Thermodynamics and kinetics of grain boundaries in ultra fine grained copper produced by severe plastic deformation

Research Thesis

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ABSTRACT

Reducing the average grain size of polycrystalline metals and alloys is a traditional way of increasing their strength. Moreover, many other attractive properties can be achieved by reducing average grain size: low-temperature superplasticity, improved magnetic properties, and homogeneity of physical properties. The recently developed technique of Equal Channel Angular Pressing (ECAP) allowed a breakthrough in decreasing the grain size of bulk materials to the sub-micrometer level. Its main principle is pressing a metal billet through an angular channel, a process that involves extremely large shear deformations forming dislocation cell structure at sub-micron scale. Subsequent pressings result in the formation of ultra-fine grains (UFG) with high-angle grain boundaries (GBs).

Many unusual properties of materials produced by ECAP are attributed to non-equilibrium grain boundaries. These GBs are expected to exhibit higher values of energy, higher amplitude of strain fields, larger free volume, and higher diffusivity than their relaxed counterparts. Although the concept of non-equilibrium state of GBs is theoretically well established, its experimental foundation is still controversial. The aim of the present study is, therefore, providing an adequate experimental proof for the concept of non-equilibrium GBs by measurements of GB diffusivity and energy in copper and copper alloys subjected to ECAP.

The diffusion of $^{63}$Ni radiotracer in Cu and Cu-Zr alloy was studied using the serial-sectioning method. The diffusion annealings were performed in the temperature range 150 °C – 350 °C for annealing times when volume diffusion is frozen and only short-circuit diffusion occurs.

The microstructure studies by Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), and Focused Ion Beam (FIB) microscopy indicated that alloying with Zr is essential for stabilizing the ECAP-processed alloys against grain growth and recrystallization. In all samples studied the experimentally-acquired diffusion profiles exhibited two distinct slopes, which are associated with "slow"- and "fast" diffusion paths. The former is very close to that of relaxed GBs in coarse-grained Cu. Based on the analysis of the activity profiles, we proposed a hierarchical microstructure model of the UFG Cu-Zr alloy studied. In this model, a cellular skeleton of "fast" GBs with the characteristic cell size in the micrometer range is embedded in a
network of "slow" GBs formed by sub-micrometer grains. This model allowed a quantitative processing of the measured activity profiles. The Arrhenius parameters of the GB diffusivities for the "slow" and "fast" GBs were determined, indicating a 3-4 orders of magnitude difference in respective pre-exponential factors.

The measured radiotracer penetration profiles in pure ECAP-ed Cu exhibited a bimodal shape similar to that observed in the Cu-Zr alloy. In contrast to the Cu-Zr alloy, the pure Cu exhibited recrystallization during all thermal annealings. The explicit expression describing the kinetics of recrystallization in ECAP-ed Cu was obtained. A model that considers diffusion in UFG polycrystal undergoing recrystallization was developed. Its main assumption is that diffusion flux is allowed in the UFG phase only, while the recrystallizing grains "freeze" the concentration of solutes existing in the UFG matrix before it was consumed by recrystallizing grain. Application of this model enabled us deriving the slow-diffusion coefficients from the experimentally measured penetration profiles. The Arrhenius parameters of the GB diffusivities for the "slow" and "fast" GBs were determined, indicating about 3 orders of magnitude difference in respective pre-exponential factors.

The relative energies of GBs in ultrafine grain copper obtained by ECAP were determined using the thermal grooving technique. The dihedral angles at the roots of GB grooves formed after annealings at 400 °C for 15 min and at 800 °C for 2h were determined with the aid of AFM. The average relative GB energies in the ECAP-ed samples annealed at 400 and 800 °C are $0.48 \pm 0.11$ and $0.27 \pm 0.07$, respectively. Theoretical estimates of the relaxation time of non-equilibrium GBs indicated that little relaxation should occur after annealing at 400 °C, while full relaxation is expected after annealing at 800 °C. It was shown that the measured difference in GB energies can be correlated with the presence of two types of GBs in the same sample exhibiting very different diffusivities.

We associated the fast-diffusion paths with unusually high GB diffusivities, and the high-energy GBs observed by AFM with the non-equilibrium GBs that were formed during ECAP. The volume fraction of such boundaries is small and they are separated by an extensive network of normal (i.e. exhibiting usual GB diffusivities and energies characteristic for annealed coarse grain polycrystals) GBs. These findings provide a solid experimental foundation for the concept of non-equilibrium GBs.
LIST OF SYMBOLS AND ABBREVIATIONS

\( b \) [m] – Burgers vector

\( B, B_0 \) [s\(^n\)] – JMAK coefficients

\( C \) [m\(^{-3}\)] – concentration

\( \bar{C} \) [m\(^{-3}\)] – average concentration weighted in two phases

\( \bar{C}_i \) [m\(^{-3}\)] – average concentration in the phase \( i \)

\( d \) [m] – grain diameter

\( D \) [m\(^2\)/s] – volume diffusion coefficient

\( D_b \) [m\(^2\)/s] – GB diffusion coefficient

\( D_{\text{eff}} \) [m\(^2\)/s] – effective diffusion coefficient

\( D_{i0} \) [m\(^2\)/s] – pre-exponential diffusion coefficient in the medium \( i \)

\( D_s, D_f \) [m\(^2\)/s] – "slow" and "fast" GB diffusion coefficients, respectively

\( D_{\text{surf}} \) [m\(^2\)/s] – surface diffusion coefficient

\( f \) – volume fraction of the short-circuit diffusion path

\( G \) [Pa] – shear modulus

\( J \) [m\(^2\)/s\(^{-1}\)] – diffusion flux

\( m \) – linearization exponent of the diffusion profile

\( n \) – JMAK exponent

\( Q \) [J/mole] – activation enthalpy for any thermally-activated process (see the context).

\( s \) – segregation factor

\( S \) [m] – Łojkowski characteristic length

\( T \) [K] – temperature

\( T_m \) [K] – melting temperature

\( \alpha, \beta \) – parameters characterizing \( B \)- and \( C \)-regime GB diffusion

\( \gamma_b \) [J/m\(^2\)] – GB energy (absolute)

\( \gamma_{\text{rel}} \) – relative GB energy

\( \gamma_s \) [J/m\(^2\)] – surface energy

\( \delta \) [m] – GB thickness

\( \varepsilon_{ij} \) – strain tensor

\( \lambda \) – volume fraction of the non-recrystallized material
ν – Poisson's ratio

ρ [m^2] – GB dislocation density

ρ_v [m^2] – bulk dislocation density

Σ – reciprocal density of CSL points

σ_{ij} [Pa] – stress tensor

τ [Pa] – sheal stress

τ_{rel} [s] – relaxation time

ϕ(m) – the slope of diffusion profile linearized with m

ψ – GB groove dihedral angle

Ω [m^3] – atomic volume
AFM – atomic force microscopy
BF – bright field
CG – coarse grain
CSL – coincident site lattice
DSC – differential scanning calorimetry
EBSD – electron back-scatter diffraction
ECAP – equal channel angular pressing
EDS – electron dispersive spectroscopy
EELS – electron energy loss spectroscopy
GB – grain boundary
HAGB – high-angle grain boundary
HRSEM – high-resolution scanning electron microscopy
JMAK – Johnson, Mehl, Avrami, Kolmogorov kinetic equation
LAGB – low-angle grain boundary
ML – modified Łojkowski model
NC - nanocrystal
OIM – orientation imaging microscopy
RMS – root mean square
SAED – selected area electron diffraction
SEM - scanning electron microscopy
SIMS – secondary ion mass spectroscopy
SPD - severe plastic deformation
S-T – Sangal-Tangri model
STEM – scanning transmission electron microscopy
STGB – symmetrical tilt grain boundary
SU – structural unit
TAP – tomographic atom-probe microscopy
TEM - transmission electron microscopy
TJ – triple junction
TWGB – twist grain boundary
UFG – ultra-fine grain
XRD – X-ray diffraction
1. INTRODUCTION

Improving mechanical properties of alloys, in particular achieving an optimal combination of strength and ductility, has always been one of the central topics in materials science. It is well known that decreasing grain size in polycrystalline materials increases their strength and hardness. Besides these mechanical properties, other attractive properties can be achieved in this manner: low-temperature superplasticity, improved magnetic properties, and homogeneity of physical properties. Conventional methods of grain refinement (rolling, forging, annealing) usually result in grain sizes in the range of tens of micrometers and anisotropic microstructure. Other methods such as mechanical alloying of nanopowders enable, indeed, obtaining bulk materials with grain sizes as small as nanometers, but they incorporate undesirable residual porosity. The growing interest in severe plastic deformation (SPD) methods of grain refinement is related to the fact that homogeneous pore-free polycrystals with ultra fine grained (UFG) microstructure (in the submicron level) can be routinely obtained by these methods.

Equal Channel Angular Pressing (ECAP) is one of the most promising SPD methods due to its potential for industrial upscaling. Its main principle is pressing a metal billet through an angular channel. Extremely large shear deformation produced in the region where the entrance and the exit parts of the channel meet leads to the formation of a pronounced dislocation cell structure at sub-micron scale. Subsequent ECAP passes, together with the rotation of the billet about the pressing direction between the passes, cause growing accumulation of dislocations in the cell walls, increase in misorientation angles between the cells and, therefore, promote the formation of high-angle grain boundaries (HAGBs).

Investigation of the special properties exhibited by alloys produced by ECAP, as well as by other SPD methods, indicates the unusual structural state of grain boundaries (GBs) in these materials. In this framework, the concept of non-equilibrium GBs has been coined, pointing on the energetically metastable state of GBs. These GBs exhibit higher interfacial energy, higher amplitude of strain fields, larger free volume, and higher diffusivity than their equilibrated counterparts.
Although the concept of non-equilibrium GBs is theoretically well-established, its experimental foundation is, still, controversial. An experimental proof for the non-equilibrium state of GBs is not easy. First, experiments involving UFG alloys at elevated temperatures are problematic because of insufficient thermal stability of the non-equilibrium GB state. For example, while several researchers reported on significantly enhanced GB diffusivity in UFG materials, others claim that it is not different from GB diffusivity in coarse-grained polycrystals. Second, the relevant data scattered in the literature are incoherent and inconclusive, since they were collected at different experimental conditions and in different materials. Third, experimental data on GB energy in UFG materials are not available at all.

