used below had a slightly different composition, Mg$_{60}$Cu$_{21}$Ag$_{7}$Gd$_{12}$. The GFA of this composition is not fully optimized, so that the critical casting diameter is slightly smaller, ca. 17 mm according to the authors, but the small specimen sizes (cast with diameters 8 mm) used here render the non-optimal alloy sufficient for all the work presented below.

The alloy used here was part of the study reported by the authors [123], but was not described explicitly in their published report, and thus its properties are almost entirely unknown. The properties reported by the authors via personal communication include: (1) the glass transition temperature $T_g$ (157°C) and characteristic crystallization temperature $T_x$ (192°C), and by extension the thermal stability $\Delta T_x = 35^\circ$C, measured by DSC at a heating rate of 20°C/min; (2) a processing temperature (i.e., liquidus temperature, and possibly an appropriate superheating to maximize GFA) of 575°C; and (3) a compressive fracture strength of 721±25 MPa (based on measurements from five rectangular specimens with edge length 4 mm and height 8 mm, tested at a constant nominal strain rate of $10^{-4}$s$^{-1}$; the error represents the standard deviation of the five values), and estimated Young’s modulus (based on ultrasonic measurements of very similar alloys) of 54±1 GPa.

According to the authors, all specimens of the monolithic alloy failed in the elastic region, with no measurable plastic strain. Although no explicit toughness data are available for this particular alloy, personal experience quickly showed that monolithic Mg$_{60}$Cu$_{21}$Ag$_{7}$Gd$_{12}$, unlike
Vit106, shatters if dropped; although this is not a quantitative measure of fracture toughness, it is certainly in sufficient agreement with the predictions of Fig. 5.1 to warrant its use in AMF.

5.2. Salt-Replication Processing

In order to provide the most direct comparison between the properties of AMF processed from Vit106 (Chapter 3) and from Mg_{60}Cu_{21}Ag_{7}Gd_{12}, attempts were first made to foam the latter alloy using replication of salt. Adaptation of the salt replication method to this alloy necessitated study along the lines presented in Section 3.1.4, i.e. identification of salts that could be dissolved from infiltrated composites without inducing corrosive attack of the alloy.

Preliminary corrosion tests on alloy specimens provided by the authors of Ref. [123] revealed catastrophic corrosion in strong acids of the sort used in Ch. 3, precluding use of insoluble salts such as BaF_{2}. Similar tests in neutral deionized water showed much slower, though still spontaneous corrosion. Tests in strong alkaline solution (NaOH, pH 13), despite the usual stability of crystalline Mg alloys in these environments [169], showed corrosion at rates approximately equal to those in water.

Based on these results, only pattern materials soluble in baths of neutral pH, such as NaCl or NaF, were investigated. Arc-melted, copper-mold-cast BMG ingots were procured from the authors [123], broken into fragments several millimeters in size, and used to pressure infiltrate loosely-packed (tap-dense) preforms of NaCl and NaF with variable particle size up to 350 \( \mu \text{m} \). Infiltration was performed in stainless steel crucibles identical to those used with Vit106, at a temperature of 575°C and with an argon pressure of 153 kPa applied for a hold time of 1–2 minutes. Infiltrated specimens were quenched in strongly-agitated chilled brine and machined into uniform cylinders using a diamond grinding wheel and diamond wafering saw.
Figure 5.2. X-ray diffraction pattern taken from an infiltrated Mg-based BMG/NaCl composite, showing that the alloy may be vitrified after infiltration of NaCl. The iron reflection dominating the pattern originates from the crucible.

A characteristic XRD pattern taken from a cross-section of one infiltrated specimen made with NaCl (before any attempt at pattern removal) is shown in Fig. 5.2. This pattern demonstrates that infiltration of NaCl with the molten alloy does not induce devitrification, and that no prominent crystalline reaction products are formed (the iron reflection present in the pattern originates from the steel crucible wall, which had not been removed).

It was concluded on this basis that processing of replicated Mg-based BMG foams using NaCl was feasible, provided that an appropriate neutral solution could be found for removal of the NaCl. Similar efforts with NaF showed that replacement of chloride ion by fluoride ion was accompanied by highly accelerated corrosion; infiltrated specimens containing NaF suffered catastrophic corrosion induced by coolant during the specimen grinding process, and therefore could not be further investigated.
Initial attempts to remove NaCl patterns (median particle size 180 µm to 320 µm, from specimens of diameter 4–6 mm) by suspension in deionized water led to massive alloy corrosion, accompanied by visible generation of hydrogen gas. This corrosion was generally not visible from the specimen surfaces, but was extensive inside the specimens, suggesting that corrosion was greatly accelerated by chloride generated internally by pattern dissolution and trapped within the resulting pore space. Attempts to facilitate removal of this harmful species, using flowing, ultrasonically-agitated, boiling, or otherwise convecting water, did not alleviate the corrosion. Unfortunately, formation of corrosion products during these experiments was also accompanied by a large volume expansion, as each such experiment was finally terminated when the specimen fractured catastrophically under the stresses induced by this expansion.

In order to avoid this spontaneous corrosion, non-aqueous neutral media were also investigated. There are several neutral solvents that have measured solubility for NaCl [115]. Some of these were tested, but found unsuitable; methanol, for example, dissolves salt but also dissolves the alloy itself, producing an opaque white gel. Other media, such as hydrazine, were too dangerous to justify testing.

The most promising results were found in ethylene glycol, against which the alloy appeared resistant. Despite the clear solubility of loose NaCl powders in glycol, however, it was found that infiltrated composites (with the same particle sizes and specimen diameters as those described above) could not be effectively leached in this medium. The most likely reason for this is that a small (but finite) alloy corrosion rate exists in glycol as well, and thus some evolution of hydrogen gas from the reduction half-cell reaction still occurs during leaching (bubble formation was indeed observed). Due to the high viscosity of glycol (even during tests near the boiling point), these bubbles could not be effectively removed from the pores of the specimen, leading to vapor barriers that effectively stopped the dissolution process (i.e., “vapor lock”). Attempts
to accelerate dissolution of the salt, and reduce the bath viscosity, by mixing small amounts of water into the glycol were found to accelerate corrosion proportionally.

Ultimately, no medium was found in which dissolution of NaCl could be effected (on specimens having sizes appropriate for mechanical testing) without simultaneously producing damaging rates of alloy attack. In light of these difficulties, a different pattern material was selected, along the lines of Ch. 4. The remainder of this chapter describes processing of these syntactic Mg-based AMF, along with basic structure and mechanical properties.

### 5.3. Syntactic Foam Processing

Although processing of syntactic foams does not permit exact comparison against the property data of Ch. 3, their processing was greatly simplified by the absence of the corrosive baths in the previous discussion. It was deemed more important to examine the fundamental nature of the mechanical properties of these AMF, than to continue attempts at producing specimens by salt replication before the fundamental ductility of the foams had been established. The foregoing discussion, is, consequently, included mainly as a guide to future researchers who may wish to pursue replication of salts further.

The pattern materials chosen for syntactic foaming were hollow iron spheres developed and provided by the Fraunhofer Institute in Dresden, Germany. Although the developers did not provide an explanation of how these spheres were fabricated, they have previously reported processing of similar spheres made from 316L stainless steel. According to this report, stainless steel spheres were fabricated by coating styrofoam spheres with a mixture of metallic powders and binders, followed by a thermal debinding and sintering treatment [2].

The composition of the spheres used in this work was determined by chemical analysis off-site, and is provided in Table 5.1. In light of the developer’s report on stainless steel sphere fabrication, and insofar as the composition in Table 5.1 is consistent with a process involving
<table>
<thead>
<tr>
<th>Cr</th>
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<th>Mo</th>
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<td>88</td>
<td>2100</td>
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<td>Balance</td>
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Table 5.1. Chemical composition of the iron spheres used in production of Mg-based syntactic AMF. Values are given in parts per million by mass (mppm).

sintering of iron powders (or iron oxide powders in a reducing atmosphere), it is suggested that the spheres here were produced by debinding and sintering of powders deposited onto sacrificial styrofoam spheres.

Measurement of thirty individual spheres using a micrometer showed a sphere diameter of $1.87 \pm 0.10$ mm and a net sphere density (sphere mass/sphere volume) of $1.0 \pm 0.1$ g/cm$^3$. Sphere wall density was measured by helium pycnometry to be $8.0 \pm 0.15$ g/cm$^3$ (close to the density of pure iron, 7.9 g/cm$^3$), giving an average sphere relative density of $12.5 \pm 1.5\%$, corresponding to an average sphere wall thickness (calculated from the relative density under the assumption of spherical particles with uniform wall thickness) of $41 \pm 5$ µm. Packing of large numbers of spheres into infiltration crucibles (inner diameter 8.1 mm) showed a mean tap-dense packing fraction of 48%. The maximum value of packing fraction which can be achieved using randomly-packed spheres is not precisely defined [183], but is in the range of $64 \pm 4\%$. The discrepancy here likely arises from the disruption in packing efficiency caused by container walls, which can be substantial when the sphere diameter is on the order of the container diameter, as was the case here [61].

Tap-dense sphere beds were placed directly into stainless steel infiltration crucibles and sintered under high vacuum conditions (10$^{-3}$–5·10$^{-3}$ Pa) for 4 h at 1250°C, followed by furnace cooling. At the conclusion of this step, spheres were found to be diffusion bonded both to one another, and to the crucible wall, and could not be removed; in this way it was assured that redistribution of spheres during infiltration, such as that seen in syntactic Vit106 AMF, could
be avoided. Following sintering, sphere beds were pressure infiltrated under conditions identical to those used above for infiltration of NaCl. Specimens were ground from their crucibles using a diamond wheel and diamond wafering saw, as in previous cases.

The density of an as-machined specimen of diameter 6.7 mm (i.e., a diameter 1.4 mm smaller than the as-cast dimensions) and height 10.1 mm, measured by dry mass and dimensions, was $2.25\pm0.01 \text{ g/cm}^3$. Assuming no uninfiltrated residual porosity, this density would correspond (using the density of the solid alloy, $4.4 \text{ g/cm}^3$, measured by helium pycnometry, as well as the mean sphere density $1.0\pm0.1 \text{ g/cm}^3$ given above) to an overall sphere volume fraction of $63\pm2\%$, higher than the value of 48% predicted by the measured packing density. If the fraction of spheres in the specimen were the expected value of 48%, a net fraction of $11.8\pm1.1\%$ residual porosity in the specimen would be needed in order to explain the discrepancy. Such a large residual porosity could not be confirmed by examination of polished cross sections (which did, however, clearly illustrate that no spheres were infiltrated internally by the matrix); it is important to note, however, that metallographic preparation was made difficult by the corrosion susceptibility of the alloy, and thus fine porosity could quite possibly have escaped detection. Most likely, the discrepancy can be explained in the same way as the parallel discrepancy in salt-replicated Vit106 foams; namely, by a combination of low levels of residual porosity with a slight increase in reinforcement packing efficiency in specimens originating from the interiors of packed beds.

A photograph showing the macrostructure of this specimen is shown in Fig. 5.3. The image demonstrates that the structure of the foam is macroscopically uniform, in agreement with observations on polished cross sections, and highlights the fact that the ratio of specimen diameter to pore size (i.e., to sphere diameter) is smaller here (ca. 4:1) than in previous discussions. The effect of this low ratio on properties is discussed below.

A cross-sectional slice of the specimen in Fig. 5.3 is shown in Fig. 5.4, showing the same overall features (although the area fraction of spheres in this cross section is estimated at 45%,
Figure 5.3. Photograph of a syntactic Mg-based AMF produced by infiltration of molten Mg$_{60}$Cu$_{21}$Ag$_7$Gd$_{12}$ into a bed of hollow iron spheres, after machining using a diamond grinding wheel and diamond wafering saw. During grinding, portions of the ductile sphere walls were pushed over the exposed sphere cavities, forming burrs that suggest in this image an erroneously high sphere wall thickness.

lower than the net value of 64% due to the poor statistical regularity caused by low specimen size/pore size ratio). The image also shows that large contiguous matrix regions (>1 mm in extent, within this 2D cross-section) exist within the structure; these features are important to note, as they most likely (though no failure strain vs. feature size data are available for this or similar alloys) are too large to allow for shear band stabilization during bending. This too is the result of large pore size; using the BCC structure as the closest periodic approximant to the sphere structure (in terms of packing fraction), it is possible to estimate that matrix regions (lying along face diagonals in the BCC structure) of ca. 1.2 mm diameter can be expected for a sphere diameter of 1.87 mm.
Figure 5.4. Optical image of a polished cross-section of syntactic Mg-based AMF. The contrast visible in the matrix of the specimen is the result of corrosion during polishing, and possibly due to devitrification of the matrix during the hot-mounting process used in metallographic preparation.

This specimen was also examined using XRD, and the resulting pattern is shown in Fig. 5.5. Although the low scattering power of Mg (particularly as part of an amorphous phase) led to poor signal strength, the pattern clearly shows the presence of an amorphous halo centered near a scattering angle of 36°. In addition, two crystalline reflections are apparent; the stronger of these originates from steel (both in the sphere wall themselves, and more importantly, from the crucible wall), while the other (appearing at approximately 40.5°) could not be identified due to poor signal strength (i.e. low volume fraction in the original phase) and the lack of secondary reflections.

The thermal stabilities of monolithic and foamed Mg$_{60}$Cu$_{21}$Ag$_7$Gd$_{12}$ were investigated using DSC at a constant heating rate of 5°C/min. Figure 5.6a shows the DSC trace of the monolithic alloy, melted and cast under conditions identical to those used in foaming experiments. Also shown is the trace of the same piece of alloy, tested a second time to illustrate the signature of the crystalline alloy (the alloy, as shown by the trace from the first test, had crystallized
Figure 5.5. X-ray diffraction pattern taken from an infiltrated syntactic Mg-based foam, showing that the alloy may be vitrified after infiltration of iron spheres. The iron reflection dominating the pattern originates from the walls of these spheres, and from the crucible wall. The phase appearing at 40.5° could not be identified.

well below the maximum temperature of the first scan, and can therefore be considered fully crystalline by the beginning of the second). Figure 5.6b shows the DSC trace of a fragment of the specimen shown in Fig. 5.3 after compression (see below). This trace was nearly identical to that of the dense alloy, with an endothermic glass transition at 144°C (compared to 145°C for the monolithic alloy) and two-stage crystallization event beginning at an onset temperature of 176°C (compared to 177°C for the monolithic alloy). These results indicate that foam processing did not lead to significant deterioration in the GFA of the alloy.

Also shown in Fig. 5.6b is the DSC trace of the alloy after vacuum annealing for 3 h at 200°C. The purpose of this heat treatment is to induce devitrification of the alloy, and comparison of the thermogram of the annealed alloy with that of devitrified Mg₆₀Cu₂₁Ag₇Gd₁₂ confirms that such a heat treatment is sufficient. This heat treatment was applied to a second syntactic foam
Figure 5.6. Results of DSC measurements performed on specimens of Mg-based BMG, using a constant heating rate of 5°C/min. (a) DSC signature of the monolithic alloy, in the as-cast and devitrified states. (b) DSC signatures of foam specimens, both as-cast and after annealing at 200°C for 3 hours.

specimen, prior to mechanical testing (see below), in order to explore the effect of crystallinity on the mechanical response of the foams.

The glass transition and crystallization onset temperatures measured here are somewhat below the values (157°C and 192°C, respectively) provided by the alloy developers. It is likely that the difference is caused by the relatively slow heating rate used here (which was chosen to give the strongest peak signal, and most clear transitions, since at the time of the measurements the heating rate used by the developers was not known). Because amorphous metals are metastable, their characteristic transition temperatures are not absolute, but kinetically limited; slower heating rates allow more time for the kinetic processes leading to these transitions to occur, and thus lead to earlier (lower-temperature) transitions than in faster experiments [70].

Based on the results of Fig. 5.5 and 5.6, it was concluded that this processing method yields amorphous syntactic foams, and that vacuum annealing of these foams at 200°C for 3 hours should be sufficient to induce complete crystallization. In the following section, the compressive
mechanical properties of these foams are measured, and compared with those of other syntactic foams in the literature.

5.4. Mechanical Properties

The amorphous syntactic Mg$_{60}$Cu$_{21}$Ag$_{7}$Gd$_{12}$ foam in Fig. 5.3 was tested in uniaxial compression at a nominal strain rate of 5·10$^{-4}$s$^{-1}$. The stress-strain curve of this foam, after compensation for load train compliance, is presented in Fig. 5.7. The specimen showed quasilinear loading up to a stress of 109 MPa and an engineering strain of 1.9%, with a loading stiffness (measured in the most linear range of loading, between 6.5 and 70 MPa) of 8.5 GPa. Macroscopic yielding in this specimen was accompanied by a steep but smooth drop in flow stress, followed by an extended Plateau region consisting of periodic increases and decreases in flow stress, punctuated by numerous serrations. Release of millimeter-size fragments of matrix material was visible throughout this Plateau region; this release was more substantial than was the case for replicated Vit106 foams, but less substantial than that observed during compression of replicated devitrified Vit106 foam. It is possible, therefore, that the loss of these fragments was responsible for the variations in flow stress in the Plateau region; however, the low diameter/pore size ratio of the specimen renders it subject to statistical fluctuations during compression [3], and thus this statement cannot be made definitively. Despite the loss of these fragments, the specimen remained mostly intact until high strains (ca. 60%). Densification began at approximately 80% engineering strain; at this point, most of the matrix material had fractured and fallen out of the crushed specimen.

The most prominent feature in the compressive behavior shown in Fig. 5.7 is the sharp loss in flow stress following yield. Although major loss in flow stress at yield is often associated with brittle foams [64], such an interpretation may not apply here, as similar (although less pronounced) stress drops have been observed previously in syntactic aluminum foams containing
Figure 5.7. Compressive stress-strain behavior of syntactic amorphous Mg$_{60}$Cu$_{21}$Ag$_{7}$Gd$_{12}$ foam. The inset shows a magnified view of the region shown in the blue box, for better visualization of the serrations in the curve.

It is unclear whether the same explanation obtains in this case. This is because stress drops at the point of macroscopic yield have only been observed in specimens, such as those listed above, where the spheres are made from a material that is stronger than the matrix. The thin-walled and annealed iron spheres in the present material are much weaker than the glassy matrix (and furthermore, the sphere walls constitute only 17% of the total solid volume in the
specimen, while the matrix constitutes 83%), implying that the strengthening effect seen in other syntactic foams should be absent in this case. In support of this argument, it is noted that the ratio of wall thickness $t$ to sphere radius $R$ is, in this work, ca. 0.04. According to the results presented by Kiser et al. [98], this ratio would be far too small to produce a significant load drop in the stress-strain curve, even for the case of strong alumina spheres in a weak aluminum matrix. However, the fractional stress drop at yield in this case (about 82%) was considerably larger than losses observed in other syntactic foams (of which the largest, 65%, was observed in an aluminum/alumina foam with an extremely large wall thickness to sphere radius ratio of 0.48 [98]).

The stress drop at yield in the present foam is, on this basis, believed to result from loss of load-bearing capacity in the amorphous matrix, rather than in the cenosphere reinforcement. As stable shear band propagation in amorphous metals does not normally lead to loss in flow stress [203, 202, 37], it is likely, moreover, that the loss in this case is the result of fracture. Thus the situation in the present foam is not dissimilar in nature to that of the ductile-matrix foams listed above, except for the fact that in this case the fracture at yield took place in the majority phase (the matrix), rather than in the minority phase (the cenosphere reinforcement). The larger volume fraction of the matrix, along with the fact that the matrix is substantially stronger than the sphere wall material, explains the relatively large loss in load-bearing capacity (i.e., the magnitude of the stress drop) accompanying macroscopic yield (i.e., matrix fracture) in the present foam.

In support of this conclusion, it is noted that no stress drop was present in syntactic foams (dimensions 36 x 40 x 53 mm$^3$) consisting of 59 vol.% unsintered iron spheres (diameter 3.7±0.2 mm, wall thickness ca. 200 microns, for a sphere relative density ca. 29%), in an aluminum-alloy matrix [153]; in that case, both the majority and minority phases were ductile, and their volume fractions were more comparable than in the present case (aluminum alloy and pure iron in a
volume ratio of 41:17, versus Mg-based BMG and pure iron in a volume ratio of 37:8), so sphere collapse was accommodated smoothly by matrix plasticity without loss in flow stress.

Examination of the exterior of the amorphous specimen (Fig. 5.8a) during compression also supports this hypothesis. Figure 5.8 shows photographic images of the specimen at nominal macroscopic strains of 0, 2.6, and 9.8%. Comparison of the image taken at 2.6% strain (i.e. during the post-yield stress drop) with the image taken prior to the test reveals at least two visible surface cracks (indicated by arrows), confirming that matrix fracture played a role in the stress-strain response of the foam in this region of the curve. At higher levels of compression, as expected, many more cracks are visible, and brooming of the specimen near the bottom platen is also visible. This brooming is believed to be the result of deteriorated local strength at the specimen faces, caused by opening of near-surface spheres during machining. These spheres, lacking the strength associated with a fully intact spherical wall, deformed at lower loads than intact spheres in the specimen interior, and thereby initiated the crush band at the platen, rather than at a random location in the gauge length, as is often the case in foam materials.

It is suggestive, if not definitive, that the number of clear local maxima in the stress-strain curve (i.e., the number of “wave”-like features in Fig. 5.7, whose maxima appear at strains of roughly 2, 14, 37, 53, 70, and >80%; the most pronounced of waves are by this estimate found at the large stress drop at yield, and at densification where the final pore space collapses) is about six, which is roughly the number of layers of spheres visible along the gauge length of the specimen (Fig. 5.3). This would suggest that the slow wave-like drops and recoveries of stress reflect the collapse of each plane of spheres, i.e. extension of the crush band through each plane, and are therefore largely an artifact of the small number of pores in the specimen, rather than an intrinsic feature of the material behavior.

The number of serrations in the stress-strain curve of Fig. 5.7 was determined using the same criteria used for the replicated Vit106 foams, i.e. by counting the number of instantaneous
drops in the curve, following macroscopic yield, which involved at least a 5% loss in flow stress. Using these criteria, the number of serrations in the curve was 36. Using the mean sample volume, volume fraction of spheres, and sphere diameter given above, it is estimated that the specimen contained 65 spheres, i.e. that there was about one serration per two spheres. Although perhaps less appropriate for this structure, in light of the small number of pores in the syntactic specimen, the same argument made in Section 3.4 can be made here: namely, that on average a pore will be associated with three unique struts. From this standpoint, there appears to be one major fracture event in this specimen for every 6 struts. This is substantially more serration activity than was present in the replicated Vit106 foams, which was estimated in this way to show one serration per 150–800 struts. Although the relatively small number of struts in the Mg-based foam naturally makes a given fracture more likely to cause a 5% loss in total flow stress (relative to the Vit106 foams, where only the largest fracture events are likely to have manifested as serrations, using the current definition), such a comparison still seems to support a greater importance of brittle fracture in the Mg-based foam.
Despite such evidence of fracture, it remains the case that macroscopic failure of the specimen did not occur until very high compressive strains, such that the total energy absorbed to a strain of 80% (this value is chosen as the onset of densification, because the definition used earlier, involving a tangent drawn at 70% strain, was not appropriate due to the later densification in the current foam) was still high, at 23.6 MJ/m$^3$ (10.5 MJ/Mg). Using the average flow stress at 25% strain, 29 MPa, the energy absorption of the syntactic Mg-based AMF falls onto the same trendline as the replicated Vit106 foams (Fig. 3.12). Such a comparison neglects the large yield strength of the syntactic foam, which may be undesirable in energy absorption applications, and the fact that the energy absorbed per unit mass is below that of the Vit106 foams. Nevertheless, it raises an important point about the seemingly-brittle behavior of this foam: evaluation of the degree of “ductilization” or “toughening” imparted by the network of ductile iron spheres in the specimen (i.e., by the foaming process) depends on how these factors are defined and evaluated. Clarification on this point is offered by comparing the behavior of the amorphous specimen to similar specimens with matrices that are known in advance to be either ductile or brittle.

The former case has been addressed by aluminum-alloy syntactic foams made with similar hollow iron spheres; the stress-strain curves of these materials show neither stress drops at macroscopic yield, nor visible variations in flow stress (either long-period fluctuations, or serrations) within the Plateau region [153]. Thus, a fully ductile matrix with ductile spheres shows a qualitatively different behavior than the specimen here; however, the possibility that the fluctuations in the present foam were caused by the small ratio of specimen size to pore size has already been noted. Thus, the comparison with aluminum-iron sphere syntactic foams is suggestive but not definitive.

The second case was addressed by compressive testing of a devitrified specimen (diameter 6.6 mm, height 10.1 mm, and density 2.31±0.01 g/cm$^3$, corresponding to an estimated sphere volume fraction of 61±2 vol.%), machined from the same casting as the amorphous specimen
Figure 5.9. Compressive stress-strain behavior of syntactic crystalline Mg₆₀Cu₂₁Ag₇Gd₁₂ foam, produced by devitrifying an amorphous foam by vacuum annealing at 200°C for 3 hours. The inset shows a magnified view of the region shown in the blue box, for better visualization of the (less-pronounced) serrations in the curve. The scales are the same as in Fig. 5.7, to facilitate comparison.

above and then vacuum annealed at 200°C for 3 hours. The effectiveness of such a devitrifying treatment has already been established above (Fig. 5.6b) using calorimetry.

The compressive stress-strain behavior of this crystalline specimen is shown in Fig. 5.9. The stiffness of this foam was similar to the amorphous specimen above, approximately 7 GPa (measured in the most nearly-linear region, between 7 and 53 MPa); however the maximum stress (i.e., strength) of this specimen was markedly lower, about 57 MPa, and thus the macroscopic yield strain was also lower, about 0.9%. The loss in strength, and elastic strain, is in keeping with the effects of devitrification on the mechanical properties of amorphous metals (Section 1.2.3), and supports the conclusion above that overall strength (and loss thereof, at yielding) arises from the matrix rather than from the spheres.
The crystalline specimen showed early behavior qualitatively similar to that of the amorphous specimen, with fragments of matrix material being expelled throughout the Plateau region, but the size of these fragments was generally smaller. It is believed that the abundance of fracture paths in the devitrified matrix (due to the large number of brittle intermetallic inclusions and grain boundaries here, as compared to the homogeneous amorphous matrix of the previous specimen, where fracture paths were likely confined to planes of maximum stress within large, uniform matrix regions) allowed such smaller fragments to form. It is further believed that the release of these smaller matrix fragments led to proportionally smaller changes in load-bearing area at each fracture, and thus to fewer and less pronounced serrations. In addition, this specimen showed obvious macroscopic cracking (i.e., shedding of large sections of matrix, corresponding to losses in the cross-sectional area of the matrix) beginning around 40% strain, where no such major failure was evident in the amorphous specimen. The lack of any substantial losses in flow stress attending these large changes in matrix cross-sectional area suggests that the load-bearing capacity of the crystalline specimen was very close to that of the sphere network itself, i.e. that the devitrified matrix added little strength to the composite. Thus, the average Plateau stress was much lower, and when the matrix fractured, the resulting serrations were less pronounced.

Photographic images showing the crystalline compression specimen at approximately the same applied strains as those in Fig. 5.8 are provided in Fig. 5.10. Once again, matrix fracture is visible in the post-peak region of the stress-strain curve (two such fractures are highlighted by arrows in the center panel), and this fracture becomes severe even at low strains of 9.9%, again confirming the importance of matrix fracture in the deformation process. Otherwise, there is little visible difference between the two specimens. It is notable, however, that because of the lower stresses carried at all times by this specimen, the energy absorption was much lower than in the amorphous specimen, at only 6.2 MJ/m$^3$ (2.7 MJ/Mg). Even with a lower flow stress of 9
Figure 5.10. Photographs taken during compression of the crystalline AMF specimen of Fig. 5.9. The images are identified by the average macroscopic strain at the time of the photograph.

MPa at 25% strain, this is unremarkable performance, and could be more easily achieved using a crystalline Al-based foam. On an energy per unit mass basis, the devitrified foam is clearly inferior to both these and Vit106 foams.

Review of the information provided thus far, without allowing interpretation of the same depth as the results in Chapter 3, still suggests important preliminary conclusions. Firstly, reinforcement of amorphous $\text{Mg}_{60}\text{Cu}_{21}\text{Ag}_{7}\text{Gd}_{12}$ with ductile metal spheres is possible without measurable deterioration of its glass-forming ability. Secondly, the post-yield compressive behavior of the resulting foam (including macroscopic strength, but also flow stresses throughout the entire Plateau region) is determined mostly by the strength of the matrix, which is usually higher in glassy than in devitrified matrices. In particular, the shape of the Plateau region of the stress-strain curve is dictated by fracture in the matrix, which for amorphous matrices (having high strength and elastic strain) leads to substantial strain energy release that manifests as fluctuations in flow stress. For crystalline matrices (which have lower strength and elastic strain),
the strain energy releases are smaller, and thus the resulting fluctuations in the stress-strain curve are also smaller.

In both specimens, matrix cracks were intercepted, deflected, and/or blunted by contact with the ductile sphere walls, and thus did not lead to immediate specimen failure. This results from the fully-interconnected structure of the sintered ductile iron sphere network, which prevents direct propagation of cracks across the specimen cross section by intercepting those cracks and dissipating their energy through local plasticity. These toughening mechanisms, however, are active in both the amorphous and devitrified foams, and are similar to those active in interpenetrating ductile-phase-toughened ceramics such as cemented carbides [23]; for this reason, they do not imply matrix plasticity of the sort seen in Vit106 foams. Rather, the mechanisms active in these materials improve energy absorption by hindering crack extension in a matrix which need not be plastic.

The prominence of matrix fracture in the compressive response in the amorphous specimen should not be surprising, in light of the fact that the features in this specimen (whose sizes are determined by the interstices of the large, and generally inefficiently-packed spheres, as discussed above) were much larger than the features of AMF appearing earlier in this work. It is, therefore, plausible that amorphous syntactic specimens would benefit from reduced feature sizes in specimens with smaller and better-packed spheres, or spheres that had been deformed by pressing prior to infiltration, in the same way that replicated Vit106 foams benefited from similar reductions in density and pore size in Chapter 3. Thus, it is possible that matrix plasticity can become active in these structures, if changes are made to bring them more into line with the replicated structures where plasticity has already been achieved.