The present research is, therefore, aimed at filling this gap in knowledge by quantifying the degree of non-equilibrium of GBs in alloys produced by ECAP. Our approach is based on the fact that on the one hand GB energy is the most direct property related with the degree of non-equilibrium, but on the other hand GB diffusivity is the physical property most sensitive to microstructure variations. Therefore, the design of concerted experiments incorporating low-temperature measurements of GB diffusivity and energy in alloys produced by ECAP is probably the most efficient way to achieve this goal. Comparing these GB properties determined in alloys produced by ECAP with those measured in equilibrated coarse-grained polycrystals may quantitatively supply us with the desirable estimation for the degree of non-equilibrium of GBs obtained by ECAP.
2. LITERATURE SURVEY

This chapter provides a survey of the published works dealing with the subject of non-equilibrium GBs. The concept of non-equilibrium GBs will be introduced starting with the motivation for developing UFG materials, reviewing the fundamentals and implications of SPD methods, and describing the physical properties of materials derived from their GB nature. The main research goal, which is quantifying the degree of non-equilibrium in GBs produced by ECAP, will be followed by a review of the documented experimental data including measurements of GB energy and diffusivity in materials produced by SPD.

2.1. The essence of ultra fine grained materials

Nanocrystalline (NC) and UFG materials exhibit superior performances and properties. These materials are attractive for many ranges of application from biomedical to aerospace industries. While high strength and good ductility rarely exist simultaneously in any material, UFG alloys exhibit the optimal combination between both. The general trend for coarse-grained (CG) materials demonstrates a trade-off between both properties: with decreasing the alloy grain size, its strength usually increases while ductility decreases [1]. The former originates from the Hall-Petch relationship:

\[ \sigma = \sigma_0 + \frac{K}{\sqrt{d}} \]  \hspace{1cm} (2.1)

where \( \sigma \) is the strength, \( d \) is the grain size, and \( \sigma_0 \) and \( K \) are constants. An inverse Hall-Petch behavior is observed below a critical grain size, which is in the nanoscale regime. On the other hand, ductility also deviates from its general trend in the UFG regime due to the operation of additional deformation mechanisms besides dislocation slip. Ductility has strong correlation with creep behavior, and in the UFG range it increases with reducing grain size. The balance between both dependences implies that sub-micron grained alloys may possess high strength concurrently with good ductility.
One of the most important properties that can be achieved in UFG materials is superplasticity, in which hundreds of percents strains are attained [2]. In an example presented by Pearson, 1950 % elongation was measured in a Bi-Sn alloy (Fig. 2.1).

Among its several modes, fine-structure superplasticity is the most relevant case to UFG materials. This phenomenon is dictated by creep, where for UFG materials the most dominant creep mechanisms are diffusional creep and GB sliding. The common feature for all creep mechanisms is the build-up of driving force for stress release when the bulk is subjected to tensile stress. In diffusional creep stress release is attained by mass transport either via lattice bulk (Herring-Nabarro creep) or via GBs (Coble creep) [3]. The parameter characterizing creep behavior is the steady-state strain rate, \( \dot{\varepsilon} \). It is obvious that in both cases \( \dot{\varepsilon} \) should strongly depend on grain size, i.e. to increase with decreasing grain size. Moreover, in Coble creep \( \dot{\varepsilon} \) is expected to increase with GB diffusivity. The accurate functional expressions for \( \dot{\varepsilon} \) depend on the geometric factors taken into account in each model, and are not of our interest. Their semi-quantitative forms, however, are given below:

\[
\dot{\varepsilon} \propto \frac{D\sigma\Omega}{kT \cdot d^2}
\]  

(2.2) for Herring-Nabarro creep, and:

\[
\dot{\varepsilon} \propto \frac{D_\delta\sigma\Omega}{kT \cdot d^3}
\]  

(2.3) for Coble creep.

Fig. 2.1: Pearson's experiment from 1934 showing 1950 % elongation of a Bi-Sn rod. After [2].
In both cases $D$ and $D_b$ are the lattice and GB diffusion coefficients, respectively; $\sigma$ is the uniaxial tensile stress, $\Omega$ is the atomic volume, $\delta$ is the effective GB width, and the term $kT$ has its usual meaning. Other mechanism relevant in UFG materials is GB sliding, which also exhibits the expected grain size dependence with a similar form of $\dot{\varepsilon}$.

It follows from the above-detailed phenomena described by Eqs. (2.2) and (2.3) that UFG materials are excellent candidates for having superplastic behavior mainly due to their sub-micron grain size. Moreover, enhanced GB diffusivity expected in UFG materials (this point will be discussed further below) should contribute to superplasticity in the same way as described by Coble creep, Eq.(2.3).

Other desirable mechanical properties of UFG materials derived from their small grain size are good wear resistance and enhanced high-cycle fatigue strength [1]. There are evidences for the improvement in other physical properties of UFG materials. Better corrosion resistance was observed in UFG-Ti [4] when compared with CG-Ti. This was explained by fast kinetics of the passivation layer growth in the UFG state, due to GBs and other lattice defects. Enhanced coercivity was measured in the UFG ferromagnetic Pr-Fe-B-Cu alloy when compared with its CG counterpart [5]. The uniformity of physical properties of UFG materials is attributed to their small grain size with respect to the dimensions of the bulk. This is important especially in low-dimensionality devices.

The potential of applying UFG materials involves two main considerations: their manufacturability and superior properties [1]. Metallic UFG bulk materials are more suitable for production methods such as forging, where time and temperature are significantly reduced owing to their enhanced ductility. This is pronounced by energy and cost savings, and is being utilized in aircraft and automobile industries [6]. Due to the increased strength of UFG alloys, the production of lightweight structures (e.g. of Al-based alloys) with high strength-to-weight ratio is another possible application field of these materials. Another example for applying the good properties of UFG alloys is for bone implants in the human body. The enhanced fatigue performance of UFG Ti makes it a good candidate for this task [1]. An example for the importance of the uniform properties obtained in UFG materials is for micro-electromechanical systems (MEMS), where UFG nickel is very promising owing to its uniform saturation magnetization in the micrometer scale [7].
In summary, the major advantage that UFG alloys exhibit is a good combination of strength and ductility. This is attained by additional deformation mechanisms becoming operative in the UFG materials - on the one hand; as well as the increased strength given by Hall-Petch behavior - on the other hand. This enables good manufacturability and superior properties of UFG alloys.

2.2. Severe plastic deformation: a method for producing UFG microstructure

Among all techniques utilized for producing nanocrystalline and UFG materials, severe plastic deformation (SPD) has proved to be very attractive. Homogeneous and isotropic submicron-grained microstructure with high fraction of high-angle grain boundaries (HAGBs) avoiding the initiation of microcracks during deformation can be produced by SPD methods. Most of the traditional processes used for grain refinement of bulk metals, such as cold rolling, are inferior to SPD since they result in an anisotropic microstructure with a high fraction of low-angle GBs (LAGBs). Other methods based on different approaches, such as gas condensation, consolidation of nanopowders, ball milling, mechanical alloying, and electrolytical co-deposition [8,9] suffer from residual porosity and the introduction of impurities. Methods based on deposition, such as chemical or physical vapor deposition as well as electrodeposition can produce nanocrystalline and UFG materials, but are not applicable for bulk materials. SPD methods enable to overcome these problems [6]. They provide grain refinement down to the submicrometer range with a homogeneous microstructure, and are suitable for the production of large materials quantities on industrial scale. Superplasticity, as well as the other superior properties typical to UFG materials detailed above, is being routinely achieved by SPD [10,11].

Equal Channel Angular Pressing (ECAP) is one of the most promising SPD methods due to its potential for industrial upscaling. Its main principle is pressing a metal billet through an angular channel. Extremely large shear deformation produced in the region where the entrance and the exit parts of the channel meet leads to the formation of a pronounced dislocation cell structure at sub-micron scale. Subsequent ECAP passes, together with the rotation of the billet about the pressing direction between the passes, cause growing accumulation of dislocations in the cell walls,
increase in misorientation angles between the cells and, therefore, promote the formation of HAGBs [12]. A schematic description of the ECAP unit is given in Fig.2.2.

![Fig.2.2: A schematic illustration of the ECAP system [12].](image)

Many factors affect the microstructure and properties of materials manufactured by ECAP. The bending angle between the two portions of the channel, $\phi$, and the external angle, $\chi$, determine the total strain per one ECAP pass, so that high values of the latter favor high misorientations (HAGBs). The expression for the total shear strain, $\tau$, for the accumulating number of passes, $N$, as a function of both angles is [12]:

$$
\tau = \frac{N}{\sqrt{3}} \left[ 2 \cot \left( \frac{\phi}{2} + \frac{\chi}{2} \right) + \chi \cdot \csc \left( \frac{\phi}{2} + \frac{\chi}{2} \right) \right]
$$

It follows from Eq.(2.3) that for the most frequently-used angles, i.e. $\phi=90^\circ$ and $\chi=20^\circ$, the total shear strain attained in each pass is nearly 1, while the effect of number of passes is cumulative. Three main ECAP processes have been suggested for the value of $\phi=90^\circ$ [6]. In the first one the orientation of billet between consequent passes is not changed (route A). In the second one (route B) the billet is rotated by $90^\circ$ between each pass (B_A: alternatively, B_C: in the same direction); and in the third one by $180^\circ$ (route C). The influence of ECAP route on microstructure and properties has
been extensively investigated. It was concluded [6,12,13] that BC is the most efficient ECAP route in terms of grain refinement, homogeneity of the microstructure, and the formation of high fraction of HAGBs.

In what follows we will consider the ECAP processing of pure copper or copper-based alloys. In addition to ECAP route, both the number of passes and the pressing temperature influence the resulting microstructure. The minimal grain size attained by ECAP of Cu samples is 200-300 nm [13-17] and is achieved already after the 1st ECAP pass. However, most GBs at this stage are of the LA type. After several passes the fraction of HAGBs increases (higher misorientation) and reaches a saturation value, and the cellular grain morphology transforms into equiaxed one. The evolution of these microstructural features affects the mechanical properties of material as well. For example, yield strength and ultimate tensile strength also increase with increasing number of passes. For copper, it was concluded [17] that 4 passes in the BC route (BC4) provide the optimal combination of high strength and ductility, as well as high GB misorientations. Concerning the effect of temperature, it was reported [12,18] that performing the ECAP process at elevated temperatures results in coarser grains having lower misorientation angles between them (smaller fraction of HAGBs) with respect to those attained at room-temperature pressing. However, equiaxed morphology of grains is easier to obtain at elevated temperatures.

A foremost feature typical to the UFG microstructure obtained by ECAP or any other SPD method is its low thermal stability. Since it was formed by a non-equilibrium process the metastable UFG microstructure is abundant of lattice defects, which are pronounced by large amount of stored elastic energy. Therefore, grain growth, recrystallization and GB recovery in SPD-processed materials are expected to occur at lower temperatures than the non-deformed materials. This factor should be taken into account in any experimental procedure [6]. Alloying with either precipitate- or solid solution-forming elements is the common method of stabilizing the microstructure of ECAP-produced UFG materials [18-25].