Finally, with regard to the issue of ductilization by foaming, the following can be stated. The capacity of both foams in this chapter to carry load to high compressive strains, despite the brittleness of the matrix in the crystalline specimen, indicates that compressive failure
strain alone cannot capture the presence or absence of local plasticity in the amorphous metal matrix. In addition, the shapes of the stress-strain curves could simply be reflections of matrix strength in each specimen (and in this case, the influence of small specimen size/pore size ratio), and hence these also are inadequate to show plasticity. Verifying the presence of shear band interruption, stable shear banding, or other mechanisms of matrix plasticity therefore requires more sophisticated methods, or at least visual confirmation of the sort provided in Chapter 3. Until such time as these methods are applied, the conservative conclusion is that macroscopic ductility was the result only of the crack-interrupting effects listed above, while simultaneous local matrix plasticity may be present but cannot be confirmed.
In this chapter and the next, two new processing methods will be described that serve to address the questions raised in Section 1.3 regarding the utility of density gradients in mass optimization of metallic foams. Both of these methods allow production of open-cell metallic foams having controllable and continuous density gradients, and both will be demonstrated through successful processing and characterization of aluminum foams showing simple, near-linear gradients.

The method of this chapter, in particular, represents the adaptation of a pre-existing foaming method, part of the general class of replication methods but distinguished from those in Chapters 3, 4, and 5 by virtue of being a *positive* replication method (where the pore space in a porous pattern is directly reproduced) rather than a *negative* replication method (where the pattern itself becomes the pore structure of the final foam). The method is described here in detail, and the resulting foam structures investigated. In addition, techniques are demonstrated for measurement of local density gradients, and used to evaluate the accuracy of the method in reproducing its designed gradient.

### 6.1. General Methodology

The method advanced here (hereafter, the *replication* method) is an adaptation of one used previously in production of uniform-density metallic foams [3]. These earlier methods begin with a sacrificial open-cell polymeric foam (hereafter, the *precursor*) whose basic structure (relative density, pore size, anisotropy, etc.) serves as a template for the final metallic product. This
precursor is invested with a ceramic slurry, and subsequently removed by pyrolysis in air. The resulting negative mold (hereafter, the *investment*) becomes the vessel for gravity or pressure casting of the molten alloy, which solidifies in the space occupied originally by the precursor and thereby creates an exact replica of the precursor foam, which is recovered by removal of the ceramic investment.

This basic procedure was altered here only through the introduction of a density gradient into the precursor prior to investment, as shown in Fig. 6.1. It therefore not only resembles the general method described above, but also shares an initial step with the approach introduced by Cichocki et al. [31] for processing of graded porous ceramics, though the methods differ substantially in their later steps and in the porosity and structure of their final products. Although the approach of Fig. 6.1 will only be demonstrated here using simple graded aluminum structures, it can be easily extended - within reasonable limits of experimental practice - to the production of graded structures having a range of pore sizes and average densities, arbitrarily-defined density gradients, and a variety of base metals.

**6.2. Processing**

Two precursors were used in this work, both of which were open-cell reticulated polyurethane foams obtained from a local supplier (Foamcraft, Inc., Skokie, IL). These precursors were nominally identical in composition and structure, with the exception of pore size; the first had relative density (measured by mass and dimensions for the foams, and by helium pycnometry for the solid polyurethane strut material) of 2.3%, and a nominal pore size of 5 mm, while the second had relative density 2.7% and nominal pore size 2 mm. These precursors, and the resulting replicated metallic foams, are referred to hereafter using the terms *coarse-pore* and *fine-pore*, respectively.
Electron micrographs illustrating the structure of the fine-pore precursor are provided in Fig. 6.2. Generally speaking, the structure is highly regular and consists of polygonal open pores defined by slender, essentially straight struts with concave triangular cross-sections and connected at relatively small nodes (Fig. 6.2a). The strut surfaces (Fig. 6.2b) are generally smooth, but do show residual evidence of the reticulation process (during which the membranes separating individual bubbles in the expanding polymer foam burst) in the form of ripples along strut edges, created by Poisson effects as the membrane material contracts into the struts under the influence of surface tension. The structure of the coarse-pore precursor was very similar to the fine-pore precursor in the figure.

As shown in Fig. 6.2a, some membranes survive the reticulation process largely intact, particularly in the fine-pore precursor. Though no such windows were visible in the final replicated specimens, it is believed that their presence contributes to higher levels of air entrapment during investment filling, and therefore to higher flaw densities (discussed below).
Slices of precursor approximately one pore thick were cut from rectangular as-received sheets of each precursor type. By counting the number of pores per linear inch along the three principal directions of these sheets, the precursor anisotropy was evaluated. No significant anisotropy was found in the coarse-pore precursor. In the fine-pore precursor, pore size was found to be approximately constant between the two in-plane directions, and close (1.90±0.17 mm) to the nominal value provided by the manufacturer (2 mm); pores in the through-thickness direction of each sheet, however, were elongated by approximately 10% relative to the in-plane directions, having size 2.25±0.21 mm. The effect of this anisotropy on processing was negligible, especially given the additional anisotropy expected to result from precursor deformation, but in order to minimize its effect on mechanical properties, mechanical test specimens were processed such that the loading direction was parallel to the through-thickness direction of the original precursor sheet.

Blocks of precursor foam were glued to a rotating support, and then cut using an electrically-heated Kanthal wire into truncated cones, as shown in Fig. 6.1. During cutting, the wire was in contact with the support, whose diameter was therefore chosen to correspond to the
largest diameter of the final precursor cone. For the purposes of demonstrating the method, this diameter \( d = 22.6 \text{ mm} \) was a factor of \( \sqrt{2} \) larger than the desired final specimen diameter \( d_o \) (16 mm as-cast, though during final machining the specimen diameters were usually reduced further, to about 14 mm, in order to eliminate near-surface flaws caused by handling of the investment). Uniform radial compression of such a region of precursor would accordingly, in the absence of significant axial deformation, yield a local density a factor \( (d/d_o)^2 = 2 \) higher than the base density of the precursor. By varying the angle of the cutting wire above the support, the height (i.e., gauge length, ca. 30 mm) and final density of the specimen were also determined.

In all cases, the minimum diameter of the precursor (farthest from the support) was equal to the desired final specimen diameter, such that the precursor at this region of the sample was effectively undeformed. The foam material between these two faces (i.e., between the support and the face farthest from it) should, therefore, have a linearly increasing diameter and thus a local relative density increasing as \( (d/d_o)^2 \) with distance from the lowest density face. Strictly speaking, this profile is nonlinear; however the concavity of the predicted profile is small (as illustrated in later sections) and thus the predicted profile may be characterized as “near-linear” with a net average foam density approximately 1.55 times that of the original precursor.

Between cutting and investment, precursors were dip-coated with a commercial isopropanol-based plaster wetting agent (Rio, Albuquerque NM, USA) to minimize entrapment of air bubbles during the investment process. Coated and dried precursors were then reshaped into uniform-diameter right cylinders, having dimensions roughly equal to the designed final sample dimensions, by insertion into oil-lubricated glass tubes (inner diameter 16 mm, wall thickness 1 mm). Care was taken during reshaping in order to minimize distortion of the structure due to friction with the walls of the tube and axial elongation resulting from Poisson effects during radial compression.
After reshaping, the precursors were invested with a commercial casting plaster (Satincast 20, Kerr Lab, Albuquerque NM) designed for investment casting of filigree jewelry. Experimentation with the water content of the plaster investment indicated that an optimal balance of high green strength (i.e., strength of the investment after setting and precursor pyrolysis) with high thermal-shock susceptibility (the method for investment removal after casting) was achieved using slightly “wet” plaster with a composition of 6 mL water per 10 g dry plaster. Plaster investments were allowed to dry and set overnight under ambient conditions.

Dip-coating prior to the investment step was successful in visibly reducing the number of replicated air bubbles found after casting for both precursors; however in the fine-pore precursor, the amount of entrapped air was still deemed unacceptably high. Accordingly, fine-pore precursors were coated, but also compressed axially after investment pouring but before setting, to squeeze out any remaining air. Original precursor height was manually restored before setting of the investment, so that the effect of this compression on the foam structure and density was minimal.

Invested precursors were removed the glass tubes after investment setting, and then heated at a rate of 2°C/min to 500°C in an open tube furnace subject to naturally-convecting air. After a dwell time of 4–6 hours to ensure complete pyrolysis of the precursor, the investments were allowed to furnace cool to room temperature at a rate not exceeding 10°C/min. Such a pyrolysis heat treatment was found to ensure complete removal of the precursor without inducing damage in the investment due to swelling and vaporization of the polymer.

Investment molds were then placed in graphite-coated quartz crucibles for infiltration by the alloy melts. Coarse-pore samples were infiltrated with 99.7% Al, while fine-pore samples (in order to ensure comparability with foams produced by the dissolution method discussed in the next chapter) were infiltrated with Al-6101 (the nominal composition of this Al-Mg-Si alloy is provided in Table 7.1). Infiltration was achieved in all cases by melting a charge of the alloy
under low vacuum at 750°C for 30 minutes, and then application of a 150 kPa pressure gradient of high-purity argon, followed by furnace cooling. Oxide scale formed during melting of the alloy charges was stripped during the infiltration process by means of a perforated graphite disk placed between the charge and investment mold. All samples remained under argon overpressure during solidification.

Several methods of investment removal were investigated. Immersion of investments in aqueous solutions of HCl, HNO$_3$, H$_2$SO$_4$, and NaOH generally led to some softening or surface erosion, but did not cause large-scale disintegration of the type needed for investment removal. Incorporation of NaCl into the plaster mix (in dry plaster:NaCl:water mass ratios from 10:6:1 to 10:5:9) was found to render the plaster susceptible to disintegration in hot water after setting; however, inclusion of the salt also led to extreme retardation of the setting reaction, such that adequate green strength could not be achieved in the invested precursors. Removal of investments using water jet spraying or other mechanical means was found to damage delicate foam struts.

The most successful investment removal approach was thermal cycling, i.e. repeated heating and quenching. Several quenchants were investigated, including liquid nitrogen, methanol/dry ice slurry, oil, NaCl brine, and water. The results in each case were similar, so water was used as the quenchant in all specimens. Specimens were repeatedly heated in air to approximately 350 °C and then drop-quenched in room-temperature water. Typically, 5–7 cycles were required for adequate investment removal in coarse-pore specimens, and 10–12 cycles for fine-pore specimens. Gentle water spraying and sonication were used between cycles to remove disintegrated plaster.

6.3. Structure

6.3.1. Architecture

Optical images of a coarse-pore graded foam sample processed by the replication method are shown in Fig. 6.3. The gradient in foam density is difficult to visualize directly in a side view
Figure 6.3. Optical micrographs illustrating the macrostructure of a coarse-pore pure aluminum specimen (diameter ca. 14 mm, relative density 3.8%) processed by the replication method outlined in Figure 6.1. (a) side view, with the low-density face at the top of the panel and the high-density face at the bottom; (b) end view of the low-density face; (c) end view of the high-density face.

(Fig. 6.3a), but can be recognized through differences in pore size and shape near the sample faces (Fig. 6.3b,c). General foam structure in the undeformed and deformed precursor regions (i.e. the low- and high-density sample faces) is illustrated with greater magnification in the SEM micrographs of Fig. 6.4a-d. Strut and pore architecture in the undeformed region (Fig. 6.3a) was similar to that of the precursor, with concave-triangular strut cross sections and relatively straight struts (Fig. 6.3b); by contrast, the deformed region (Fig. 6.3c) showed evidence of elastomeric precursor deformation in the form of strut buckling, twisting, and rotation (Fig. 6.3d).

The most common defects observed in graded foam specimens were thin layers of retained plaster on interior surfaces, which were more prominent in fine-pore samples and in regions where precursor deformation created “pockets” where the investment was less exposed. These layers are not expected to affect foam properties substantially, as the plaster investment is unusually
weak and brittle on account of its water-rich composition; however retained plaster leads to increased mass and, consequently, increased calculated relative density in foam specimens.

The effect can be numerically estimated as follows: a representative cylindrical foam specimen of diameter 16 mm and height 30 mm has a bulk volume of $6 \text{ cm}^3$. According to manufacturer data for Duocel® aluminum foams having pore density 10 ppi and relative density 3% (comparable to fine-pore graded specimens described here), the internal surface area of a sample with this volume would be approximately $35 \text{ cm}^2$. The density of dried plaster investments was
measured by helium pycnometry to be 2.55 g/cm$^3$. Therefore the total mass of a uniform layer of plaster with thickness 5 microns (which is considered a high but plausible estimate based on SEM observation of retained surface plaster) is estimated as 0.044 g. Such a mass adds to the measured bulk density by 0.0074 g/cm$^3$, which would add to the measured relative density (calculated assuming that all mass represents aluminum) by ca. 0.3%. As discussed below, this error would often be sufficient to explain deviations between radiographic and tomographic measurements of density and those based on dry mass and volume. The effect is, proportionally speaking, even more severe in the case of fine-pore precursors with higher specific surface area.

The next most commonly observed structural flaws were caused by replication of air bubbles trapped during investment pouring. These flaws, an example of which is shown in Fig. 6.4e, were substantially decreased in number by use of a wetting agent. However some bubbles were found in every specimen. They, like the retained plaster deposits, were more common in fine-pore specimens (due to increased drag on rising bubbles, and due to the higher numbers of intact membranes in fine-pore precursors) and in regions where the precursor had been deformed (due to an excess of re-entrant features in the deformed precursor where bubbles could be trapped). These flaws, like the retained plaster, serve to increase the final measured foam relative density beyond that of the precursor.

The third, and by far most rare, types of structural flaw were regions of incomplete infiltration or other major defects (Fig. 6.4f). Incomplete infiltration was most likely associated with mechanical damage (i.e., collapse of the open channels formerly occupied by the precursor) caused by handling the investment after the pyrolysis step, and/or by the weight of aluminum charges during the infiltration step. Pyrolysis of the precursor weakens the investment primarily by replacing the tough polymer foam with a fully-interconnected network of open channels, but also leads to drying out of the excess water in the plaster. Removal of this excess water is believed to induce microporosity, and contributes visibly to the weakness of the investments.
after pyrolysis. Though excess water thereby increases the likelihood of damage, investments were necessarily water-rich to increase their susceptibility to thermal cycling.

### 6.3.2. Radiographic Density Profiling

Characterization of any density-grading process must involve not only structural investigation, but also mapping of local density within graded specimens. In this work, density mapping was performed radiographically, because small sample sizes and surface irregularity (due to relatively large pore sizes) made other nondestructive analyses (e.g., modified Archimedes methods, or measurement of properties, such as moment of inertia, that are sensitive to internal mass distribution) difficult, and because radiography provides structural information (e.g., strut sizes and conformations) that is more difficult to access by these other methods. Two forms of radiographic analysis were compared in this work, the first being direct radiographic imaging using a white x-ray source, the second being 3D micro-computed tomography. Tomographic methods are presented below in Section 6.3.3.