Based on numerous microstructural observations and mechanical testing of SPD-processed alloys, Valiev and co-workers [6] have suggested a hypothesis that GBs in UFG materials produced by SPD are in a highly non-equilibrium metastable state. These non-equilibrium GBs are characterized by higher interfacial energy, higher long-range strain fields and higher free volume with respect to GBs in the pre-
deformed state. These properties are derived from the presence of high density of extrinsic dislocations, which are not needed to accommodate the given GB misorientation.

There have been several attempts to confirm the concept of non-equilibrium GBs by direct atomic structure observations using high-resolution Transmission Electron Microscopy (TEM). For example, Horita and co-workers [26] revealed a zigzag, highly stepped configuration of GBs in UFG copper. Similar atomic GB configurations were reported by the same authors in a UFG Al-3% Mg alloy [27]. These highly-distorted, stepped GBs rotated and got flattened after several minutes of irradiation by the electron beam (Fig. 2.3). These observations, as well as an increased density of lattice dislocations found in the vicinity of these GBs were considered as a proof of the non-equilibrium state of GBs.

Fig. 2.3: High-resolution TEM image of a GB in UFG Al-3%Mg alloy: (a) the as-pressed state; (b) after several minutes of electron irradiation. After [6].

However, the atomic structure observations alone cannot prove the non-equilibrium character of the GBs since it is known that well-annealed GBs may also be faceted and dissociated at a wide range of scales: from the micron [28] down to the atomic scales [29]. Furthermore, only the value of Gibbsian GB energy can be considered as a quantitative criterion for deviations from equilibrium. All experimental evidence for non-equilibrium character of GBs based on microscopic observations
reported so far (e.g. [10]) can rarely reveal any quantitative feature and are, therefore, insufficient. The next section comprises a brief review of materials properties derived from GB nature, followed by the theoretical background underlying the nature of non-equilibrium GBs.

2.3. Physical properties of materials derived from GB character

Many physical properties of materials can be directly associated with GB structure. Among them are: creep and plastic behavior, corrosion and fracture resistance, intergranular cavity and wetting, and microstructural evolution such as grain growth, recrystallization, etc. All of the above can be classified in two categories: properties determined by either GB energy or diffusivity [30].

The thermodynamic definition of interfacial (GB) energy is the reversible work per unit area required for an infinitesimal increase of the interface (GB) area. This definition of GB energy has a geometrical sense. In this terminology, a GB is regarded as a planar defect within the perfect lattice. In the perfect lattice, each atom is bounded to its neighbors by a constant number of bonds with certain energy per bond. In the vicinity of the GB plane some of these interatomic bonds are broken or distorted. The excess interfacial energy is associated with these broken bonds (considering bonding energy as negative, a broken bond means a higher energetic state). According to this concept, it is obvious why GB energy depends on crystallographic orientation and structure, as well as on chemical composition of the GB.

Since the diffusion coefficient in crystalline solids increases with the increase in concentration of vacancies [31], the GB diffusion should be particularly sensitive to GB structure [32].

In view of the above, it is expected that both GB energy and diffusivity should have the same qualitative dependence on the structure of the GB. Indeed, experimental evidence indicates an increased energy and diffusivity in the GBs with high free volumes, and vice-versa. Sharp minima (cusps) in the misorientation dependencies of both energy and diffusivity were identified in many experimental studies at the low-\(\Sigma\) coincident site lattice (CSL) misorientations [32]. Such cusps can be also observed in the misorientation dependence of other GB properties related to GB diffusivity and energy. Several detailed examples were given by us elsewhere [30].
In summary, many physical properties of materials depend on GB energy and diffusivity, which are closely correlated with the GB free volume. Therefore, due to larger amount of absorbed dislocations, it is expected that non-equilibrium GBs should possess higher energy and diffusivity, and different physical properties if compared with their equilibrated counterparts.

2.4. Non-equilibrium GBs: theoretical aspects

Contemporary models of GB structure can be divided in two main categories: atomic matching models and dislocation models. Any model of GB structure should be judged in terms of its ability to provide a quantitative prediction of physical properties. Therefore, the fundamental model for LAGB structure-energy relationship, the Read-Shockley model, will be outlined in the present section. Subsequently, utilizing the Read-Shockley approach, the model of Nazarov for non-equilibrium GBs will be introduced.

2.4.1. Conventional models for GB structure

The Read – Shockley model is an example of dislocation model [33]. It was developed for LAGBs, and later has been extended for HAGBs. For the clarity of explanation, let us regard the simplest configuration: symmetrical tilt GB (STGB) with a low misorientation angle. This GB can be described as an array of edge dislocations, as shown in Fig. 2.4.

Fig. 2.4: A wall of edge dislocations accommodates the difference in orientation across a low-angle STGB [34].

- 16 -
If \( h \) is the average distance between two adjacent dislocations and \( b \) is the Burgers vector absolute value, then \( \frac{b}{h} = \sin \theta \), where \( \theta \) is the tilt angle. Similarly, a twist GB (TWGB) can be described as an array of screw dislocations, except of a slight difference: unidirectional array of screw dislocations forms a planar shear, rather than twist. It means that two orthogonal arrays of screw dislocations are needed to produce a twist, and that a TWGB can be represented by a network of screw dislocations (Fig.2.5). Therefore, the density of screw dislocations in the case of TWGB should be twice that of STGB for the same \( \theta \) (either twist or tilt) [34].

![Diagram](image)

Fig. 2.5: A network of perpendicular screw dislocations accommodates the difference in orientation across a low-angle TWGB [34].

The GB energy can be obtained by summation of the energies of all dislocations in the unit area of GB:

\[
\gamma = \gamma_0 \sin \theta \left[ A - \ln \left( \sin \theta \right) \right]
\]

(2.4)

where:

\[
\begin{align*}
(a) \quad \gamma_{0,STGB} &= \frac{Gb}{4\pi(1-\nu)} \\
(b) \quad \gamma_{0,TWGB} &= \frac{Gb}{2\pi} \\
(c) \quad A_{STGB} &= \frac{4\pi(1-\nu)B_e}{Gb^2} \\
(d) \quad A_{TWGB} &= \frac{2\pi B_s}{Gb^2}
\end{align*}
\]

(2.5)

\( G \) is the shear modulus, \( \nu \) is Poisson’s ratio, and \( B_e \), \( B_s \) are the dislocation core energies per unit length (for edge and screw dislocations, respectively).

The model considers two contributions to the GB energy: the first one is related with the dislocation core energy, and can be only roughly evaluated. The second term
is associated to the elastic strain field energy. In any case, GB energy increases with the increasing density of GB dislocations. The model deals with LAGBs ($\theta \leq 20^\circ$), therefore: $\sin \theta \approx \theta$. For higher values of $\theta$ the dislocation cores overlap, and a meaningful distinction between a dislocation strain field and a core region becomes impossible.

The dislocation model described above is applicable to pure tilt (symmetrical) and pure twist GBs only. Read and Shockley [33] generalized it for any configuration of GB, which can be expressed as a mixture of pure tilt and pure twist components. For the LAGBs, this model provides a good description of the structure-energy relationship. Further extensions of the Read-Shockley model considering HAGBs have also been proposed [35,36], however the basic concept remained the same.

Additional models for the GB structure-energy relationship have been developed based on the approach of atomic-matching. The CSL model [37] regards the misorientation between two lattices forming a given GB. Its main concept is that for particular misorientation a given fraction of the lattice sites from both sides of the boundary coincide. The GB faceted plane follows such coincident sites, in order to form a closely-packed structure having the lowest possible interfacial energy [38]. The structural units (SU) model [39,40] describes the GB structure in terms of periodic arrays of atomic polyhedra, each one having its own energy. The shape of polyhedra, as well as their relative numbers and periodicity depend on both lattice misorientation and GB plane inclination. The total GB energy is, therefore, the sum of polyhedra and inter-polyhedra bonding energies, where large SUs are more energetic. The Wynblatt-Takashima [41] model considers the GB plane as an interface between two independent surfaces, each one having its own energy. The GB energy is, therefore, an average of the respective surface energies plus a term that depends on the twist angle between two lattices. This latter term depends on the free volume associated with the interface formed by two contacting surfaces. The detailed description of these models was given by us elsewhere [30], and will not be repeated here. It can be concluded from all of these models that GB energy increases with increasing GB free volume. A striking example taken from the work of Wynblatt and Takashima [41] is given in Fig. (2.6). This trend is general, and is valid for any of the modeling approaches.
Fig. 2.6: Results of computer simulations for the (111)(511) GB in Cu. The plot shows the dependence of one of the components of GB energy on a dimensionless parameter of free volume [41].

In summary, the modeling of GB structure-energy relationship follows two different approaches: GB dislocations and atomic-matching. The first one is applicable for quantitative calculations of strain field energy, while the dislocation core terms describing the most significant deviation of GB structure from the atomic bonding in the perfect lattice, can be only approximatey evaluated. The second approach is a complementary to the first one, enabling the quantitative estimation of atomic mismatch in the GB. In all cases, GB free volume is a key parameter determining the GB energy, and is essential for understanding the concept of non-equilibrium GBs. The introduction of models for non-equilibrium GBs in the following section will be given in terms of dislocation models.

2.4.2. Modeling of non-equilibrium GBs

The first model of non-equilibrium GBs was proposed for NC materials. While in CG polycrystals adjacent crystallites are free to minimize the boundary energy by translations in the interatomic scale reaching at the energetically-stable configurations, in NC materials the constraints exerted by the neighboring GBs and triple junctions (TJs) are stronger and limit the rigid-body relaxation [8]. Thus, a non-equilibrium GB is formed. However, this model is expected to work only in NCs with the grain size of up to a few tens of nm, and is insignificant in the polycrystals with sub-micron grains.

Another way by which non-equilibrium GBs are formed is the accumulation of lattice dislocations. For instance, Grabski and Korski (1970) observed an increase of GB energy in Cu due to the absorption of lattice dislocations during migration of GBs.
They concluded that these GBs transform into a non-equilibrium state. Based on this approach, Nazarov [43-46] has developed a structural model that elucidates the properties of non-equilibrium GBs.

The starting point for the model is the Read-Shockley model for LAGB detailed above (section 2.4.1), where the GB structure was described in terms of periodic dislocation arrays. Hence, all GB properties are expressed as the sum of contributions of individual dislocations forming the GB. In particular, the total GB energy is the energy of the elastic field which is a superposition of the elastic strain fields of individual dislocations. Contrary to this description, non-equilibrium GBs evolve during plastic deformation by absorbing the lattice dislocations, which form non-periodic, disordered arrays at GBs. These trapped dislocations dissociate into two different components with the Burgers vectors normal \((\pm b_n)\) and tangential \((b_t)\) to the GB plane. While the tangential components are glissile and form pile-ups at triple lines, the normal ones are sessile. Both dislocation assemblies (pile-ups of glissile extrinsic GB dislocations and disordered networks of sessile GB dislocations) form the non-equilibrium state, as illustrated in Fig. 2.7. The separation between absorbed dislocations is denoted as \(h\), and is a random variable [43]. The separation between GB dislocations in the equilibrium state is, however, constant (does not deviate much from its average value) and is denoted as \(h_0\).