Direct imaging of coarse-pore graded specimens was performed with radiographic equipment housed by the Conservation Department of the Art Institute of Chicago for nondestructive analysis of artwork and historical artifacts. Transmitted radiographic images were captured on fine-grain x-ray sensitive film (Kodak Industrex MX125), exposed to x-rays generated by an articulating white x-ray source positioned 81 cm from the sample and operated at 25–60 kV accelerating voltage and 5–20 mA source current. Graded foam specimens were imaged in transmission in both the stationary state and during rotation about their long axes, as explained below. In each case, accelerating voltage, current, and exposure time were selected by examination of exposed films to give good contrast with minimal saturation of the film; optimal values were 60 kV, 5 mA, and 30 s for stationary images, and 25 kV, 20 mA, and 480 s for rotating
images. In the latter case, the period of sample rotation (ca. 0.3 s) was kept much smaller than the total exposure time, to ensure that a sufficient number of sample rotations were captured.

Exposed films were scanned and digitized, and the resulting images analyzed using the absorption equation, \( I/I_0 = e^{-\mu x} \), where \( I/I_0 \) is the normalized transmitted intensity for a particular pixel in the image, \( x \) is the thickness of aluminum separating the source and detector at this pixel (which is related to the foam relative density through the known sample thickness at each point), and \( \mu \) is the characteristic x-ray absorption length. Strictly, a single value of \( \mu \) cannot describe transmission of a white x-ray beam in this equation, as x-ray absorption is strongly energy-dependent and this leads to preferential absorption of the lower-energy regions of the incident spectrum (a phenomenon known as “beam hardening”). Nonetheless, an adequate effective value of \( \mu \) can be determined for a given experiment using an appropriate series of stacked foils, a wedge, or other standard of known and varying thickness.

For this method, the effective absorption coefficient was calibrated using a layered aluminum kitchen foil standard included in each exposure. The standard was designed to present a series of sixteen path lengths spanning the range of path lengths believed to exist in the graded specimens. After analysis of transmitted intensities through each region of the standard using the absorption equation (wrinkles in the foil standard sometimes caused deviations in intensity, such that only those paths that gave uniform intensity were used), an individual effective value of \( \mu \) was fitted for each specimen; these values were reproducible between exposures and gave values near \( \mu = 300 \text{ m}^{-1} \). A schematic of the foil standard and a representative calibration dataset are provided in Fig. 6.5.

Radiographs of stationary coarse-pore samples, due to low foam density and sample size/cell size ratio, contained many pixels with direct line-of-sight to the x-ray source. As a result, saturation of the films occurred for all but the shortest exposure times. Noise in these pixels (from source fluctuations during short exposure, and to finite intensity resolution during digitization)
sometimes led to intensities $I > I_0$, giving spurious negative path lengths that diminished overall accuracy of the measurement. Rotating samples about their long axes throughout longer collection times reduced this noise and ensured that all pixels showed $I < I_0$, improving the accuracy of the density calculation. Even in rotating samples, however, data near the sample edges are subject to numerical noise, due to the vanishing projected thickness of the cylindrical specimens and slight precession of the sample resulting from small misalignment; as such, data near the sample edges were truncated. Radiographs of the sample from Figs. 6.3-6.4, both stationary and rotating and after this truncation, are shown in Fig. 6.6a and 6.6b.

The mean relative density of each cross-sectional plane along the long axis of the specimens was calculated from radiographs of rotating samples by weighted averaging (taking into account that pixels near the center of the image represented larger sample volumes than those near the edges), giving net density profiles which could be compared to those predicted from initial precursor dimensions, to assess the accuracy of the replication process. The profile calculated
Figure 6.6. Radiographic images of the graded specimen of Figure 6.3a, with the low-density face at the top of the panel and the high-density face at the bottom. (a) radiograph of the stationary specimen; (b) radiograph of the rotating specimen. Radiographs have been contrast-enhanced for better visualization.

from the data in Fig. 6.6b is shown in Fig. 6.7, along with the predicted profile. The measured profile appears to track the prediction accurately across the entire gauge length of the sample, with large variability that likely reflects the large pore size of the sample, rather than any inherent noise in the measurement (see the discussion of tomographic profiling below). The overall relative density of the sample calculated from radiographic density profile (Fig. 6.7) was 3.5%, while the value from sample mass and dimensions was 3.8% and the value predicted from the precursor dimensions was 3.6%. This error is considered acceptable in light of the fact that: (a) large pore sizes made measurement of foam dimensions less precise; and (b) the radiographic value was derived entirely from measurements with no assumptions beyond the use of a single representative value of $\mu$. The codes used for calibration and analysis of these data are provided in Appendix B.1.
6.3.3. Tomographic Density Profiling

The structures and density profiles of coarse-pore replicated foams were also analyzed tomographically using synchrotron x-radiation at the Advanced Photon Source of Argonne National Laboratories (Argonne IL, USA). Tomographic reconstruction was achieved using a series of 1500 transmitted radiographs, spaced evenly within one 180° half-rotation of the specimen, taken with a monochromatic 30 keV beam having ca. 15 mm illuminated width. The effective height of the beam (that is, the height of the region for which the intensity of the incoming beam was at least 50% of its maximum value; only this region was used for measurements, in order to avoid errors due to poor signal strength associated with the natural intensity profile of the beam) was 5 mm. Tomographic 3D renderings (Fig. 6.8) of the low- and high-density faces of the specimen shown in Fig. 6.3a illustrate the general shape of the struts in each face, and reinforce the observation above that the concentration of defects was higher in the higher-density region (i.e., where the precursor had been compressed).
Reconstructed cross-sectional images were also binarized using an adaptive thresholding technique and analyzed for area/volume fraction (codes are provided in Appendix B.2), leading to the density profile shown in Fig. 6.9a. This profile is in good agreement with both the predicted and radiographic profiles (Fig. 6.7). However, binarization gives the potential for systematic errors in area fraction: experimentation with various thresholding levels led to fluctuations in overall sample density on the order of 0.3%, sufficient to explain the difference between the calculated density (3.3%) and the corresponding value (3.5%) determined by radiography. It is unlikely, however, that binarization fully accounts for the discrepancy with the value determined from physical measurements (3.8%). Also notable is the fact that the tomographic profile approximately reproduces the prominent features (i.e., larger minima and maxima) of the radiographic profile, confirming that these fluctuations represented real local density fluctuations associated with the large pore size, rather than artifacts from the measurement technique.

Radial density variations (as might occur, for example, if the outermost layer of the precursor were to deform preferentially during reshaping, leaving the inner “core” relatively undeformed) were investigated by calculating density profiles independently for two roughly equal volumes in the sample, one representing this inner cylindrical “core” of the sample, the other representing
Figure 6.9. Relative density profiles calculated from full 3D tomographic data. (a) total relative density profile; (b) relative density profiles plotted separately for the innermost and outermost 50 vol.% of the structure; (c) magnified view of the boxed region in panel b. The predicted profile is shown as a smooth line in each panel for reference.
the outermost “tube.” As shown in Fig. 6.9b, no consistent density differences were found between these regions. On finer scales (Fig. 6.9c), however, the profiles for these two subvolumes were anti-correlated, indicating that precursor deformation was often localized in one or the other region (that is, either the interior or near-surface region), with the other sustaining less deformation. Since this radial density gradient depended on position along the gauge length, the subvolume which deformed the most was most likely determined by statistically-distributed weak points in the structure, and therefore varied along the length of the sample in such a way that the overall density profile was approximately correct.
CHAPTER 7

Density-Graded Metallic Foams by Chemical Dissolution

The second density-grading method (hereafter, the dissolution method) was investigated for its simplicity and for its potential to enhance the density gradients produced in open-cell foams using other grading methods, for example the replication method of Chapter 6. In this method, the first step involves identification of minimally-damaging conditions for free corrosion of the alloy used in the target foam, as judged by microscopic observation and mechanical testing. A sample of the foam is then exposed to these conditions and allowed to corrode freely, but in a nonuniform fashion, by varying the exposure time of different regions of the foam to the dissolution bath. This variation in exposure time is accomplished, in the simplest case, by fixing the sample to a stationary support and then lowering the dissolution bath level by slowly draining the bath through an exhaust port. A schematic illustration of this process is provided in Fig. 7.1.

Figure 7.1. Schematic representation of the dissolution method for production of density-graded metallic foams.
7.1. Experimental Methods

The starting materials chosen for development and demonstration of the dissolution method were sheets of Duocel® open-cell aluminum foam provided by ERG Aerospace (Oakland, CA). The nominal pore density of the foams was 20 pores per linear inch (PPI), corresponding to pores approximately 1–1.5 mm in diameter, and the designed relative density was 10%. Though the exact processing of Duocel foams is proprietary, it is believed they are processed by the replication casting method described in Chapter 6; whether or not this is true, it remains the case that their structure is very similar to other foams processed with that method, including those described in that chapter.

The base alloy used in Duocel® foams is aluminum 6101 (hereafter, Al-6101), and sheets were provided by the manufacturer in the optimally-age-hardened or T6 condition, where strengthening is achieved in Al-6101 through the precipitation of Mg₂Si. This treatment involves solutionizing at 527°C for 8h, prior to water quenching and aging at 177°C [18]. In order to investigate the effect of Mg₂Si precipitates on dissolution characteristics, certain foam specimens were restored to the solution-treated (ST) condition by annealing at 530°C for 30 min.

Quadrilateral foam samples (ca. 10 × 10 × 5 mm³) were cut using a diamond saw from an as-received foam sheet and immersed in stirred 1000 mL baths of aqueous NaOH, KOH, Ca(OH)₂, and HCl, whose pH was set and monitored using a pH meter equipped with a glass electrode. Changes in solution pH (towards neutrality) were observed during dissolution experiments, particularly at low HCl and NaOH concentrations. Therefore, solutions were replaced at intervals of less than 15 h for the pH 3 HCl solution (in which the average pH change was +0.082/h) and the pH 10 NaOH solution (average pH change -0.21/h). In the more concentrated solutions, with rates of pH change of +0.003/h (pH 1) to -0.015/h (pH 13), the solutions were replaced whenever necessary, in order to maintain their pH values within 15% of the target values.
Mass losses were measured after every few hours of immersion, following washing in deionized water and ethanol and drying. Dissolution rates were then estimated from mass losses using manufacturer-provided data for foam surface areas, under the assumption of uniform corrosion. These specific surface areas decreased with relative density, and the values were 19.0, 17.4, 15.3, and 12.3 cm\(^{-1}\) for 10, 8, 6 and 4% dense foams, respectively. Interpolated specific surface areas were used for estimating true mass losses and corrosion penetration rates.

For comparison between dissolution rates in the foamed and monolithic alloy, bulk specimens (6 × 25 × 1.5 mm\(^3\)) of known surface area were cut from Al-6101-T61 extruded bus bar having a rectangular section of 6.35 × 50.8 mm, manufactured by Central Steel and Wire Company (Chicago, IL). Cut specimens were polished with 1200 grit SiC paper and cleaned in order to remove surface oxides and flaws, and then exposed to the same dissolution conditions used with foam samples. Certain specimens were solution-treated at 530°C for 60 min. The chemical compositions of the foam and bulk alloy are shown in Table 7.1. For comparison, the nominal chemical composition of Al-6101 is also given [18].

The effects of dissolution on foam architecture and surface condition were evaluated using optical and scanning electron microscopy. In addition, three foam specimens were selected for detailed analysis using a commercial micro-computed tomography (\(\mu\)CT) system (\(\mu\)CT 40, Scanco Medical, Bassersdorf, Switzerland) with a white x-ray source operating at an accelerating
voltage and source current of 45 kV and 177 µA, respectively. For each of these specimens, five volumes (thin slabs with thickness ca. 600 µm and spanning the entire cross section, equally spaced along the gauge length) were reconstructed with an isotropic spatial resolution near 15 µm. The data were binarized using the threshold value which gave greatest correspondence between the calculated tomographic relative density, averaged over all five volumes, and the relative density measured by dry mass and dimensions for an as-received foam sample. The densities of the two other specimens, which had been dissolved in alkaline solution, were then evaluated using the same threshold value. Two structural indices, the mean trabecular (i.e., strut) thickness and the structure model index were evaluated using the µCT software package. The details of these calculations are described elsewhere [80, 79], but it is noted that both algorithms were designed for model-independent quantitative analysis of trabecular bone, whose structure is quite similar to that of Duocel® foams.

7.2. Dissolution of Al-6101

Changes in relative density with immersion time were measured in foams (having initial relative densities ca. 10–13%) using Ca(OH)$_2$, KOH, NaOH, and HCl solutions of varying concentration. Immersion in Ca(OH)$_2$ led to formation of thick surface films, and therefore to increasing density, and was thus discarded as a possibility for grading. Immersion in all other solutions led to decreasing density, as shown in Figure 7.2. To emphasize differences in dissolution rate (i.e., slope) between specimens, the data are normalized by initial foam density.

After about one week of immersion, measurable density changes occurred in foams exposed to solutions with pH outside the range ca. 3–10. As expected, dissolution rates increased quickly as pH values moved farther from neutrality. Dissolution rates were generally similar for both heat-treatments (T6 and ST, represented by open and closed markers, respectively), though slightly
accelerated dissolution was sometimes noted in T6-treated samples. As discussed below, damage through preferential attack of grain boundaries and precipitates likely caused this acceleration.

Dissolution rates for foam specimens in NaOH solutions (Fig. 7.1a) were marginally higher than dissolution rates in KOH solutions (Fig. 7.1b) of comparable strength, and substantially higher (by approximately fifty times, when equal concentrations are compared) than those measured in acidic HCl solutions (Fig. 7.1c). It was therefore determined that strong alkali solutions offer the greatest potential for density reduction or grading of Al-6101 foams on practical timescales, and these dissolution conditions were selected for further analysis. For reasons discussed in the next section, it was further determined that NaOH solutions are preferred to KOH solutions, despite their similarity in dissolution rates.

Foam dissolution rate data such as those shown in Fig. 7.1 are necessary to implementation of the dissolution method for density grading. Measuring such data would not, however, have been necessary if they could be calculated from a known relationship between dissolution rates in foam and monolithic specimens (for which literature data are more extensive). There are reasons to believe that the relationship will be other than 1:1, i.e. that corrosion rates in foam specimens will be different than those in bulk specimens of the same composition. These reasons include differences in grain size, surface state, and surface curvature. In addition, Sakashita et al. [160] has reported a diameter dependency for dissolution of high-carbon steel wire in aqueous NaCl solution, explaining the effect in terms of reduction of dissolved oxygen or promotion of a cathodic reaction involving hydrogen ions.

In order to explore this relationship, dissolution rates in rolled Al-6101 sheet were measured under the same dissolution conditions shown in Fig. 7.1a, and the results are shown in Fig. 7.3. As shown in the figure, dissolution rates in the bulk material were similar to those measured in foams (consisting mainly of thin struts), indicating that there was no significant size effect in the dissolution rate of Al-6101 in NaOH solution.
Figure 7.2. Normalized rates of dissolution for commercial Al-6101 foams in aqueous solution. (a) NaOH solution; (b) KOH solution; (c) HCl solution. Data courtesy of Dr. Y. Matsumoto of the Oita National College of Technology (Oita, Japan).
Figure 7.3. Comparison between dissolution rates of foamed and bulk Al-6101 in aqueous NaOH solution of pH 13. Data courtesy of Dr. Y. Matsumoto of the Oita National College of Technology (Oita, Japan).