Fig. 2.7: The formation of a nonequilibrium GB structure. (a) Trapping of lattice dislocations by the boundary. (b) Dissociation of the trapped dislocations into two components resulting in disordered arrays.
In general, the densities of dislocations with $+b_n$ and $-b_n$ are different, so that $\langle h \rangle \neq h_0$. Consequently, the misorientation increases with the increase of net GB dislocation density. Since the inter-dislocation separation, $h$, is now a random variable, its variance:

$$D_h = \langle h^2 \rangle - \langle h \rangle^2$$  \hspace{1cm} (2.6)

expresses how the structure of GB is far from equilibrium or the degree of non-equilibrium. This definition is essential because it is the basis for the subsequent quantifications of non-equilibrium GB properties. For instance, the root mean-squares (RMS) of stress field components exerted from a fragment of GB with the length $L$ will be calculated according to the 1st and 2nd order moments [44] defined as:

$$\left\langle \sigma_{ij}^n (x, y) \right\rangle = \frac{1}{L} \int_{y'}^{y'} \frac{1}{L} \sigma_{ij}^n (x, y - y') dy'$$  \hspace{1cm} (2.7)

where $n$ denotes the $n$th-order moment, and $\sigma_{ij} (x, y - y')$ is a stress component at the $(x, y)$ position induced by one dislocation located at $y'$ along the non-equilibrium GB. Eq. (2.7) enables calculating the complete tensor of the explicit values ($xx$, $yy$, and $xy$ components) of $\left\langle \sigma_{ij}^2 \right\rangle$.

Utilizing the conventional approach in the theory of elasticity, i.e. employing stress-strain relationships, the total elastic energy associated with the non-equilibrium boundary can be obtained by the volume integral:

$$E_{el} = \iiint \sigma_{ij} \cdot \varepsilon_{ij} dV$$  \hspace{1cm} (2.8)

Eq. (2.8) can be expressed in terms of the 2nd-order moments of the stress components, so that the following properties of non-equilibrium GBs are quantified: the RMS strain in the vicinity of GB, the GB excess elastic energy, and the GB excess volume. They are given in expressions (2.9)-(2.11), respectively:

$$\varepsilon_{rms} = 0.13 b \cdot \sqrt{\rho \cdot \ln \left( \frac{d}{b} \right)}$$  \hspace{1cm} (2.9)
\[
\gamma_{\text{ce}} = \frac{Gb^2 \cdot \rho_v d}{12\pi(1-\nu)} \ln\left(\frac{d}{b}\right) \tag{2.10}
\]

\[
\Delta = 0.14 \cdot b^2 \rho_v \ln\left(\frac{d}{b}\right) \tag{2.11}
\]

where \(\rho_v\) is the density of dislocations in the bulk SPD-metal \((\rho_v \approx 6 \cdot 10^{15} \text{ m}^{-2})\), \(d\) is the grain size and all other parameters have their usual meaning. For instance, it was assessed \[46\] that for Cu with \(d \approx 200\) nm the elastic energy of non-equilibrium GBs should be about 1.2 J/m\(^2\), i.e. about twice its equilibrium value.

As mentioned above, the pile-ups of glissile \(b_t\) dislocations near the triple lines cause local changes in misorientation, a term that was defined as disclination. Similarly, each disclination has its own contribution to the above-listed properties and their total effect was also modelled \[46\]. It was concluded that the contribution of disclinations to the GB excess energy and volume expansion is minor: about one order of magnitude less than the values given by Eqs.(2.10) and (2.11). Their contribution for the RMS strain is, however, more significant, and should be taken into account.

In summary, non-equilibrium GBs are assumed to consist of lattice dislocations absorbed in preferred sites. The model for non-equilibrium GBs applies the theory of elasticity to calculate the stress field exerted from this non-periodic array of dislocations. It provides the expressions for RMS strain, excess energy, and free volume of the non-equilibrium GBs. All of the above are significantly larger than the relaxed GBs.

### 2.4.3. Relaxation of the non-equilibrium state

It follows from the description of how non-equilibrium GBs are formed (section 2.4.2) that they are metastable configurations of dislocations and, therefore, may relax in a thermally-activated process. The kinetics of relaxation must be considered when designing any GB-related experiment in SPD-processed materials, especially in GB diffusion experiments \[47\]. The following sections review the main attempts made so far to estimate the GB relaxation kinetics. The common assumption of all models is that since the GB dislocations forming the non-equilibrium state are
sessile, GB relaxation is possible only by dislocation climb. The following models estimate the kinetics of climb.

### 2.4.3.1. The approach of Lojkowski

One of the fundamental models aimed at the evaluation of the relaxation time of GBs was proposed by Lojkowski and Fecht [48]. The general principle of the model is regarding the Burgers vector of a given GB dislocation as a continuous variable. The relaxation process is regarded as the expansion of GB core, until the complete detachment of the dislocation from the GB. This process is driven by the gradient of strain field exerted from a given GB dislocation, and is enabled by the self-diffusion flux of atoms along the GB. This classical attitude yields an equation of motion in a strained GB. The relaxation time is derived from this kinetic equation, and has been expressed in several quantitatively-equivalent forms. One of these forms [49] which is convenient for practical use is given in Eq. (2.12):

\[
\tau \approx \frac{10.9 \cdot kT G \Omega \delta D_p}{S^3}
\]  

(2.12)

where \( \tau \) is the relaxation time, \( \delta \) is the GB thickness, and \( S \) expresses a characteristic dimension of length related with the dislocation strain field. \( S \) is generally evaluated as the extinction distance, where the dislocation TEM image loses its contrast (or, roughly, the inter-dislocation separation). From TEM observations in Al, \( S \) was evaluated as 60 nm. The value of \( \tau \) calculated from this model agrees with TEM observations, in which changes in the contrast around GBs occurred at elevated temperatures [48,49]. However, there are some problematic points concerning this model. First, the extinction of contrast in the vicinity of GBs does not necessarily indicate GB relaxation and allows alternative interpretations rather than dissociation of the GB dislocations. In this case, the real time of relaxation can be much larger. Second, the analysis of Lojkowski is based on GB diffusion flux driven by the strain field gradient of a single dislocation. This incorporates a "hidden" assumption that vacancy sources are available in the vicinity of each GB dislocation. This is equivalent, as well, to comparing \( S \) with the diffusion length, thus leading to underestimation of the relaxation time.

A similar approach was proposed by Nazarov et al. [50]. His model, however, treats a periodic array of dislocations in the GB, which is a more realistic
approximation. The other assumptions are the same as in the model of Lojkowski. The resulted equation of motion for dislocation climb was solved numerically and an expression for the relaxation time was obtained:

$$\tau \approx \frac{0.03 \cdot kT}{G\Omega \delta D_b} S^3$$

(2.13)

The relaxation time estimated in this model is 3 orders of magnitude smaller than in the model of Lojkowski. Concerning this difference, the explanation offered by Nazarov is that Eq. (2.13) expresses the spreading time of GB dislocations, which is usually entitled as "relaxation time". However, for large dislocation densities (i.e. in non-equilibrium GBs) the relaxation time can be much larger than the spreading time. Nevertheless, the true meaning of the parameter $S$ is, still, questionable.

2.4.3.2. The approach of Varin & Kurzydlowski

The model proposed by Varin and Kurzydlowski [51] attempts to solve the problem of small relaxation times predicted by previous works. The main assumption of the model is that GB relaxation occurs by volume diffusion of atoms and vacancies towards the TJs. Dislocation climb takes place along the GBs, until their annihilation at the TJs. As dislocation is absorbed in the TJ, an infinitesimal displacement of the TJ occurs. Correlating between the numbers of GB dislocations absorbed at TJ and the total strain involved in this process, and substituting the resulted equation in Ashby's expression for the deformation rate due to volume diffusion, a new kinetic equation is obtained. Eq. (2.14) describes the time-dependent density of GB dislocations, $\rho(t)$:

$$\frac{\rho}{\rho_0} = \exp\left(-\frac{20G\Omega D}{\pi (1-\nu)kT \cdot d^2 \cdot t}\right)$$

(2.14)

where $\rho_0$ is the initial ($t=0$) density of dislocations and the other parameters have their usual meaning. It should be remarked that contrary to the previous models, the dependence on grain size, $d$, is prominent in Eq. (2.14). Such dependence was missing in the previous works. Additionally, the kinetics is determined by bulk diffusivity, $D$, rather than GB diffusivity, $D_b$. This means that, according to Eq. (2.14), the relaxation kinetics should be slower than that predicted by Eqs. (2.12) and (2.13). Determining an
arbitrary condition for equilibration, for instance when dislocation density drops to 10% of its initial value, an expression for the relaxation time is obtained:

$$\tau = \frac{2.3\pi(1-\nu)kT \cdot d^2}{20G\Omega D}$$  \hspace{1cm} (2.15)

Varin and Kurzydłowski provided experimental support for their model [51]. However, in some cases the relaxation times calculated according to Eq. (2.15) were longer than observed in experiments.

2.4.3.3. The approach of Sangal & Tangri

The advantages of Varin and Kurzydłowski model include a good agreement of its predictions with experimental results, and a reasonable functional dependence of the relaxation time on grain size. However, some of the experimental data could not be explained by this model. For example, the relaxation time of GBs in austenitic steel with grain size 3.4 µm annealed at 800 ºC is predicted by Eq. (2.15) as 11 h. Experimental data based on the measurement of yield stress indicates a recovery at this temperature after 5 min only [52]. Sangal & Tangri [53] took a note of this underestimation of relaxation times, and suggested a revised approach.

Their model assumes GB relaxation by a flow of vacancies in the bulk towards the TJs, driven by a stress field induced by the TJs. Figure 2.8 illustrates the main principles of the model. It describes an array of GB dislocations at a GB of the length $d$. For the simplicity, all dislocations have the same Burgers vector in $z$ direction. The resulting strain field of the dislocation array exerts the climb forces on the edge dislocations near the TJs. In the configuration illustrated in Fig. 2.8, the climb stress, $\sigma_{zz}$, is compressive near the position $A$, and is tensile near the position $B$, so that vacancies are attracted to $A$ and emitted from $B$.

The expression for the concentration of vacancies, $C$, is determined by their chemical potential. The latter can be expressed in terms of the climb stress, $\sigma_{zz}$, and the resulting expression for $C$ is:

$$C = C_0 \exp\left(\frac{\Omega \cdot \sigma_{zz}}{kT}\right),$$  \hspace{1cm} (2.16)

where $C_0$ is the equilibrium concentration of vacancies.
An expression for the radial and angular \((r, \theta)\): polar co-ordinates) distribution of \(\sigma_{zz}\) near \(A\) and \(B\) is obtained from the theory of elasticity. Substituting this expression in Eq. (2.16), we obtain the radial and angular distribution of vacancies near the TJs, \(C(r, \theta)\). The average concentration of vacancies (over all directions) near the positions \(A\) and \(B\) is calculated by:

\[
\bar{C}(r_{A,B}) = \frac{1}{\pi} \int_0^\pi C(r_{A,B}, \theta) d\theta
\] (2.17)

Assuming that the diffusion of vacancies towards the TJs satisfy steady-state conditions, we obtain new boundary conditions for \(\bar{C}(r_{A,B})\), which are:

\[
\bar{C}(r_{A,B}) = C_0 \left(1 + \frac{G\Omega \rho}{4\pi(1-\nu)kT} \left[1 - 2\ln\left(\frac{b}{d}\right)\right] \frac{\ln(d/2r_{A,B})}{\ln(d/2b)}\right)
\] (2.18)

where the signs \(-\) and \(+\) stand for the positions \(A\) and \(B\), respectively. Eq. (2.18) incorporates some approximations: the dislocation core width, \(r_0\), was roughly evaluated as \(r_0 = b\). The location where the concentration of vacancies reaches its equilibrium value ("infinity", or far enough from the TJs) was evaluated as the half grain size, \(d/2\).
The annihilation rate of dislocations is calculated from the vacancy flux, $J$, at any of the TJs $A$ and $B$. According to Fick's 1st law:

$$\vec{J} = -D_v \vec{\nabla} C,$$

(2.19)

where $D_v$ is the vacancy diffusion coefficient, and can be expressed as: $D = \Omega C_0 D_v$ ($D$ is volume self-diffusivity). The vacancy flux can be simply correlated with the density of remaining GB dislocations, and the concentration gradient appearing in Eq. (2.19) can be evaluated from the expression (2.18). The result is a differential equation for the density of GB dislocations. Its explicit solution yields the kinetic expression:

$$\frac{1}{\rho(t)} = \frac{1}{\rho_0} + \left( \frac{G\Omega D(1-2\ln(b/d))}{(1-v)kT \cdot d \cdot \ln(d/2b)} \right) \cdot t$$

(2.20)

The functional dependence of $\rho$ on time, temperature and grain size confirms our expectations: a larger grain size results in an increase of the relaxation time, and increases the annealing time and temperature required for GB relaxation. The relaxation times calculated from Eq. (2.20) are in a good agreement with experimental data describing the change in yield stress due to annealing [52].

In summary, different models have been suggested for estimating the GB relaxation times. The approach of Lojkowski and Nazarov considers GB diffusion in the small regions comparable in their size with the inter-dislocation separation. Therefore, it predicts a relatively fast relaxation kinetics. These models were experimentally verified by TEM observation. However, two points are still questionable: the assessment of strain field from TEM images, and correlating this value with the real diffusion length. The approaches of Varin & Kurzydłowski as well as Sangal & Tangri consider volume diffusion of atoms and vacancies driven by the stress fields near GB dislocations. In these models the diffusion length is considered as comparable with grain size, and, therefore, they predict relatively slow relaxation kinetics. Some of the experiments on GB relaxation support these models, too. It seems that each model is working under certain specific experimental conditions that should be considered in the experimental work.
2.5. Experimental observations

It was shown that the concept of non-equilibrium GBs is theoretically well-established. This section reviews the experimental works in which the GB diffusivity and energy in UFG alloys produced by SPD methods were measured. These works provide an experimental support of the concept of non-equilibrium GBs.

2.5.1. Measurements of diffusion in UFG materials

It is well known that GB diffusion coefficients are very sensitive to the finest details of the GB structure (see section 2.3). Whereas the difference in energies of random HAGBs rarely exceeds 10-20% [32], the corresponding diffusivities can differ by orders of magnitude. It is therefore very attractive to employ GB diffusion measurements for quantification of the degree of GB non-equilibrium. Based on the correlation between GB structure and diffusivity (see section 2.4.1), non-equilibrium GBs are expected to possess higher values of diffusivities [54].

The problem of GB diffusivity in UFG materials has been addressed in several experimental studies; however, the results of these studies are contradictory and inconclusive. While several authors reported a significant enhancement of GB diffusivities in UFG materials, others claimed that the GB diffusivities in UFG and coarse-grained materials are very close to each other. For instance, Kolobov et al. [55] investigated GB diffusion of Cu in UFG Ni processed by ECAP using the secondary ion mass spectroscopy (SIMS) technique. The values of diffusion coefficients measured in the range of 150 - 200 °C were by about 5 orders of magnitude higher than in the coarse-grained state. At the same time, pre-annealing of the sample at 250 °C prior to diffusion annealing led to a drastic decrease of GB diffusivity. It was concluded that the non-equilibrium GBs exhibit high diffusivities and relax during the pre-annealing, which results in diffusivity decrease. Similar conclusions were drawn in the work of Herth et al. [56], where the GB self-diffusivity in NC Fe-alloys decreased by one order of magnitude after the pre-annealing treatment. These results were compared with positron annihilation lifetime experiments, indicating a decrease in GB free volume with annealing time. Although these findings provide evidence for the unusual diffusion properties of GBs in UFG materials, they indicate the problematic nature of such experiments: relaxation of GB structure at elevated temperatures before or during the diffusion anneal may significantly modify the GB diffusion.
In contrast with the above reports, Würschum et al. [57] have found that the diffusion coefficient of $^{59}$Fe along the GBs in UFG Pd was comparable with that for CG Pd. Similarly, Fujita et al. [58] investigated short-circuit diffusion in ECAP-processed UFG Al and Al-3 wt.% Mg alloy containing small precipitates for suppressing grain-growth. No enhanced diffusivity was observed, despite the stabilized microstructure. The same authors reported on an increase in GB diffusivity obtained in UFG Al-Mg and Al-Zn alloys produced by ECAP [59], but associated it with the larger fraction of HAGBs existing after ECAP. Both authors concluded that even if the non-equilibrium GBs exist in the as-deformed state, they rapidly recover during initial stages of diffusion annealing.

Besides direct measurements of GB diffusivity, an indirect experimental support for the hypothesis of non-equilibrium GBs was provided in the studies of grain growth [60] and GB sliding-controlled creep [61] in UFG Cu. For instance, some models relate the grain growth kinetics with the GB diffusivity according to:

$$d^2 - d_0^2 = \frac{4\gamma\Omega}{\delta}D_{b0} \cdot \exp\left(-\frac{Q}{kT}\right) \cdot t \quad \text{(2.21)}$$

where $d_0$ is the initial grain size, $D_{b0}$ is the pre-exponential factor of GB diffusion coefficient, $Q$ is the activation enthalpy for GB migration (which is closely related to that of GB diffusion), $\gamma$ is the GB energy, and all other parameters have their usual meaning. Lian et al. [60] have shown that grain growth in SPD-produced Cu begins at $0.32T_m$ (where $T_m$ is the melting temperature of pure Cu), and, using the Eq. (2.21), estimated the parameters of GB self-diffusion from the kinetics of grain growth. The activation energy for GB diffusion at low temperatures was 71 kJ/mole, while at higher temperatures it increased to 107 kJ/mole. This increase in activation energy was explained by relaxation of the non-equilibrium structure of GBs. However, in view of the recent data on the purity effect on GB self-diffusion in copper [62] this conclusion has to be treated with caution: the activation enthalpy of 72 kJ/mol was measured for GB self-diffusion in high-purity copper, whereas a less pure material exhibited values of 80 to 90 kJ/mol.

The hypothesis of non-equilibrium GBs is often employed for interpretation of unusual mechanical properties of UFG materials produced by SPD. For example, GB
sliding is an important deformation mechanism in UFG materials. Models of GB sliding predict that the strain rate is proportional to GB diffusion coefficient:

\[ \dot{\varepsilon} = \frac{D_b}{kT} \left( \frac{\sigma}{E} \right)^2 \cdot \left( \frac{b}{d} \right)^2 \]  

(2.22)

where \( E \) is the modulus of elasticity. Estimates of the copper GB self diffusivity from the creep data based on Eq. (2.22) gave relatively low values of the activation energy for GB self diffusion in the range of 70-78 kJ/mole [61]. This was interpreted in terms of non-equilibrium GBs with high diffusivity. However, again, this value agrees well with the data for high-purity coarse-grained copper. A main drawback of such experiments is that they rely on semi-quantitative models relating the measured properties to GB diffusion, so that no definitive conclusion as to the occurrence of non-equilibrium GBs can be drawn.

The cited investigations do not prove the existence of non-equilibrium GBs with an anomalously high diffusivity. Moreover, even the direct measurements of GB diffusion in UFG alloys provide the contradictory results that cannot be considered as an unequivocal proof of the existence of the non-equilibrium GBs with anomalously high diffusivity. It can be concluded that diffusion behavior of GBs in UFG alloys is still far from being understood.

2.5.2. Characterization of UFG materials by X-ray diffraction

X-ray diffraction (XRD) measurements provide valuable data on NC materials. XRD patterns of UFG materials differ from XRD patterns of their coarse-grained counterparts by an increased integral intensity of the background and by a peak broadening. The former is caused by diffuse scattering enhanced by lattice defects, while the latter is associated with high level of strain and small grain size [6]. Regarding XRD data collected from UFG materials, the term "strain" requires further clarification. When the mean interplanar \( d \)-spacing remains constant, but is accompanied with large random variations having a finite root-mean-square (RMS) value, an XRD peak broadening is observed. This strain is defined as RMS strain. XRD peak broadening in UFG materials indicating microstrain fluctuations has been observed [6, 63-66] and was ascribed to the highly non-equilibrium state of GBs. The values of RMS strain calculated from the XRD peaks were in the range of \((5-10) \times 10^{-3}\),
in correspondence with the values expected by Nazarov in his models of non-equilibrium GBs [43-46].

At this point it should be noted that the term "strain" refers also to a uniform change in the interplanar \(d\)-spacing. Such homogeneous strain is pronounced by an angular shift of the XRD peak. XRD peak shifts have been predicted by Alexandrov and Valiev [67] in their simulation of XRD patterns collected from NCs. It was associated with grain sizes that are comparable with the strain fields induced by the GBs (20-30 nm), so that the RMS strain becomes homogeneous. According to this explanation, a shift of XRD peaks is not expected in UFG-materials \((d \leq 1 \, \mu m)\) at all, since their grain size is much larger than the characteristic size of strained zone at the GBs.

In summary, XRD peak broadening observed in UFG materials produced by ECAP can be explained by the existence of non-equilibrium GBs. However, XRD peak broadening is only indirect evidence. In addition to RMS strain, the decreasing grain size also contributes to the peak broadening.