Figure 7.4 shows dissolution rates in NaOH solutions of various pH, presented as penetration rates in order to facilitate comparison with literature data. For pH values between 10 and 12, dissolution rates increased near-linearly from 0–15 mm/y. However, in pH 13 solution, dissolution accelerated to $\sim 70$ mm/y ($\sim 8 \mu$m/h). It has been reported [18] that general-use 1100-H14 aluminum alloy shows an average dissolution rate of 2 mm/y or more in NaOH solutions exceeding pH 11, and this rate increases rapidly with a further rise of pH. Although dissolution of the present Al-6101 in NaOH solution is not well documented, it is noted that T6 and ST foams seem to have a more rapid penetration rate of 4–5 mm/y at pH 11, as compared to Al-1100-H14.

### 7.3. Structure

Although the mechanical properties of reticulated aluminum foams have been studied extensively, there is little knowledge about the effect of strut surface condition on foam properties [64, 3]. Nonetheless, it is plausible that the quality of the surfaces in a dissolved or corroded foam will affect overall mechanical properties, because: (i) during strut bending, the dominant
Figure 7.4. Dissolution rates as a function of NaOH concentration (molarity and pH) for Al-6101 foams and bulk specimens.

deformation mode in low-density foams, deformation initiates at strut surfaces where the local strain is highest; (ii) most deformation, at least at low strains, is concentrated in the struts, whose low thickness renders surface effects proportionally more important; and (iii) corrosive damage may extend beyond the surfaces in certain cases, such as grain pullout or severe pitting. Achieving maximum performance from partially-dissolved aluminum foams therefore requires identifying the least-damaging immersion conditions, as discussed below.

Figure 7.5 shows SEM images taken from Al-6101 foam specimens in the T6 and ST conditions, following dissolution in room-temperature HCl solution of pH 2. A layer of corrosion product (made particularly apparent by contrast with NaOH-treated foams, Figs. 7.6–7.7) is visible on the internal surfaces of the T6-treated specimen (Fig. 7.5a), and evidence of large-scale damage in the form of sharp crack-like pits and grain pullout (Fig. 7.5b) is seen in several places. Though the number and severity of these damaged regions were decreased by the solution treatment (Fig. 7.5c), the corrosion product remained and several deep pits and large area reductions (Fig. 7.5d) were still visible, identifying HCl as a highly-damaging immersion solution.
Figure 7.5. SEM micrographs of T6-treated foams after immersion in a pH 2 HCl solution at 23°C. Panels (a) and (c) show strut and node surfaces for foams with 7.5 and 5% relative densities, respectively; Panels (b) and (d) show individual strut of foams with 7.5 and 5% relative densities, respectively.

Figure 7.6 shows SEM images of T6-treated Al-6101 foams after dissolution in pH 13 NaOH solution at room temperature. Shallow, hemispherical corrosion pits were uniformly distributed on the surfaces of struts and nodes. Although one quarter of the foam mass had been dissolved (reducing the relative density of the foam, shown in Fig. 7.6b, from 10% to 7.5%), struts with sharp edges remained. These edges have largely disappeared from the struts of the foam having relative density 5% (Fig. 7.6d), while the hemispherical pits on grain boundaries become larger and etched grain boundaries are visible. Struts appeared to preferentially thin near the middle of their lengths, and at times were even cut into two halves by complete dissolution of their thinnest section.

Solution-treated Al-6101 foams (Fig. 7.7) were investigated in the same manner. The density of the hemispherical corrosion pits decreased, and strut and node surfaces with minimal damage
and shallow pit depth were obtained. Even in foams reduced to relative densities of 5%, sharp strut edges remained and grain boundaries were not etched. Thus, after solution-treatment was performed to solutionize Mg$_2$Si precipitates, Al-6101 foams were dissolved more uniformly, and reductions in strut and node sizes were possible without significant visible damage, despite the fact that this was the most rapid dissolution medium identified earlier (Fig. 7.2).

The foam samples shown in Fig. 7.7 were analyzed tomographically, along with a solution-treated as-received sample, and the results of this analysis (values are averages over the five thin-slab volumes taken from each sample, and errors are standard deviations) are summarized in Table 7.2. Tomographic relative densities were within 8% relative deviation from those measured by mass and dimensions in each case (though the as-received sample was used for threshold calibration), with low standard deviations of less than 0.1 vol.%. With decreasing relative
Figure 7.7. SEM micrographs of ST-treated foams after immersion in a pH 13 NaOH solution at 23°C. Panels (a) and (c) show strut and node surfaces for foams with 7.5 and 5% relative densities, respectively; Panels (b) and (d) show individual strut of foams with 7.5 and 5% relative densities, respectively.

density, mean strut thickness (this is the standard terminology, although the term could be replaced by 'effective diameter') decreased, as expected. The values calculated for mean strut thickness are also in rough agreement with predictions from SEM examination, though it is noteworthy that the method of calculation of strut thickness is volume-weighted and thus tends to emphasize thicker node-like features, leading to overestimates for strut thickness [79].

More significantly, the difference in strut thickness between as-received and moderately-dissolved (7.5%) foams is smaller than the difference between moderately- to severely-dissolved (5%) foams. Due to their higher specific surface area (i.e., high aspect ratio), struts may be expected to bear a disproportionate fraction of the total alloy loss, as was apparent in SEM examinations (Figs. 7.5–7.7). Consequently, it is also anticipated that relative decreases in strut thickness (reflecting only the dissolution of struts) will outpace those of average foam
Table 7.2. Tomographic parameters calculated from three foam specimens, solutionized and then dissolved in room-temperature NaOH solution of pH 13. Error values represent standard deviations based on 5 measurements taken along the gauge length of each sample.

<table>
<thead>
<tr>
<th>Physical $\rho/\rho_s$ (%)</th>
<th>Tomographic $\rho/\rho_s$ (%)</th>
<th>Mean Strut Diameter ($\mu$m)</th>
<th>SMI (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.7</td>
<td>8.9 ± 0.6</td>
<td>289 ± 5</td>
<td>3.25 ± 0.08</td>
</tr>
<tr>
<td>7.5</td>
<td>7.9 ± 0.7</td>
<td>273 ± 7</td>
<td>3.29 ± 0.04</td>
</tr>
<tr>
<td>5.1</td>
<td>5.1 ± 0.3</td>
<td>233 ± 7</td>
<td>3.58 ± 0.09</td>
</tr>
</tbody>
</table>

density (reflecting both struts and more slowly-dissolving nodes), as described in Chapter 3 for Vit106 foams dissolved in acid solutions. In the case of the Vit106 foams, it is recalled that foam strength also decreased more rapidly with density than in conventional metallic foams, a reflection of the relative importance of struts (as compared to nodes, which deform only slightly at low macroscopic strains) in determining foam mechanical properties.

To quantify the effect of such preferential strut attack more precisely, the non-dimensional structure model index (SMI) of each sample was also calculated, and the results are included in Table 7.2. The SMI is used to characterize the conformity of the real structure to various model structures, e.g. plates (SMI = 0), cylindrical rods (SMI = 3), or spheres (SMI = 4), based on changes in surface area attending small “dilations” of the structure outwards along its surface normals [80]. An SMI of 3.25 for the as-received foam suggests a structure composed mostly of rods (i.e., struts), with some spherical features (i.e., nodes). Increases in SMI with dissolution indicate evolution towards more spherical features, or a decrease in the proportion of rod-like struts, in agreement with the discussion presented above. The fact that changes in SMI accelerate between 7.5% and 5% relative density again suggests that high levels of dissolution cause proportionally greater changes to foam architecture than moderate degrees of dissolution.
7.4. Mechanical Properties

In accordance with the observations above, a series of foams with relative densities near 10% (as-received), 7.5%, 6.25%, and 5% was created by dissolution under minimally-damaging conditions (NaOH solutions of pH 13). To further study optimized conditions, specimens were produced using solutions at both room temperature and 70°C, and in both ST and T6 conditions. To investigate the effect of the HCl-induced microstructural damage seen in Fig. 7.5, ST and T6-treated specimens were also created using room-temperature HCl solutions of pH 1.

This series of foam specimens (all in the T6 condition for mechanical testing, though some samples had been solutionized before dissolution) was tested in displacement-controlled uniaxial compression at a nominal strain rate of $10^{-3} \text{s}^{-1}$. Each specimen had a rectangular cross-section and a minimum dimension seven times the pore size or greater, to avoid statistical variation in foam properties [3]. However, due to the limited dimensions of the as-received foam sheet, and the fact that the specimen longitudinal direction was kept perpendicular to the sheet plane to minimize the effects of anisotropy, the specimens were limited to aspect ratios averaging 1.3. Stress-strain data were corrected for compliance in the same manner described in previous chapters. Three representative stress-strain curves, representing the as-received foam as well as two partially-dissolved specimens, which were solutionized, dissolved in room-temperature NaOH solution of pH 13, and then aged back to the T6 condition, are shown in Fig. 7.8.

In most cases (eleven of fifteen tested specimens), the linear initial loading regions of the stress-strain curves were separated from the subsequent Plateau regions by a local maximum in flow stress. In these cases, this local maximum stress was taken as the foam strength. In the remaining specimens (four of fifteen), no distinct maximum stress was found, the transition between initial loading and Plateau regions being essentially monotonic. In these cases, foam strength was determined by the intercept of two tangent lines extrapolated from the initial loading and Plateau regions of the stress-strain curves. Initial stiffness in the foam specimens was
Figure 7.8. Representative compressive stress-strain curves for foams dissolved uniformly in room-temperature NaOH (pH 13). The highest-density specimen was in the as-received condition, while the two partially-dissolved specimens were solution-treated prior to dissolution, and then aged to the T6 condition before mechanical testing.

...determined using data from several loading/unloading cycles taken near the point of macroscopic yield, after compensation for load train compliance. Complete unloading was avoided during these cycles to prevent sample resettling, and data near the maximum applied stress were discarded to avoid the effects of plasticity.

Yield strength for all tested specimens is compiled as a function of relative density in Fig. 7.9a. As shown in the figure, there was a noticeable loss of strength in the HCl-treated samples when compared to the NaOH-treated samples. However, among the NaOH-treated samples, there was no significant difference in strength between samples dissolved in room-temperature and 70°C heated solutions. There was also no consistent difference in strength between foams dissolved in the ST and T6 conditions, despite the differences in strut surface appearance (Figs. 7.6 and 7.7). Though more data would be needed to identify subtler differences,
the available data suggest that the presence of visible cracks, grain pullout, thick corrosion product layers, and other forms of severe damage incurred during HCl treatments are sufficient to affect foam strength, as might be expected. By contrast, moderate surface pitting such as that seen in the NaOH-treated specimens did not lead to major changes in foam strength, perhaps due to the relative notch-insensitivity of ductile aluminum struts.

A notable feature of the data, however, is that the relative loss in strength with decreasing density was more rapid than predicted by conventional scaling laws. To illustrate this point, a best-fit line having a slope of 1.5 (corresponding to the exponent of Eqn. 1.2) is provided in Fig. 7.9a. The data for foams with densities in the range ca. 6–10% could reasonably be fit to such a line, but when data for foams near 5% density are included, a higher slope (the best-fit value found by allowing a variable exponent in the power-law equation) near 4 is suggested. This indicates that modest changes in density (from 10 to ca. 6%) are accommodated without severe damage or fundamental changes to the structure of the foam, whereas more substantial dissolution (below ca. 6%) causes strut damage and/or a qualitative change in the shape of the...
struts themselves. This observation is in agreement with the SEM and tomographic analyses presented in the previous section, as well as with similar accelerated strength losses in the replicated AMF of Chapter 3.

Figure 7.9b shows initial stiffness for the same series of foams, as a function of relative density. The same trends are apparent, with visible differences between HCl- and NaOH-treated foams, but no significant differences between room-temperature and heated NaOH solutions, or between foams dissolved in NaOH in the ST and T6 conditions. Similarly, while the higher-density points (ca. 6% and higher) could be described by the conventional relationship of Eqn. 1.1 (illustrated by a best-fit line of slope 2), the points near 5% density appear to fall below the prediction, leading again to a higher overall slope of 4 (i.e., a faster loss in stiffness than would be expected from normal foam processing methods). In this case, the deviation from conventional behavior is more pronounced, and occurs quite distinctly between 6.25% and 5%. Thus the foam stiffness data corroborate the observation, suggested by the strength data, that the severity of surface pitting is less important a predictor of mechanical properties for these foams than relative density.

7.5. Density Grading

Dissolution in temperature-controlled NaOH baths of pH 13 was used to create two density-graded specimens using the approach shown in Fig. 7.1. The first specimen consisted of an Al-6101-T6 foam of size 19 × 5 × 50 mm³, and the second of a similar foam of size 9.5×5×50 mm³. The first specimen was placed in a room-temperature bath with a rate of change of fluid level of 6 mm/h, while the second was placed in a heated bath of temperature 70°C with a more drainage rate of 60 mm/h. These rates were chosen, based on measured rates of change in relative density under the corresponding conditions, to grade the foam specimens to minimum densities of approximately 5% (i.e. density gradients of about 2:1, as in the replicated foams of
A photograph of the graded foam produced using the room-temperature solution is shown in Fig. 7.10a. The structure of the region not exposed to solution (at the top of this image) is characteristic of the as-received foam; an electron micrograph demonstrating this fact is provided in Fig. 7.10b. By contrast, the structure of the low-density region, exposed to the longest immersion time (Fig. 7.10c), shows evidence of heavy dissolution. In this heavily-corroded structure, evidence of damage is already visible.

This specimen was mounted in epoxy resin and polished to a 0.1 μm finish using an aqueous Al₂O₃ suspension. The longitudinal gradient in the area fraction of the foam was calculated by digital image analysis, from which the gradient in relative density was inferred. The measured gradient is shown in Fig. 7.11, which shows that relative density decreased from 10% to 5% near-linearly with the distance from the upper (unexposed) edge. The rapid density change near the
bottom (maximally-exposed) edge, at a position of 30 mm, was due to strut fracture by severe dissolution, as well as handling damage, consistent with the study of mechanical properties presented above, as well as the image in Fig. 7.10c.

The graded foam produced using a heated solution is shown in Fig. 7.12. Although much more rapid density grading was indeed possible in this way, visible corrosion damage in the graded T6-treated foam was more severe, as evidenced by large corrosion pits on strut surfaces. This damage was less pronounced after solution treatment, but still visible, and thus the details of the resulting profiles were not investigated.

From these preliminary experiments, it is concluded that optimal control of both solution pH and temperature are required in order to reduce density while leaving the struts and nodes of density-graded foams intact. However, under such conditions it is believed that density-graded foams with minimum relative densities near 5% can be reliably obtained using this method.
Figure 7.12. Photograph of a commercial Al-6101 foam graded by nonuniform exposure to a heated (70°C) NaOH solution of pH 13.
CHAPTER 8

Conclusions and Future Work

8.1. Amorphous Metal Foams

At the time of this writing in September of 2006, the field of amorphous metal foams is just entering its fourth year. Naturally, a great number of challenges have been raised over these years which have not yet been addressed, and which must therefore become objects of future study. These challenges pertain to all aspects of the field, from basic processing to property characterization and applications study. The following sections analyze each of these individually, and propose appropriate areas for future study.