2.5.3. Utilization of Differential Scanning Calorimetry for UFG materials

The physical principle of Differential Scanning Calorimetry (DSC) is heating the investigated sample together with a reference one and measuring the heat required to maintain identical temperatures of both samples. Thus, the beginning of an exothermal reaction within the sample is denoted as an abrupt decrease of the heat supplied by the system. Peaks in the DSC curve (supplied heat vs. temperature), either negative or positive, may indicate phase transformations. Therefore, DSC is used as a supplementary tool in the studies of phase transformations in materials.

The thermodynamic parameter that has the strongest correlation to the GB degree of non-equilibrium is the GB energy, \(\gamma\). So far, the GB energy has been measured in UFG materials with the aid of DSC. For instance, Huang et al. [68] measured the enthalpy released during grain growth in nanocrystalline copper (with an initial average grain size of 8.5 nm) produced by compaction of nanoparticles. The value of GB energy extracted from the enthalpy release was 0.7 J/m\(^2\), about the same as the well-known value for pure copper, 0.6 J/m\(^2\), which was measured by Hilliard et al. [69] using the thermal grooving method. Concerning the effect of plastic deformation, it was shown that UFG copper exhibits a more intensive exothermal peak.
with respect to cold-rolled copper due to higher values of elastic and capillary energy stored in the former [70]. By comparing experimental results obtained by DSC and by other characterization techniques, a more comprehensive view of the physical processes in UFG alloys can be achieved. For example, the comparison of the DSC peak integral intensity of ball-milled metals with the extent of XRD peak broadening shows that the heat released is proportional to the square of RMS strain [63]. The energy released is, therefore, associated with strain relaxation.

Further progress in the investigation of GB energy after SPD was reported by Zhilyaev et al. [71], who performed the DSC measurements of the enthalpy released during grain growth in UFG nickel samples produced by several variants of SPD. These values of released enthalpy were correlated with the GB energy considering the initial and final grain size, as well as other geometrical factor. The estimated values of GB energy in the SPD-produced nickel were higher by a factor of about 1.4-1.7 than the values of GB energy in relaxed nickel samples.

In the thorough work of Tschöpe, Birringer and Gleiter [72] the heat released in NC Pt samples was correlated with their grain size. It was shown that although grain growth begins only at 500 K, exothermal peaks are observed already at 400 K. Analysis of the peak shape also indicated two-stage heat releasing processes. Other experiments in NC metals using the DSC technique [64,66] indicate the presence of exothermal peaks at temperatures lower than the threshold temperature of grain growth. These findings imply that the process of non-equilibrium GB relaxation may occur prior to recrystallization and grain growth.

In spite of the fact that DSC can provide quantitative estimation of GB energy, this technique suffers from several drawbacks. First, the value of $\gamma$ can be measured only indirectly. Though the heat released ($\Delta H$) during grain growth is associated with the decrease of the total interfacial energy, the relationship between $\gamma$ and $\Delta H$ is not trivial, since it depends on the grain size distribution and grain morphology. Second, the magnitude of $\Delta H$ measured by DSC is associated with a large population of GBs in one sample, and the distinction between two or more GB populations having different values of energy is impossible. Third, the defects other than GBs (such as lattice dislocations) may contribute to the amplitude of the exothermal peak, $\Delta H$, measured by DSC. Thus, only the upper limit of $\gamma$ can be obtained in the DSC measurements.
Another drawback of this method is its applicability in the ultrafine-grain regime only. As grain size increases, the total area of interface decreases and the amplitude of the released heat falls below the detection limit of the instrument.

2.6. Summary and research goals

UFG materials exhibit an attractive combination of structural and functional properties. One of the most effective ways of producing UGF alloys is by SPD. Many unusual properties of UFG alloys produced by SPD can be understood in terms of the hypothesis of non-equilibrium GBs. Theoretical models have been developed for describing the formation and relaxation of non-equilibrium GBs, as well as for predicting their physical properties. Besides the theoretical aspect, there have been several attempts to verify the concept of non-equilibrium GBs experimentally. This includes TEM observations of the GB strain fields and atomic structure, GB diffusion experiments, X-ray diffraction analyzes and DSC measurements.

It follows from the above review that a solid experimental proof of the hypothesis of non-equilibrium GBs in SPD-processed UFG materials is still missing. The results of diffusion measurements in UFG alloys are contradictory. Moreover, to the best of our knowledge no direct measurements of GB energy in alloys produced by SPD were reported in the literature. Other experimental attempts to confirm the hypothesis of non-equilibrium GBs are indirect, and allow several alternative interpretations. Providing such a proof is a challenging task because of the low thermal stability of the microstructure of UFG materials and the high driving forces for the relaxation of non-equilibrium state.

Therefore, the main objectives of this research are quantifying the degree of non-equilibrium of GBs in UFG Cu alloys produced by ECAP by studying the GB diffusivity and energy, and comparing them with those of equilibrated GBs in annealed polycrystals of identical chemical composition. The reasons for the choice of GB energy and diffusivity in the context of this study are the following:

- GB energy is the most direct indicator of the degree of GB non-equilibrium, since the non-equilibrium, metastable GB by definition exhibits higher energy than its fully equilibrated counterpart (which is an absolute minimum of energy);
GB self-diffusion is a kinetic parameter extremely sensitive to GB structure and GB free volume.

This research is expected to contribute to the understanding of the unusual mechanical and functional properties of UFG materials obtained by SPD methods. The detailed quantitative knowledge of the kinetic and energetic properties of GBs in this new class of UFG materials will be helpful in the search for new application areas for these materials.
3. EXPERIMENTAL METHODS

This chapter provides a description of the experimental strategy and methods implemented in this research. The first section of this chapter describes the methodology utilized to achieve the research goals. The second section deals with the characterization techniques that were employed.

3.1. Research methodology

The two main experimental parts forming the backbone of this research are measuring GB diffusivity as well as relative GB energy in ECAP-processed alloys, and comparing the results obtained with those of relaxed samples. Therefore, the appropriate metallic systems should first be selected so that both thermally-stable UFG as well as relaxed microstructures can be examined. Second, the whole set of thermal treatments involved in both parts of the experimental work should be selected, considering the stability of microstructure. For this purpose, the microstructure of the alloys should be characterized prior to annealing and after it.

3.1.1. Selection of the alloys

As mentioned above, it is very important to retain the microstructure obtained after SPD processing at the temperatures which are as high as possible. Indeed, significant relaxation of the GB structure can occur during thermal annealing of pure metallic specimens produced by ECAP [16]. Moreover, GB migration during diffusion annealing will complicate considerably the processing of penetration profiles obtained in diffusion experiments [73]. Therefore, alloying with either precipitate- or solid solution-forming elements is the common approach applied for stabilizing the ECAP-produced specimens in several metallic systems [19-25]. Among all metallic systems produced by ECAP, Cu-alloys are probably the most widely-investigated ones [13-17, 26, 60, 61, 66, 74, 75], therefore we selected copper alloys in order to achieve the research goals. In addition to pure Cu, a Cu-Zr alloy having a small Zr content was selected. In this range of compositions, we expect the presence of Cu₅Zr precipitates dispersed within the Cu matrix, as shown in the Cu-Zr phase diagram [76].
The Cu-0.17 wt.% Zr alloy was selected for the experiments since it was established that in an alloy with similar composition the grain size of about 400 nm obtained after 4 passes of ECAP kept constant during annealing up to 500°C [19]. This improvement in stability with respect to pure Cu is well demonstrated in Fig. 3.2.

Fig. 3.1: The Cu-rich part of the Cu-Zr phase diagram showing the two-phase region of Cu + Cu₅Zr [76].

Fig. 3.2: The grain size of several Cu alloys produced by ECAP plotted against annealing temperature (after [19]).
3.1.2. Preparation of samples: ECAP and surface treatment

Ingots of Cu-0.17 wt.% Zr alloy (further denoted as "Cu-Zr alloy") were prepared from pure components by casting in vacuum. The material was provided by Prof. G. Gottstein (RWTH Aachen). The initial average grain size in the ingots was 300 µm. Billets from this material with the dimensions of 10 mm × 10 mm × 70 mm were processed at room temperature by 4 ECAP passes according to route B_C (90° rotations about the workpiece axis between the passes).

Copper (99.98 wt.% Cu, further denoted as "pure Cu") ingots with the diameter of 50 mm were supplied by RAFAEL Ltd. and processed in the ECAP method in the same B_C route. The major impurities (>1 wt. ppm) are: O (29 wt. ppm), P (18 wt. ppm), Ag and Fe (5 wt. ppm each).

After a usual polishing routine (SiC papers and diamond paste with 6 µm particle size), electrochemical polishing was performed in all samples (in a 50 % wt. H₃PO₄ solution, 2.1V) for 1 h prior to any annealing procedure in order to enable surface stress relaxation.

3.1.3. Design of diffusion experiments

The diffusion experiments should be properly planned by selecting the appropriate physical conditions and combination of characterization techniques. In our experiments, Ni was selected as the diffusing element due to its chemical resemblance to Cu.

According to the conventional classification of Harrison [77], diffusion in polycrystals can be divided into the 3 main kinetic regimes. In \( A \)-regime the polycrystal behaves as a homogeneous medium with an effective diffusivity, \( D_{eff} \), which is a weighted average of the bulk \( (D) \) and GB \( (D_b) \) diffusion coefficients [31]. The expression for the effective diffusion coefficient is:

\[
D_{eff} = f \cdot D_b + (1 - f) \cdot D
\]  

(3.1)

where \( f \) is the volume fraction of GBs in the material. It should be noted that the weighted average diffusion behavior in bulk containing dislocation cores, as well as other short-circuit diffusion paths, can also be expressed by Eq. (3.1) after some modifications. The physical case denoted as \( A \)-regime prevails where the bulk
diffusion length is much larger than the grain size, \( d \), i.e. at high temperatures or, alternatively, long annealing times \( (t) \):

\[
\sqrt{Dt} \gg d ,
\]  

(3.2)

The other extreme case is \( C \)-regime, in which the diffusion flux is confined within the GB cores (volume diffusion is "frozen out"). An intermediate case is the \( B \)-regime, where the solute atoms diffuse preferentially along the GBs, with subsequent leakage into the bulk. The analytical models for processing of experimental diffusion profiles are available for all three regimes, and also for the case of GB migration during diffusion annealing [78-80]. The distinction between the two relevant diffusion regimes, \( B \) and \( C \), requires the following definitions:

\[
\alpha \equiv \frac{s\delta}{2\sqrt{D}t} ; \quad \beta \equiv \frac{s\delta D_b}{2D\sqrt{D}t}
\]  

(3.3)

where \( s \) is the segregation factor, and \( \delta \) is the GB width (\( \delta \approx 0.5 \text{ nm} \)). While \( \alpha \) expresses the ratio between boundary width and bulk diffusion length, \( \beta \) denotes the ratio between the amount of material penetrating into the GBs and into the bulk.

The most simple case in type-\( C \) diffusion, that demands \( \alpha \gg 1 \) (practically: \( \alpha > 10 \)). This type of diffusion occurs at low temperatures, or alternatively short annealing times. Relying on the theory of diffusion [78], the complete forms of solution for the diffusion equation in the \( C \)-regime are the same as for diffusion in homogeneous semi-infinite media, depending on the boundary conditions. In the case of constant surface concentration \( C_0 \) (for instance, an infinitely thick layer deposited on the surface) the dependence of mean concentration \( \bar{C} \) on the depth, \( x \), is given by:

\[
\bar{C} = C_0 \cdot \text{erfc} \left( \frac{x}{2\sqrt{D}t} \right)
\]  

(3.4)

In the case of an instantaneous diffusion source (for instance, a thin layer of tracer on the surface) the solution of concentration is:

\[
\bar{C} = \frac{A}{\sqrt{t}} \exp \left( -\frac{x^2}{4D_b t} \right)
\]  

(3.5)

where \( A \) is a time-independent constant.
Type-B diffusion (α < 1 and β >> 1) occurs at higher temperatures. The solutions for this case are based on Fisher's approximate analysis [81], which is valid for the condition of constant surface concentration. The exact and extensive analysis of this case was performed by Whipple, Suzuoka, and Le-Claire. We present here the most practical solution given by Suzuoka [82], where the GB diffusion coefficient can be derived from plotting the average concentration in the $x^{6/5}$ co-ordinates. For a constant surface concentration:

$$P \equiv s \delta D_h \approx 1.322 \sqrt{\frac{D}{t}} \left( \frac{-\frac{\partial \ln C}{\partial x^{6/5}}}{\delta} \right)^{-\frac{5}{3}}$$  \hspace{1cm} (3.6)$$

This solution is valid for $\alpha < 0.1$ and $\beta > 10$.

The solution for an instantaneous source is:

$$P \equiv s \delta D_h \approx 1.308 \sqrt{\frac{D}{t}} \left( \frac{-\frac{\partial \ln C}{\partial x^{6/5}}}{\delta} \right)^{-\frac{5}{3}},$$  \hspace{1cm} (3.7)$$

and is valid for $\alpha << 1$ and $\beta > 10^4$.

It should be remarked that contrary to the solution in C-regime, which yields the GB diffusion coefficient directly, experiments in B-regime yield the parameter $P$ only.

In view of the above, the temperatures selected for diffusion-annealing should be as low as possible for two main reasons: preserving the stability of microstructure, and working at C-regime, where the mathematical analysis of results is more straightforward. It should be noted that in the case of non-stable microstructure the derivation of diffusion coefficient can be very complicated. A mathematical analysis of the case in which $D$ is time-dependent [83] (e.g. decreases exponentially with time during GB relaxation) indicates that in the simplest case:

$$D_{exp} = \int_{t'}^{t} D(t') dt',$$  \hspace{1cm} (3.8)$$

where $D_{exp}$ is the value of diffusivity measured experimentally. This underlines the importance of ensuring microstructure stability [47].

An additional consideration taken into account in the determination of annealing temperatures is that the latter should be divided into equal intervals in the reciprocal temperature scale. This ensures a more statistically-reliable expression of the
diffusivity when plotted in an Arrhenius diagram. In the present grinder sectioning technique (see below, section 3.2.4.) an average characteristic diffusion length $\sqrt{D_b t}$ of at least 10 µm is necessary for getting reliable concentration-depth profiles. Therefore, the lower limit of all annealing times was determined according to this relationship using the diffusivity values obtained in preliminary experiments. The time and temperature conditions were selected regarding these considerations, as shown in Table 3.1.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Time [s]</th>
<th>$\alpha/s$</th>
<th>$(\alpha/s)s^{rel}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>424</td>
<td>$1.71\cdot10^6$</td>
<td>$1.66\cdot10^3$</td>
<td>$1.01\cdot10^5$</td>
</tr>
<tr>
<td>437</td>
<td>$7.81\cdot10^5$</td>
<td>$9.48\cdot10^2$</td>
<td>$5.03\cdot10^4$</td>
</tr>
<tr>
<td>457</td>
<td>$2.84\cdot10^5$</td>
<td>$4.05\cdot10^2$</td>
<td>$1.76\cdot10^4$</td>
</tr>
<tr>
<td>474</td>
<td>$1.08\cdot10^5$</td>
<td>$2.27\cdot10^2$</td>
<td>$8.44\cdot10^3$</td>
</tr>
<tr>
<td>493</td>
<td>$4.68\cdot10^4$</td>
<td>$1.15\cdot10^2$</td>
<td>$3.63\cdot10^3$</td>
</tr>
<tr>
<td>513</td>
<td>$1.8\cdot10^4$</td>
<td>$6.36\cdot10^1$</td>
<td>$1.71\cdot10^3$</td>
</tr>
<tr>
<td>553</td>
<td>$3.6\cdot10^3$</td>
<td>$2.11\cdot10^1$</td>
<td>$4.29\cdot10^2$</td>
</tr>
<tr>
<td>623</td>
<td>$3.6\cdot10^3$</td>
<td>$1.35\cdot10^1$</td>
<td>$1.83\cdot10^1$</td>
</tr>
</tbody>
</table>

Table 3.1: Temperatures and durations of diffusion annealings selected in the present study. $s^{rel}$ is the segregation factor of Ni at relaxed GBs in high-purity coarse-grained Cu after Divinski et al. [84].

In order to verify that C-regime conditions prevail in our experiments, the values of $\alpha$ from Eq. (3.3) were calculated. The inequality $\alpha>1$ determines the upper limit for annealing time. The bulk diffusion coefficient $D$ was taken from the investigation of Bernardini and Cabane [85]:

$$D = 7.0\times10^{-5} \exp\left(-\frac{225 \text{ kJ/mol}}{RT}\right) \text{m}^2/\text{s}. \quad (3.9)$$

The segregation factor $s^{rel}$ of Ni at relaxed GBs in high-purity coarse-grained Cu was recently determined by the radiotracer measurements in Harrison’s B and C regimes [84]:
\[ s^{rel} = 0.55 \exp\left(\frac{16.6 \text{ kJ/mol}}{RT}\right) \tag{3.10} \]

Generally, different segregation behaviors at relaxed and non-relaxed GBs could be expected. Therefore, in Table 3.1 the values of the parameters \(\alpha/s\) and \((\alpha/s)s^{rel}\) are listed. Direct measurements \[84\] have shown that Ni does segregate at HAGBs in coarse-grained copper with the segregation factor ranging from 30 to 50 in the temperature interval under consideration. Note that the condition \(\alpha/s > 1\) corresponds safely to the C-regime of GB diffusion.

3.1.4. Thermal GB grooving for measurements of the relative GB energy

The conventional method for measuring GB energy is by the geometry of its equilibrium groove where it intersects a free surface. A GB intersecting the surface tends to form a groove. The rate of grooving depends on the dominating mechanism of mass transport. The physical theory of GB groove growth was formulated by Mullins \[86,87\] for three possible mechanisms: surface diffusion, evaporation-condensation through the vapor phase and volume diffusion in the lattice (Fig. 3.3). All three processes are driven by the chemical potential gradient caused by the surface curvature, and by nature become operative at elevated temperatures.

Fig. 3.3: The 3 possible kinetic mechanisms for GB groove growth: surface diffusion, volume diffusion inside the lattice and evaporation – condensation through the vapor phase.
Under the assumption of full surface isotropy, the condition for mechanical equilibrium at the triple line is:

$$\gamma_{rel} = \frac{\gamma_b}{\gamma_s} = 2 \cdot \cos \left( \frac{\psi}{2} \right)$$

(3.11)

where $\gamma_b$, $\gamma_s$ and $\gamma_{rel}$ are the excess Gibbsian energy of the GB and of the surface, and the relative dimensionless GB energy, respectively. $\psi$ is the dihedral angle at the triple line. The geometric meaning of Eq.(3.11) is illustrated in Fig. 3.4.

Comparing between the several grooving mechanisms mentioned above [86,87], it has been concluded that for low temperatures or, alternatively, short annealing times, the dominating mechanism is surface diffusion [30]. At longer annealing times the better alternative option is performing grooving experiments in the solid-liquid interface, where the liquid phase is a molten metal. This method has been studied by several authors [88-93]. The metallic system selected as the liquid phase should satisfy the following conditions:

- It should possess as lower melting temperature as possible;
- It must significantly dissolve the atoms of the substrate (copper);
- It must wet the (copper) surface.

According to the above, the most suitable metal for wetting the Cu surface is Pb, with the melting temperature of 327 ºC. The Pb-Bi eutectic alloy has a lower melting temperature of 125 ºC [76]. This option, however, involves experimental difficulties. Firstly, it requires the removal of the (solidified) liquid phase after grooving, which
complicates the experimental procedure. Secondly, it is known that Bi considerably segregates into Cu GBs and, therefore, modifies their energy [90, 93] as well as kinetic parameters [94].

In view of these considerations and since we are interested in working at low temperatures and short annealing times, we performed our grooving experiments with the samples of pure Cu, i.e. without wetting by a liquid metal.

In this part of experimental work we utilized pure-Cu only. The samples were prepared in the same procedure detailed above (see section 3.1.2.). All heat treatments were conducted in a quartz-tube reactor under a constant flow (0.25 cm³/s) of dry Forming gas (90%N₂-10%H₂) at atmospheric pressure. The furnace is equipped with a magnetic knob that enables inserting the samples immediately when the temperature is stabilized. The temperature was measured directly at the sample position. Two different annealing conditions were selected:

- The first set of samples (denoted as class 1) was annealed at 400 °C for 15 min., so that thermal grooving is activated – on the one hand; however, no considerable relaxation of GB energy is allowed – on the other hand. Thus, the energetic state of the sample is close to the as-deformed state.

- The second set of samples (denoted as class 2) was annealed at 800 °C for 2h. At these conditions we expect a significant relaxation of the GBs.

### 3.1.5. Microstructure characterization

For characterization of the microstructure of the samples studied we used a combination of several techniques. Transmission electron microscopy (TEM), enabled us to observe the microstructure of the as-pressed, UFG samples due to its capability of providing high resolution images taken from a relatively small field of view (several micrometers). For determining the misorientation between individual grains and between the copper matrix and Cu₅Zr precipitates the selected area electron diffraction (SAED) technique in TEM was employed. Energy dispersive X-ray spectroscopy (EDS) operated in the scanning mode (STEM) was also applied in order to estimate the nickel solute concentration in the vicinity of the copper GBs. High-resolution field emission gun scanning electron microscope (SEM) equipped with EDS detector and dual focused ion beam (FIB) microscope were utilized to observe the coarse-grained
microstructure of samples after annealing. The FIB technique was selected owing to the good orientation channeling contrast it provides, the simplicity of sample preparation, and the possibility to image large areas with spatial and orientational resolution superior to that of SEM. In this manner, microstructure observations were held prior to heat-treatments and after them; thus supplying us with additional information about the influence of heat-treatments on the microstructures.