8.1.1. Processing

The first significant conclusion drawn from this work is that processing of AMF is possible using liquid-state approaches and commercially-relevant alloys. This was, at the start of this work in 2001, not an obvious conclusion, on account of the contamination sensitivity and cooling rate requirements of such alloys. The work presented here demonstrates that liquid-state foaming of commercial amorphous metals is possible, and further, that the resulting properties (discussed below) are promising enough to warrant further study.

As discussed in Section 2.3, processing of AMF in general has already advanced considerably, with proven methods for fabrication of open- and closed-cell foams ranging in density from 15% to more than 90% of the bulk, containing spherical and angular, isotropic and anisotropic porosity ranging in size from the nanometer to the millimeter scale. Yet despite this rapid progress, AMF processing cannot yet fulfill the most important claim put forth here, namely, that these
materials will eventually represent a simpler means of achieving mechanical performance criteria, from the standpoint of processing, than will crystalline metal foams made from high-melting alloys. Doing so will require still more advances, in terms of optimization of current methods and development of new ones.

Many of the key advances needed to extend the use of AMF beyond academics can be made by improving the glass-forming ability and cost effectiveness of their base alloys, e.g. by reducing precious and toxic metal components and increasing the robustness of BMG against crystallization induced by contaminants. However, the fruits of such advances are not limited to AMF, but rather benefit the entire field of amorphous metals. Thus these topics are already the subject of intensive research within that community (the successes of which are reflected in the thousand-fold increase in castable dimensions over the last 40 years [84]). In light of this fact, alloy development need not be a goal for the AMF community in particular; the more relevant concern there is how to minimize the complexity and cost of the foaming processes themselves.

Several of the published foam processing methods, unfortunately, are themselves both complex and costly. The replication method of Chapter 3 is no exception, as its use of fluoride-bearing strong acids makes strong demands on the corrosion resistance of both the BMG and associated processing equipment (this method does, however, enjoy generality in every other respect). A similar limitation applies to the powder-based methods of Lee and Sordelet [107, 108], which employ identical strong acid treatments for removal of placeholders, and which involve the added complexity of powder processing and consolidation. Although these reports also suggest that large (8–8.5 mm diameter [107, 108]) extruded samples could be effectively leached, considerable difficulty in selective phase dissolution has been reported with crystalline Ni-based metals [158, 159]. This difficulty arose mainly from the diminishing transport kinetics of species involved in dissolution reaction, as the reaction moved inwards through a specimen; the result of this deceleration was that only thin sections of nanoporous material could be processed in the
time window in which more damaging reactions began occurring [158]. Similar difficulties may also occur in future AMF produced by this technique.

Both the replication and selective dissolution methods, therefore, would benefit significantly from replacement of their current placeholding phases by water-soluble substitutes. Use of NaCl, which has been demonstrated in both Zr-based [149] and Pd-based [186] alloys, offers a clear advantage from this standpoint; however, it is not clear that NaCl will be generally applicable in liquid-state foaming, due to its low melting point and high vapor pressure (Section 3.1.4), and early experiments (not reported elsewhere in this work) involving co-extrusion of Vit106/NaCl powder blends revealed a strong tendency of NaCl to become segregated during consolidation. It is instead suggested here, based on preliminary experiments performed by coworkers, that a compromise may be offered by use of water-soluble alkaline-earth oxides such as CaO, SrO, or NaAlO\(_2\). These oxides are thermodynamically stable, with respect to reduction by components in the melt [155], but react with water to form soluble hydroxide species such as Ca(OH)\(_2\) and Sr(OH)\(_2\) [115]. Lime (CaO), in particular, is readily-available on account of its importance in the cement industry.

A second limitation of salt-replication methods, in their present form, is poor control over relative density. In NaCl-based AMF methods [186, 149], little or no effort was made to vary the volume fraction of salt patterns in order to vary the relative density or structure of the final AMF. Although different relative densities were studied in this work, changes in relative density were accomplished primarily through corrosive dissolution of the amorphous phase, which is highly inefficient and which produced different density-scaling behavior than in conventional foams. There is, consequently, an outstanding need for study of how relative density changes can be more efficiently produced in replicated structures. The obvious approach for such study would be to study the effect of pattern pressing and/or sintering, along the lines of recent study of the effects of these procedures on the properties of replicated Al foams [65]. Limited
study along these lines was attempted here, but was hindered by the difficulty of achieving densification during sintering of BaF$_2$, without severe evaporation losses, and by difficulty in achieving adequate infiltration in pressed salt patterns.

More troublesome than replication methods, from the standpoint of complexity and cost, are AMF methods based on gas entrapment. In the first of these methods, demonstrated by the Johnson group [168, 167], water vapor released from boron oxide powders constitutes the driving force for foaming. While the approach was successful in a Pd-based alloy, both water vapor and boron oxide should be expected to contaminate less-noble glass-forming melts. Thus, the future of this method depends on identifying similar agents capable of binding non-reactive gases and then releasing them in a controlled fashion after dispersion a glass-forming melt. The difficulty of identifying such an agent can be appreciated by considering the difficulties encountered during parallel investigation of blowing agents for aluminum [12, 94], which certainly represents the easier of the two systems from a processing standpoint.

Similar difficulties are faced by the method of Wada and Inoue [187, 190, 189], based on charging high-temperature Pd-based glass-forming melts for several hours under 150 atmospheres of pure hydrogen. In addition to the substantial safety issues attending scaleup of such a process, it is again unclear whether the method can be applied to less noble alloys. Yet despite these difficulties, gas entrapment methods remain important for the future of AMF because they illustrate the excellent foam structures made possible in AMF by elegant decoupling of pore formation and vitrification. Successful generalization of these methods to commercial alloy systems would represent a major step in AMF processing.

Once processing of stand-alone AMF has been more thoroughly developed, it will become necessary to investigate AMF-core sandwich structures. It is likely, given the established benefits of geometric confinement of shear bands in monolithic amorphous metals [202, 37, 118], and the observed suppression of microfracture induced by confinement during densification in
AMF (Section 3.4), that sandwich structures with AMF cores will show marked improvements in performance relative to stand-alone AMF. It is further believed that sandwich structures can be produced on research scales with only minimal modifications to preexisting foaming processes, though difficulties in diffusion bonding AMF cores to faceplates (without inducing crystallization) may necessitate development of integral processing methods where facing layers are formed or bonded before or during foaming (e.g., roll-cladding of facing materials onto powder compacts prior to SCL-state foaming). The high specific strength and excellent wear-and corrosion resistance of amorphous metals make them natural first choices for facing materials, especially using integral methods for which amorphous metal facings would be natural. Crystalline metallic facings should also be considered, due to their high uniaxial ductility in both tension and compression, though bonding of crystalline facings may come at the cost of added processing difficulty and increased likelihood of inducing brittle crystalline phases near the core/facing interface.

8.1.2. Properties

The single most important conclusion drawn from this work is that foam architectures can indeed be successful in inducing shear band stabilization in amorphous metals, and that AMF can on this basis show compressive ductility on par with metallic foams made from ductile crystalline metals. To the author’s knowledge, the work described here represents the only published evidence of this fact, as the available data from other researchers show compressive behavior which is qualitatively different from that of low-density crystalline metallic foams, generally on account of the higher relative densities of these other published AMF. To illustrate this fact, a compressive stress-strain curve from this work (representing a replicated Vit106 foam of relative density 18%) is shown alongside that of a higher-density foam (representing a hydrogen-blown Pd-based foam of relative density 64% [187]) in Fig. 8.1. The stress-strain curve of the AMF
Figure 8.1. Comparison between the compressive stress-strain curves of representative AMF specimens from this work and the work of the Inoue group in Japan \cite{187}. The inset shows a magnified view of the low-strain region of each curve.

from this work is qualitatively the same as that of a ductile crystalline metallic foam, while the higher-density Pd-based specimen shows very different behavior, with higher strength but lower failure strain. The difference between these behaviors may be crucial in certain applications, most notably impact absorbers.

Substantial work, however, is still needed in the documentation and understanding of the properties of AMF, in particular mechanical properties. Nothing is known, for example, of the tensile or bending properties of AMF, or of fracture toughness, fatigue strength, or high strain-rate behavior. Documentation of these properties, important for the eventual application of AMF (for example, as structural or impact-resistant paneling or load-bearing biomaterials), is however less pressing than the need for fuller understanding of the basic compressive behavior of
AMF. This need is best illustrated through examination of the available compressive mechanical property data.

Of all the porous amorphous metals reported to date, the most thoroughly-documented are those in this work, and the hydrogen-blown Pd-based AMF of Wada and Inoue [187, 190, 189]. The available mechanical data from these two sets of foams seem to show discrepancies, however. Specifically, normalized stiffness and strength are higher in the hydrogen-blown foams, even when the trend of the lower-density replicated foams is extended to higher densities. This suggests that there may be a difference in the underlying deformation mechanisms.

To illustrate this point quantitatively, the mechanical properties (relative stiffness and strength, as functions of relative density) of both sets of foams are compared in Fig. 8.2. Fitting the replicated foam data using the appropriate empirical scaling relationships (Eqn. 1.1 and 1.2), and extending these fits to the higher densities represented by the Pd-based samples, reinforces the notion that the behavior of these two materials is regulated by different mechanisms.

Several explanations can be put forth to rationalize these observations. Firstly, the Pd-based AMF have closed-cell structures, which tend to be somewhat stronger and stiffer than open-cell structures of equal density [3]. Secondly, with regard specifically to strength, the pores in the Pd-based structure are spherical, minimizing loss in strength associated with stress concentrations when compared to angular pores. Thirdly, the higher-density Pd-based foams most likely derived their ductility from composite toughening, rather than through stable shear banding in strut-like features, as indicated by examination of deformed specimens in each case [187]. As such, they failed primarily through axial deformation, as in a composite matrix, rather than through the bending modes characteristic of the lower-density replicated AMF. Since the load-bearing capacity of a metallic glass feature such as a strut is substantially higher in axial loading than in bending, loss in strength is expected to accompany the transition between axial and bending-dominated deformation modes, especially since collapse in bending is partly controlled by the
Figure 8.2. Comparison between the mechanical properties of replicated Vit106 foams in this work and hydrogen-blown Pd-based foams described in Ref. [187]. (a) Normalized compressive strength. (b) Normalized stiffness. Also shown are least-squares regression fits to the empirical scaling equations [3] most relevant to each structure.
tensile strength. A similar loss in stiffness may occur during the transition to bending-dominated deformation, since elastic deflection of a long beam subjected to bending, e.g. in a cantilever, is generally higher than the deflection of an identical beam deforming axially under the same load. However, this effect is less pronounced than for strength, due to the absence of tension-compression asymmetry in alloy stiffness.

Although the differences in strength and stiffness between the lower-density replicated AMF and the higher-density gas-blown AMF can be rationalized in this fashion, the relative contributions of each of these factors are still unclear and in need of further study. To point out examples, it has already been stated that the difference in mechanical properties between open- and closed-cell foams is usually small, suggesting that this factor may not account for the discrepancy [3]. The significance of pore angularity appears evident in the loss of stiffness and strength in NaCl-replicated Pd-based BMG foams [186], when compared to closed-cell, spherical-pore foams of equal density [187, 190, 189]. It is also generally supported by the strong sensitivity of BMG toughness to crack tip radius (or, in this case, to the local curvature at the edge of a pore) [111]. However when two high-density porous Pd-based BMG containing elongated pores were compared (one whose pores had major axes parallel to the stress axis, and therefore whose edges of greatest stress concentration were subjected to tension, and one whose pores were perpendicularly oriented), significant differences in ductility were not accompanied by any large differences in strength [189], suggesting that pore angularity may not be the primary source of strength differences in Zr-based and Pd-based foams. If, as these observations would seem to suggest, the difference in strength and stiffness originate largely from the difference between bending- and axially-dominated local deformation modes, the question remains as to whether the transition between these modes is a function only of relative density, or of pore morphology as well. Consequently, investigation of samples in the region lying between these
two datasets, i.e. in the range of 25–40% relative density, is of key importance in understanding how to maximize strength in AMF.

A compilation of all published mechanical property data for porous amorphous metals is shown in Fig. 8.3. The left panel (Fig. 8.3a) shows normalized compressive strength (compressive strengths were once again used for normalization, despite the arguments put forth in Section 3.3, because tensile strengths were generally not known) as a function of relative density; the right panel (Fig. 8.3b) shows compressive failure strain, also as a function of relative density. This compilation is, admittedly, incomplete, as in certain cases the strength of the dense alloy was not known or not provided, or stress strain curves were not plotted in their entirety and thus failure strains were unknown. However in order to avoid misrepresentation, only those data stated, tabulated, or plotted explicitly by their authors are shown in the figure.
The trends displayed by the larger set of strength data in Fig. 8.3a confirm the observations made above, and reinforce the need for more data in the lower regions of relative density. The parallel trend in compressive failure strains (Fig. 8.3b), however, seems to suggest that activation of the stable shear banding processes occurs at higher relative densities than reflected in the strength data. Thus, an additional discrepancy, between the locations of the transition in strength and that in ductility, must be explored using AMF in a broader relative density range, perhaps 25–60%. More data in this range should help decide whether there is indeed any discrepancy between the transitions, or whether the appearance of one is an artifact produced by large scatter in the available data.

Of particular interest, from this standpoint, would be syntactic foams like the Mg-based AMF of Chapter 5; these foams have highly spherical pores with alloy volume fractions that fall naturally into the range in question. Indisputable evidence of matrix plasticity in such foams would, accordingly, have strong bearing on the questions raised above, and it is believed that such plasticity could be accomplished by minimizing the relative density and pore size in these foams (as described previously). Naturally, success with this method would also expand the field of AMF in other ways, as well as contributing to the fundamental understanding of deformation in syntactic foams by providing a new basic structure for study (namely, a syntactic foam in which the matrix is both stronger and more brittle than the sphere wall material).

Until such time as more data become available, it will be difficult to draw conclusions about the governing factors in the mechanical properties of AMF, e.g. the influence of open vs. closed cells, pore angularity, and most importantly, relative density. Without such conclusions it is impossible to ascertain how close available AMF are to maximizing their structural potential, and how competitive they may (or may not) eventually be with crystalline metallic foams.
8.1.3. Applications

On account of their high cost, and the processing limitations described above, it is only appropriate at the moment to discuss AMF applications which are both low-volume and relatively cost-insensitive. Of the applications proposed in Section 2.1, the two that best fit these criteria are vehicular/structural armor and bone replacement materials. The following discussion, pertaining to these applications, should be taken to refer to Vit106 foams, as application of the Mg-based alloy of Chapter 5 is not realistic until such time as the corrosion resistance of such alloys can be improved, and as application of Pd-based foams is, even for low-volume, high-cost niche applications, implausible.

In light of the rising importance of protective armors for both military and civilian vehicles and buildings over recent years, it is possible that high-strength AMF sandwich panels could be retrofitted onto such objects in order to increase their resistance to attack via explosives. In these cases, the principal benefit of AMF would be their high specific strength, which should provide superior energy absorption relative to aluminum foams or other materials by making use of the higher allowed stresses in vehicles and buildings. Indeed, it has already been shown here (Fig. 3.12) that Vit106 foams show markedly superior energy absorption (about two-fold on an energy/volume basis, though somewhat less on an energy/mass basis) relative to foams made from crystalline aluminum alloys. The principal areas of research required for further development of such applications would be study of facing materials having appropriate mechanical properties, the fabrication of sandwiches using these facings, fatigue strength, and high strain-rate mechanical properties (including ballistic penetration).

Use of AMF as orthopaedic biomaterials, specifically as bone replacements of the sort used in total hip replacement surgery, is an application for which a firmer literature basis can be found. As discussed previously (Section 2.1), the benefits of AMF in this context would be higher specific
strength (allowing for smaller, less intrusive implants than the Ti-based foams currently being developed [48]), low modulus (i.e., better stiffness matching with host tissue [146]), wear and corrosion resistance (minimizing release of particulate debris that often causes inflammation and failure in the host tissue), and, in most cases, lack of magnetism (simplifying noninvasive post-operative evaluation). The principal areas of research required in development of this application would include further investigation into the biocompatibility of BMG, and the development of glass-forming compositions (such as the Ni-free Zr-based alloy developed by Buzzi et al. [20]) free of toxic components. In the case of salt-replicated foams, which are the most likely of the available structures to find application as bone replacements (due to their open structures, and pore sizes large enough to accommodate bone ingrowth [48, 146]), the effect of residual salt deposits and corrosion layers would need particular attention.

8.2. Density-Graded Metallic Foams

The primary motivation for investigating density-graded foam materials is the potential for optimization of mechanical response at minimum mass. Unfortunately, even less mechanical property data are available in the case of density-graded metallic foams than was the case for amorphous metal foams. Consequently, the most important topic for future research is investigation of the mechanical behavior of density-graded foams, and the study of the relationships between this behavior and that of uniform-density foams of equivalent density, which are by comparison very well documented.

With regard to the work of Chapter 6 in particular, several points can be made. Because the structure and properties of polymer foams are more easily controlled than those of metallic foams, replication methods enjoy the advantage of high flexibility in foam density and local architecture. The method also allows for design of complex, non-monotonic density profiles, and can be applied in principle to any alloy system which is investment castable. On the other
hand, the densities which can be achieved using this method have not been fully explored, and there is clear evidence of structural flaws in foam regions replicated from highly-compressed precursors. In addition, difficulty in adequate investment filling and removal have presented themselves at small pore sizes. Future work should therefore emphasize a more comprehensive study of the mechanical properties of foams having simple density profiles such as those studied here, in order to better understand the influence of flaws on mechanical behavior. In addition, the practical limits of the method, in terms of relative density and pore size, should be sounded, as well as any deterioration of mechanical properties caused by exceeding these limits. This latter objective can be achieved without major modifications to the method, by analysis of new specimens having greater than two-fold increases in local density and pore sizes below 2 mm.

The dissolution method of Chapter 7 also enjoys flexibility in foam density and structure, a result of decoupling the foaming and density-grading steps. With these steps separated, the dissolution method can be applied, in principle, to any open-cell metallic foam irrespective of the method by which it was foamed. In practice, however, it is unclear whether non-damaging chemical dissolution is possible using these other alloy systems. Further work is therefore necessary to examine the generality of the process.

Future work is also clearly needed to establish the real viability of producing graded structures. Although the specimens described in this work represent an adequate first demonstration of the principle of grading by chemical milling, the sizes of these specimens were not appropriate for mechanical testing, and hence the properties of foam graded by this method are still unknown. Without production of a suitable mechanical test specimen, it is likewise unclear that capillary effects (that is, wicking of the bath into the pores of the precursor) will allow controlled grading over relevant length scales. This will be particularly problematic in specimens with smaller pore sizes; thus, grading of fine-pore specimens should also be demonstrated,
and the effects of capillarity, and potentially of differential aeration cells formed near the bath surface, documented.

Naturally, one of the principle reasons for investigating grading by dissolution was to augment the density gradients of specimens produced using the replication method. Thus an important advance could also be made by processing of such a hybrid specimen with a much more pronounced gradient, and evaluation of its mechanical properties. Before such data could be properly interpreted, however, the mechanical properties of foams graded through each individual process would need to be better characterized than they presently are.
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APPENDIX A

Effective Yield Stress for Struts with Triangular Cross-Section

Evaluation of the fully plastic moment of a strut having uniform equilateral triangular cross-section (with edge length \(a\)) proceeds under the same assumptions and with the same approach as outlined in the text for square cross-sections. For simplicity, the triangular strut is assumed to bend in a plane intersecting one of its edges along the entire length of the beam, and passing through the midpoint of the opposing face (i.e., a vertically-oriented plane extending perpendicularly to the cross-section in Fig. A.1). Depending on the sign of the applied moment, one of the two cases represented in Fig. A.1 applies. For the case represented in Fig. A.1a, the area of the tensile region is \(A_T = \frac{z^2}{\sqrt{3}}\). The area of the compressive region is \(A_C = \sqrt{3} \cdot \left(\frac{a^2}{4} - \frac{z^2}{3}\right)\), found as the difference between \(A_T\) and the total strut area \(A_{tot} = \sqrt{3} \cdot \frac{a^2}{4}\). Introducing these quantities into the force balance equation, Eq. 3.3, and solving for \(z\) locates the plastic neutral axis:

\[
(A.1) \quad z = \frac{a}{2} \cdot \left( \frac{3\sigma_C}{\sigma_C + \sigma_T} \right)^{\frac{1}{2}}
\]

where \(T\) and \(C\) are the magnitudes of the tensile and compressive strengths, as in the main text. The centroid of the tensile region lies at a distance equal to one-third the height of the triangle above its base, or \(y_T = \frac{z}{3}\). The centroid of the isosceles trapezoidal compressive region lies at a distance \(\left(\frac{h}{3}\right) \cdot \frac{(2a' + b')}{(a' + b')}\) above the bottom edge of the strut, where \(h\), \(a'\), and \(b'\) are the height, upper, and lower base of the trapezoidal region, respectively (Fig. A.1a). Noting that this bottom edge is at a distance \(a \cdot \sqrt{3}/2 - z\) from the neutral axis, the distance
Figure A.1. Schematic cross-sectional view of a strut of equilateral triangular shape, subjected to bending in a plane oriented perpendicularly to the page. In (a) the applied moment produces tension along the edge of the strut and compression along the opposing face; in (b) it has the opposite sense, producing compression along the edge and tension in the face.

\[ y_C = \frac{3a^2 - 2z^2 - \sqrt{3}az}{6z + 3\sqrt{3}a} \]  

Introducing the distances \( y_T \) and \( y_C \), the areas \( A_T \) and \( A_C \), and Eq A.1 into the moment balance equation (Eq. (5a)) and solving for \( M_p \) gives the fully plastic moment of the beam under the assumed loading conditions:

\[ M_p = \frac{a^3}{4} \cdot \left( \frac{\sigma_C \cdot \sigma_T}{\sigma_C + \sigma_T + \sqrt{\sigma_C \cdot (\sigma_C + \sigma_T)}} \right) \]

Since the area of a triangular strut of edge length \( a \) is not equal to the area of a rectangular strut of edge length \( a \), a foam composed of such struts need not be of the same relative density as the foam represented by the rectangular strut of Fig. 7. Thus we calculate the effective edge length \( h_e \) of a rectangular strut with equal cross-sectional area to the strut in Fig. A.1a, by equating their respective areas, with the result that \( h_e = 3\frac{1}{2} \cdot \frac{a}{2} \). Expressing Eq. A.3 in terms of
this quantity gives:

\[ M_p = \frac{h_e^3}{4} \cdot \frac{8}{3^4} \cdot \left( \frac{\sigma_C \cdot \sigma_T}{\sigma_C + \sigma_T + \sqrt{\sigma_C \cdot (\sigma_C + \sigma_T)}} \right) \]

Equating Eqs. A.4 and (5b) provides the effective yield stress:

\[ \sigma_{y,e} = \frac{h_e^3}{4} \cdot \left( \frac{\sigma_C \cdot \sigma_T}{\sigma_C + \sigma_T + \sqrt{\sigma_T \cdot (\sigma_C + \sigma_T)}} \right) \]

Performing the same analysis for an oppositely-oriented applied moment (Fig. A.1b) gives a similar result:

\[ \sigma_{y,e} = \frac{h_e^3}{4} \cdot \left( \frac{\sigma_C \cdot \sigma_T}{\sigma_C + \sigma_T + \sqrt{\sigma_T \cdot (\sigma_C + \sigma_T)}} \right) \]

Using \( \sigma_T = 1200 \) MPa and \( \sigma_C = 1800 \) MPa for Vit106, Eqs. A.5 and A.6 provide values \( \sigma_e = 1424 \) MPa and \( \sigma_e = 1548 \) MPa, respectively. Since both loading configurations are equally likely for any given strut within a foam, we take the effective yield stress of a triangular beam to be the mean of these quantities, 1486 MPa.
APPENDIX B

Scripts for Calculations Described in the Text

B.1. Scripts for Density Profile Analysis from Radiographic Images

The script provided here was designed to analyze TIFF-formatted image files for the analysis of relative density profiles, as described in Section 6.3.2). The script was designed to run with Matlab Student Version 6.5.

```matlab
% ScoutView.m
%
% Takes two grayscale images (TIFF format), one representing the entire
% foam sample, and the other representing a suitable area of background,
% and calculates the relative density profile for the sample by assuming a
% cylindrical sample geometry. User must input sample dimensions and
% effective linear absorption coefficient for the radiation and base
% alloy used.
%
% Alan Brothers
% 7/06

clear; 
home; 
clc; 

%prompt for an image file and store grayscale values in the 2nd order matrix gs
filename = input('Enter image file name (tiff files only, inverted from the films, no extension): ','s');
gs = imread(filename,'tiff');
clear('filename');

%prompt for a background image and use it to determine average grayscale value of the background
bgfilename = input('Enter background file name (tiff files only, inverted from the films, no extension): ','s');
bg = imread(bgfilename,'tiff');
bg1 = mean(bg);
background = mean(bg1');
clear('bgfilename','bg','bg1');
```
%prompt for the physical dimensions represented by the image
sampleheight = input('Enter the height of the sample represented by this image, in millimeters: ') / 1000;
samplediam = input('Enter the diameter of the sample represented by this image, in millimeters: ') / 1000;

%prompt for the percentage of the sample width to use (to eliminate noisy edges)
widthfrac = input('Enter the percentage of the diameter to use in calculation of densities (to avoid numerical errors near the sample edge): ') / 100;

%prompt for the effective linear absorption coefficient
mu = input('Enter the effective linear absorption coefficient (\(\mu\)) in \(1/m\); calibrated value is near 609: ');

%prompt for the number of layers, then determine how many pixel rows will %go into each layer, and determine how many of the bottom rows will not be %included.
numlayers = input('Enter number of vertical layers to analyze: ');
rowsperlayer = floor(size(gs,1)/numlayers);
lostrows = rem(size(gs,1),numlayers);

%calculate the number of points in the image that show higher intensity %than the background
badpixcnt = 0;
for i=1:size(gs,1)
    for j=1:size(gs,2)
        if gs(i,j)>background
            badpixcnt=badpixcnt+1;
            gs(i,j)=background;
        end
    end
end
badpixfrac = badpixcnt/((size(gs,1)*size(gs,2)));
clear('i','j','badpixcnt');

%inform user of these values
sprintf('The density profile will contain %d points, each representing %d pixel rows.\nThe bottom %d pixel rows will be ignored.\nThe fraction of bad pixels in the image is %1.3d.',
numlayers,rowsperlayer,lostrows,badpixfrac)
clear('badpixfrac');

%cutoff the unused layers from the matrix
gs = gs(1:numlayers*rowsperlayer,:); %bin the pixel rows into layers and store the layers in the new matrix gsl
for i=1:rowsperlayer:size(gs,1)+1-rowsperlayer
    layer = gs(i:i+rowsperlayer-1,:);
    layer = mean(layer);
    gsl((i+rowsperlayer-1)/rowsperlayer,:) = layer;
end clear('i','layer');

%compute pathlengths
pathlengths = -(1/mu)*log(gsl/background);

%finish transforming to relative density by adjusting for sample shape
samplecenter = round(size(gsl,2)/2);
for j=2:size(pathlengths,2)-1
    radialdist = (samplediam/2)*abs(j-samplecenter)/samplecenter;
    reldens(:,j) = pathlengths(:,j)/sqrt(samplediam^2-4*radialdist^2);
end clear('samplecenter','j','radialdist');

%cut the edges off of the sample data
pixtrimmed = round(((1-widthfrac)*size(reldens,2)));
pathlengths = pathlengths(:,pixtrimmed:size(pathlengths,2)-pixtrimmed);
reldens = reldens(:,pixtrimmed:size(reldens,2)-pixtrimmed);

%find avg relative density in each layer
for i=1:size(pathlengths,1)
    pathtot(i) = sum(pathlengths(i,:));
end
layerheight = sampleheight/size(pathlengths,1);
pixwidth = samplediam/size(pathlengths,2);
metalvol = pathtot*layerheight*pixwidth;
reldensavg = metalvol/(layerheight*pi*(samplediam^2)/4);
clear('i','metalvol');

%the overall relative density of the sample
reldensnet = mean(reldensavg);
sprintf('The calculated average relative density of the sample is %1.3d.',reldensnet)
B.2. Scripts for Density Profile Analysis from 3D Microtomographic Data

The scripts provided here were designed to convert raw binary data, the output from 3D x-ray microtomography experiments at Argonne National Laboratories, into a series of useable images with a standard TIFF formatting. They are further designed to perform dynamic thresholding on these images, and thereby to determine the density profile of the specimen being reconstructed. Scripts are also provided to perform this analysis separately on two regions from within the specimen, as described in the text (Section 6.3.3). All scripts were designed to run with Matlab Student Version 6.5.

B.2.1. maketiffs.m

% Maketiffs.m
%
% Maketiffs.m
% Convert signed 16-bit grayscale raw data files into uncompressed
% TIFF-formatted 16-bit indexed image files. The dimensions of the image are determined by
% the parameters 'width' and 'height', and each raw data file contains a stack
% of 'stacknum' individual images. The program will convert all raw data
% files having the correct base file names provided that the filenames end in a sequence of
% 4-digit numbers, e.g. 0001, 0002, etc. as defined by the array
% 'fileindexlist'.
clc;
% Lay out the input file names
fileindexlist = [‘0000’; ’0001’; ’0002’; ’0003’; ’0004’; 
’0005’; ’0006’; ’0007’; ’0008’; ’0009’; 
’0010’; ’0011’; ’0012’; ’0013’; ’0014’; 
’0015’; ’0016’; ’0017’; ’0018’; ’0019’; 
’0020’; ’0021’; ’0022’; ’0023’; ’0024’; 
’0025’; ’0026’; ’0027’; ’0028’; ’0029’; 
’0030’; ’0031’; ’0032’; ’0033’; ’0034’; 
’0035’; ’0036’; ’0037’; ’0038’; ’0039’];
fileindexlist = cellstr(fileindexlist);
basefilename = ’0_6.taurec’;
filenameextension = ’.img’;

% Define the size of each image (width and height), and the number of 
% images in the stack (stacknum)
width = 1299;
height = 1299;
stacknum = 16;

% Loop through the files in the slice
for j=1:length(fileindexlist)

  % Construct the current file name
  fileindex = char(fileindexlist(j));
  fullfilename = strcat(basefilename,fileindex,filenameextension);

  % Read data from the file as double format, so that math can be used on it
  fullstack = multibandread(fullfilename,[1299,1299,16],’int16=>double’,0,’bsq’,’ieee-le’);

  % Loop through the individual images in the stack and write them out as 
  % .tiff files
  for i=1:stacknum

    % Select a layer for reformatting
    layer = fullstack(:,:,i);

    % Determine the range of intensity values
    layergrange = max(max(layer)) - min(min(layer));
    % Renormalize image to have dynamic range [0,1]
layer = layer/layergsrange;
layer = layer - min(min(layer));
% Convert the double formatted data to unsigned 16-bit integer format
layer = uint16(round(layer*65535));

% Write out an image file
outputfilename = strcat(basefilename,fileindex,'-',int2str(i),'.tiff');
imwrite(layer,outputfilename,'compression','none');
fprintf('Writing layer number %d/%d of stack number %d/40...
',i,stacknum,j)
end
end

B.2.2. croptiffs2.m

% This script takes a series of .tiff images in the current directory and
% extracts the center of each image by zeroing the grayscale values of all
% pixels lying outside a user-defined radius, centered at the pixel center
% of the image. Images cropped in this way are output with '-cX' appended
% to their original filenames, where X is the pixel radius outside of which
% the pixels were zeroed. The output image size is reduced to the smallest
% size encompassing the whole nonzeroed image.
%
% Alan Brothers
% Northwestern University
% August, 2005
clc;

% Lay out the input file names
fileindexlist = ['0025';'0026'];
fileindexlist = cellstr(fileindexlist);
basefilename = '0_4.taurec';
stacknum = 1;

% Prompt for the pixel radius outside of which the data are zeroed
pixradius = input('Pixel radius for circular cropping: ');
pixradius = round(pixradius);
fprintf('
Estimated true radius: %.1f
',(pixradius/1299)*15.588)
% Loop through the files with the defined base file name
for j=1:length(fileindexlist)
    for i=1:stacknum

        % Construct the current file name
        fileindex = char(fileindexlist(j));
        fullfile = strcat(basefilename,fileindex,'-',int2str(i));

        % Read the image in as a 2x2 array
        rawimage = imread(fullfile,'tiff');

        % Isolate the region of interest in the image
        imagecenterx = round(size(rawimage,1)/2);
        imagecentery = round(size(rawimage,2)/2);
        %rawimage = rawimage(imagecenterx-pixradius:imagecenterx+pixradius,imagecentery-pixradius:imagecentery+pixradius);

        % Determine the pixel center of the smaller selected image
        imagecenterx = round(size(rawimage,1)/2);
        imagecentery = round(size(rawimage,2)/2);

        % Print status message
        fprintf('
Cropping file %s...
',fullfile);
        fprintf('Writing file %s...
',outputfilename)

    end
end

for k=1:size(rawimage,1)
    for l=1:size(rawimage,2)
        % Determine the pixel distance from the image center
        pixdist = sqrt((k - imagecenterx)^2 + (l - imagecentery)^2);
        % Zero out pixels that are outside the radius
        rawimage(k,l) = double(rawimage(k,l))*(pixdist <= pixradius);
    end
end

% Write out the cropped images
outputfilename = strcat(basefilename,fileindex,
    '-','c',int2str(pixradius),'tiff');
fprintf('Writing file %s...
',outputfilename)
imwrite(rawimage,outputfilename,'compression','none');
B.2.3. findmodes.m

% This script takes a series of .tiff images and determines the modal
gray scale value of all pixels lying within a hard-written pixel radius.
The output is written to a text file from which the modal values may be
looked up (rather than recalculated) when other scripts require them. The
output filename includes the pixel radius used.

% Alan Brothers
% Northwestern University
% September, 2005
clc;

% Lay out the input file names
fileindexlist = ['0000';'0001';'0002';'0003';'0004';
                 '0005';'0006';'0007';'0008';'0009';
                 '0010';'0011';'0012';'0013';'0014';
                 '0015';'0016';'0017';'0018';'0019';
                 '0020';'0021';'0022';'0023';'0024';
                 '0025';'0026';'0027';'0028';'0029';
                 '0030';'0031';'0032';'0033';'0034';
                 '0035';'0036';'0037';'0038';'0039'];
fileindexlist = cellstr(fileindexlist);
basefilename = '0_6.taurec';
stacknum = 16;
outerradius = 600;
numfiles = length(fileindexlist)*stacknum;

% Create output matrix
outputmatrix = zeros(numfiles,1);

% Loop through the files with the defined base file name
for j=1:length(fileindexlist)
    for i=1:stacknum
        tic;

        % Rest of the code
        toc;
    end
end
% Update the row number for the output matrix
rownumber = (j-1)*stacknum+i;

% Construct the input file names
fileindex = char(fileindexlist(j));
fullfilename = strcat(basefilename,fileindex,'-',int2str(i));

% Read the full (uncropped) image in as a 2x2 array
fprintf('
Image %s: Loading image...
',fullfilename)
fullimage = imread(fullfilename,'tiff');

% Determine the pixel center of the full image
fullimagecenterx = round(size(fullimage,1)/2);
fullimagecentery = round(size(fullimage,2)/2);

% Move through the full image one pixel at a time
for k=1:size(fullimage,1)
    for l=1:size(fullimage,2)
        % Determine the pixel distance from the image center
        pixdist = sqrt( (k - fullimagecenterx)^2 + (l - fullimagecentery)^2 );
        % Zero out pixels that are outside the outer radius
        fullimage(k,l) = double(fullimage(k,l))*(pixdist <= outerradius);
    end
end

% Read the nonzero pixels into a temporary array and determine the
% modal grayscale value
fprintf('Image %s: Determining grayscale mode...',fullfilename)
fullimage = reshape(fullimage,size(fullimage,1)*size(fullimage,2),1);
fullimage = fullimage(fullimage>0);
[modeval junk] = mode(double(fullimage));
fprintf('(%d)
',modeval);
clear junk;

% Write mode to the output matrix
outputmatrix(rownumber,1) = modeval;
fprintf('Image %s: File %d of %d completed in %3.1f
',fullfilename,(j-1)*stacknum+i,numfiles,toc)
% Generate the output file
outputfilename = strcat(basefilename,'modes-','radius-',int2str(outerradius),'.txt');
fprintf('
Writing modal values to %s...
',outputfilename)
dlwrite(outputfilename,outputmatrix,'	');

B.2.4. mode.m

function [result,percents]=mode(x)

%MODE
% Finds the mode of a 2d matrix.
% [result percents]=mode(matrix)
% where result is the mode of the matrix
% and percents is the amount of difference within the mode
% ORIGINALLY TABULATE.m by B.A. Jones
% Changes by David Li, UCSB updated: 4-8-2004

[Mo,No]=size(x);
x=reshape(x,Mo*No,1);

y = x(find(~isnan(x)))+1;

maxlevels = max(y(:));
minlevels = min(y(:));
[counts values] = hist(y,(minlevels:maxlevels));
total = sum(counts);

result=-1;
index=1;
while(counts(index) ~= max(counts))
    index=index+1;
end
result=values(index)-1; %disp(result);

percents =counts(index)/total;

B.2.5. thresh.m

% This script takes a series of cropped .tiff images in the current directory and
% thresholds them into black and white using about 10 levels equally spaced 
% between user-defined upper and lower grayscale limits. The script outputs 
% the resulting area/volume fractions (i.e. the fraction of pixels having 
% grayscale values exceeding each of those thresholds) to a tab-delimited 
% text file, with the top row being the grayscale threshold values 
% themselves. The name of this file is printed to the screen by the script. 
% 
% Alan Brothers 
% Northwestern University 
% August, 2005

clc;

% Lay out the input file names
fileindexlist = ['0000';'0001';'0002';'0003';'0004'; 
    '0005';'0006';'0007';'0008';'0009'; 
    '0010';'0011';'0012';'0013';'0014'; 
    '0015';'0016';'0017';'0018';'0019'; 
    '0020';'0021';'0022';'0023';'0024'; 
    '0025';'0026';'0027';'0028';'0029'; 
    '0030';'0031';'0032';'0033';'0034'; 
    '0035';'0036';'0037';'0038';'0039'];
fileindexlist = cellstr(fileindexlist);
basefilename = '0_6.taurec';
stacknum = 16;

% Prompt for lower and upper values, and determine the 1/10th step size
lowerlim = input('Lower limit for threshold, as a multiple of the modal value: '); 
upperlim = input('Upper limit for threshold, as a multiple of the modal value: '); 
threshstep = (upperlim-lowerlim)/10;
cropradius = input('Pixel radius used for cropping? '); 
cropradius = round(cropradius);

% Determine the number of columns needed for the threshold volume 
% fractions, and create the output matrix 
count=0; 
for i=lowerlim:threshstep:upperlim
    count = count+1;
end
numfiles = size(fileindexlist,1)*stacknum;
outputmatrix = zeros(numfiles+1,count);
clear count;

% Loop through the files with the defined base file name
for j=1:length(fileindexlist)
    for i=1:stacknum

        tic;

        % Construct the current file name
        fileindex = char(fileindexlist(j));
        fullfilename = strcat(basefilename,fileindex,'-',int2str(i)
        ,'','-c',int2str(cropradius));

        % Read the image in as a 2x2 array
        fprintf('
Image %s: Loading...
',fullfilename)
        rawimage = imread(fullfilename,'tiff');

        % Read the nonzero pixels into a temporary array and determine the
        % number of such pixels (the total 'area' after cropping)
        fprintf('Image %s: Isolating nonzero elements...
',fullfilename)
        image = reshape(rawimage,size(rawimage,1)*size(rawimage,2),1);
        image = image(image>0);
        imagesize = size(image,1);

        % Determine the modal value of the image
        [modeval junk] = mode(double(image));
        clear junk;

        % Print status message
        fprintf('Image %s: Thresholding...
',fullfilename)

        % Update the row number for the output matrix
        rownumber = 1+(j-1)*stacknum+i;

        % Generate thresholded data and write it to the output matrix
        for k=lowerlim*modeval:threshstep*modeval:upperlim*modeval
            % Threshold the image to a logical array
            threshedimage = image(image>k);
            % ... (remaining code)
% Determine the number of pixels exceeding the threshold value
% and thereby the volume fraction
volfrac = size(threshedimage,1)/imagesize;
% Determine the column number for the output
colnumber = 1+round((k/modeval-lowerlim)/threshstep);
% Label the output column with the current threshold value
outputmatrix(1,colnumber) = k/modeval;
% Output the volume fraction to the output matrix
outputmatrix(rounumber,colnumber) = volfrac;
end
fprintf('Image %s: Completed in %3.1f seconds...
',fullfilename,toc)
end
end

% Generate the output file
outputfilename = strcat(basefilename,'-c',int2str(cropradius),
'-t-',sprintf('%1.1f',lowerlim),'-',sprintf('%1.1f',upperlim),'.txt');
fprintf('
Writing threshold data to %s...
',outputfilename)
dlmwrite(outputfilename,outputmatrix,'	');

B.2.6. ringthresh.m

% This script takes a series of cropped .tiff images in the current directory and
% thresholds them into black and white using about 10 levels equally spaced
% between user-defined upper and lower grayscale limits. The script outputs
% the resulting area/volume fractions (i.e. the fraction of pixels having
% grayscale values exceeding each of those thresholds) to a tab-delimited
% text file, with the top row being the grayscale threshold values
% themselves. The name of this file is printed to the screen by the script.
%
% Used for outer, annulus regions of images. The properties of the inner
% core of the image can be determined from this data and data taken
% from the entire image.
%
% Alan Brothers
% Northwestern University
% August, 2005

clc;
% Lay out the input file names
fileindexlist = ['0016';'0017';';'0018';'0019';
  '0020';'0021';'0022';'0023';'0024';
  '0025';'0026';'0027';'0028';'0029';
  '0030';'0031';'0032';'0033';'0034'];
fileindexlist = cellstr(fileindexlist);
basefilename = '0_4.taurec';
stacknum = 16;
umfiles = length(fileindexlist)*stacknum;

% Prompt for inner and outer radii, and threshold multiplier
innerradius = input('Inner pixel radius of annulus: ');
innerradius = round(innerradius);
outerradius = input('Outer pixel radius of annulus: ');
outerradius = round(outerradius);
threshlim = input('Threshold value, as a multiple of the modal value: ');

% Create output matrix
outputmatrix = zeros(numfiles,1);

% Loop through the files with the defined base file name
for j=1:length(fileindexlist)
  for i=1:stacknum
    tic;

    % Construct the input file names
    fileindex = char(fileindexlist(j));
    fullfile = strcat(basefilename,fileindex,'-',int2str(i));
    ringfile = strcat(basefilename,fileindex,'-',int2str(i),'-ID',
     int2str(2*innerradius),'-OD',int2str(2*outerradius));

    % Read the full (uncropped) image in as a 2x2 array
    fprintf('
Image %s: Loading uncropped image...
',fullfile);
    fullimage = imread(fullfile,'tiff');

    % Determine the pixel center of the full image
    fullimagecenterx = round(size(fullimage,1)/2);
    fullimagecentery = round(size(fullimage,2)/2);
for k=1:size(fullimage,1)
    for l=1:size(fullimage,2)
        % Determine the pixel distance from the image center
        pixdist = sqrt( (k - fullimagecenterx)^2 + (l - fullimagecentery)^2 );
        % Zero out pixels that are outside the outer radius
        fullimage(k,l) = double(fullimage(k,l))*(pixdist <= outerradius);
    end
end

% Read the nonzero pixels into a temporary array and determine the
% modal grayscale value
fprintf('Image %s: Determining grayscale mode...
',fullfilename)
fullimage = reshape(fullimage,size(fullimage,1)*size(fullimage,2),1);
fullimage = fullimage(fullimage>0);
[modeval junk] = mode(double(fullimage));
clear junk;
clear fullimage;
clear fullimagecenterx;
clear fullimagecentery;

% Print status message
fprintf('Image %s: Analyzing annular image...
',ringfilename)
ringimage = imread(ringfilename,'tiff');

% Update the row number for the output matrix
rownumber = (j-1)*stacknum+i;

% Generate thresholded data and write it to the output matrix
k = threshlim*modeval;
threshedimage = ringimage(ringimage>k);
% Determine the number of pixels exceeding the threshold value
% and thereby the volume fraction
volfrac = size(threshedimage,1)/round(pi*outerradius^2 - pi*innerradius^2);
% Output the volume fraction to the output matrix
outputmatrix(rownumber,1) = volfrac;
fprintf('Image %s: File %d of %d completed in %3.1f seconds...
',
        ringfilename,(j-1)*stacknum+i,numfiles,toc)
end
% Generate the output file
outputfilename = strcat(basefilename,'-ID',int2str(2*innerradius),
'-OD',int2str(2*outerradius),'-t-',sprintf('%1.2f',threshlim),'.txt');
fprintf('
Writing threshold data to %s...
',outputfilename)
dlmwrite(outputfilename,outputmatrix,'\t');