3.2. Experimental techniques

The above-detailed methodology utilized in this research requires selection of the appropriate experimental techniques. Such description is given in this section, according to the following sequence: techniques for microstructure characterization, techniques for measurement of diffusion behavior, and techniques applied for evaluation of relative GB energy.

3.2.1. Transmission Electron Microscopy (TEM)

Observations of the as-deformed microstructure were carried out by the JEOL FX-2000 Transmission Electron Microscope (TEM) with LaB₆ filament operating at 200 kV. TEM samples were cut along the pressing direction into slices of 500 µm thickness. Further electrochemical etching (10 min in 50 wt. % H₃PO₄ solution at 2.1v) was performed to obtain a thickness of about 100 µm. Discs of 3 mm in diameter were cut and thinned by electrojet polishing in the same solution with the current of 50 mA. Bright field images were taken to characterize the microstructure. Qualitative data of misorientation was obtained by the selected-area electron diffraction (SAED) using a 2 µm² aperture.

3.2.2. High-resolution Scanning Electron Microscopy (HRSEM)

High-resolution field emission gun Scanning Electron Microscope (SEM, LEO982 Gemini, Zeiss – Leica) equipped with energy dispersive X-ray spectroscopy (EDS, ThermoNoran) was used for observations of the samples surface. Images were taken with the annular in-lens detector, accelerating voltage of 20 keV and working distance 5 mm.
3.2.3. Focused Ion Beam (FIB)

Dual focused ion beam (FIB) microscope (Strata-400) operated with a 30 keV liquid-Ga\(^+\) source was selected owing to the good orientation channeling contrast it provides, the simplicity of samples preparation, and the possibility to image large areas with spatial and orientational resolution superior to that of SEM. Images in the FIB microscope were taken after mechanical polishing and removal of the upper surface electrochemically, as detailed above (section 3.2.1) in order to eliminate the effects of surface polishing. The ion beam currents were in the range of 28-280 pA, depending on the magnification.

3.2.4. The Radiotracer technique for diffusion measurements

GB diffusion in this alloy was measured using the \(^{63}\)Ni radiotracer. Commercial \(^{63}\)Ni radioisotope purchased as hydrochloric solution was deposited by drying a droplet of a dilute solution at the sample surface. Each sample was wrapped with Cu foil and annealed in a glass ampoule under purified argon atmosphere. The temperature was measured and controlled by certified thermocouples with an accuracy of \(\pm 1\) K. After the annealing treatment all samples were reduced in diameter by grinding in order to eliminate effects of lateral diffusion. The diffusion penetration profiles were determined by the serial-sectioning technique [95] using a precision parallel-grinder with special abrasive Mylar foils having 3, 9 or 12 \(\mu\)m particle size. The section thickness was determined from the density and the mass reduction by weighing the sample after each sectioning on a microbalance with an accuracy of several \(\mu\)g, which translates into the accuracy of about 0.01 \(\mu\)m in thickness measurements. The tracer concentration is proportional to the specific counting rate which is the ratio of the counting rate after background subtraction and the section mass. The \(^{63}\)Ni isotope emits only soft \(\beta\)-radiation. Its radioactivity is collected onto the grinding foils and measured in an appropriate nuclear counting device (Liquid scintillation analyzer TRI-CARB 2500 TR PACKARD, Remcor products Co.). For liquid scintillation counting each grinding foil with the removed material was dissolved in a counting vial in a scintillation cocktail. In this manner, any loss of activity was avoided and equal counting conditions for all sections were provided. The half-life of \(^{63}\)Ni radioisotope is about 100 years, so that no half-life correction was required.
3.2.5. Secondary Ion Mass Spectroscopy (SIMS)

The technique of secondary ion mass spectroscopy (SIMS, Cameca ims-4f) operated in the dynamic mode [96-99] was selected for shallow depth-profiling. Sputtering of \( \mathrm{O}_2^+ \) primary ion beam with the impact energy of 8 keV toward a \( 100 \times 100 \ \mu\text{m}^2 \) crater stimulates secondary ions, which are collected from a field analysis of \( 30 \times 30 \ \mu\text{m}^2 \) at the center. By choosing oxygen as the primary ion beam we suppress surface roughening owing to preferential oxidation of the bottom of the facets formed during sputtering [100, 101]. This process hinders the growth of the facets amplitude and preserves the high depth resolution. The raw output for each element is the number of counts per unit time vs. time. The time scale can be converted into a length scale by measuring the crater depth in a profilometer at the end of sputtering, assuming constant sputtering rate. This method provides a practical detection limit of less than 1 ppm and high depth resolution in the nanometer range, but has poor lateral resolution of the order of tens of microns.

3.2.6. Electron Dispersive Spectroscopy (EDS) in the STEM

The Cu/Ni and Cu-Zr/Ni interfaces were prepared after electrochemical deposition of a thick (30 \( \mu\text{m} \)) layer of Ni on the electrochemically-etched (see section 3.2.1) surface. A thin lamella containing the Cu/Ni interface for TEM observation was cut in the FIB from the bulk diffusion-couple in the lift-out method [102] and thinned by ion milling (see section 3.2.3). The preparation of Cu-Zr/Ni sample was different. A 3 mm-radius semi-circular slice from this interface was cut and ground mechanically to a final thickness of 70 \( \mu\text{m} \), with the Ni layer on its flat side. Further thinning was performed by ion milling in the FIB operated with initial current of 21 nA in the standard cross-section method [102]. The subsequent stages of ion milling were performed with currents reducing down to 48 pA at the final (cleaning) stages. The final thickness of the lamella was about 100 nm.

The chemical analysis of both Cu/Ni and Cu-Zr/Ni interfaces was performed in a Tecnai G\(^2\) T20 S-Twin TEM microscope operated in the STEM mode (STEM resolution <1 nm). The EDS detector (EDS resolution 132 eV) is mounted in a certain angular location with respect to the eucentric position, where the X-ray signal was acquired by tilting the sample by 16° towards the detector to obtain a minimal
background intensity [103, 104]. Measurements were performed at a constant spot size (typically 50 nm) and for constant acquisition times (100 s) enabling the collection of sufficiently intensive signals (at least $10^4$ counts) for a reliable composition analysis [105].

3.2.7. Atomic Force Microscopy (AFM)

The measurements of GB groove dihedral angles were performed by AFM (AutoProbe CP - Park Scientific, USA operated in the contact mode). Scans were done with the CSC11/50 Ultrasharp W$_2$C-coated Si tips with the 50 nm nominal radius of curvature. GB groove profiles taken from the AFM images across the GB grooves and after a routine flattening operation enabled us to calculate the relative values of GB energies. A process for correction of the values of dihedral angles measured by the AFM tip was proposed by us [106], regarding the effect of the finite radius of curvature of the AFM tip. In the present case we did not implement this correction procedure, since we were interested in the general distribution of GB energies only.

3.2.8. Orientation Imaging Microscopy (OIM)

Orientation Imaging Microscopy (OIM) was applied as an auxiliary tool for the interpretation of our main results. The OIM option is part of the TSL-EDXA system for Electron Back-Scattered Diffraction (EBSD), and is mounted on a Sirion high-resolution Scanning Electron Microscope (SEM). The system includes acquisition hardware (DigiView1612 CCD Camera), data collection software, and analytical software for OIM.

3.2.9. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was utilized as a supplementary tool for finding out whether exothermal reactions take place in the samples in the range of working temperatures. DSC scans were performed in the METTLER TOLEDO STAR System with heating rate of 10 ºC/min starting from room temperature up to 300 ºC in an Ar-flow atmosphere. The weight of the samples examined was in the range of several mg.
4. RESULTS

In accordance with the research goals defined in chapter 2, the experimental results are divided into two major sections: measurements of GB diffusivity and GB energy in the Cu-alloys subjected to ECAP. Since the microstructure of samples plays a key role in understanding of the results, the characterization of the samples microstructure subsequent to ECAP (as-pressed) is presented in the 1st section. The following two sections (2nd and 3rd) present the radiotracer diffusion results obtained under the conditions of stable microstructure (Cu-Zr alloy), and in dynamic conditions (pure Cu), respectively. Each section describes microstructure characterization after the annealing processes. The 4th section relates to the measurements of relative GB energy in the Cu samples. Finally, supplementary methods that were applied are introduced in the 5th and 6th sections: EDS analysis of the diffusion profile and DSC analysis of the as-deformed material, respectively.

4.1. Microstructure Characterization: as-pressed specimens

Both pure Cu (99.98% wt.) and Cu-Zr (Cu-0.17 wt.% Zr) samples were processed according to the ECAP B4 route. Their microstructures were characterized mainly by SEM and TEM after the procedure of sample preparation detailed in section 3.2.

4.1.1. The Cu-Zr specimens

According to the binary Cu-Zr phase diagram (Fig. 3.1) the maximum amount of Cu5Zr precipitates in the Cu-0.17 wt.% Zr alloy equilibrated at room temperature is about 0.8 wt. %, which is slightly below the detection limit of X-ray phase analysis. SEM images of the sample surface after polishing and electrochemical etching indicate the presence of large (~5 μm in diameter) spherical precipitates and of lamellar colonies of Zr-rich phase (see Fig. 4.1). The spherical shape of individual precipitates is probably a result of the electrochemical etching. EDS analysis of these precipitates confirms the expected stoichiometric composition of Cu5Zr. Estimation of the Cu5Zr precipitates volume fraction using the SEM micrographs indicated that approximately 0.05 wt. % of Zr are bound within these precipitates. The remaining 0.13 wt. % of Zr are either homogeneously dissolved in the Cu matrix or bound in fine precipitates whose size is below the resolution limit of SEM.
Fig. 4.1: SEM micrograph of the surface of etched as-pressed Cu-Zr alloy showing the distribution of precipitates (a). The round shaped precipitates (b) have the stoichiometric composition of Cu₅Zr.

SIMS analysis was implemented in the dynamic mode for in-depth chemical analysis. A 100×100 µm² crater was sputtered by an O₂⁺ primary ion in the conditions detailed in section 3.2.5. The signal of secondary ions was collected from the regions that do not contain large Cu₅Zr precipitates, as shown in Fig. 4.1. The isotopes detected are ⁶³Cu and ⁹³Zr, which are 70% and 17% of the total Cu and Zr isotopes, respectively. SIMS analysis revealed homogeneous distribution of Zr in Cu matrix up to the depth of 4 µm, measured with depth steps of 70 nm. The calculation of Zr content was done considering the frequency of these isotopes as well as the relative sensitivity factor of Zr within a Cu matrix. Regarding the level of accuracy common in such assessments (factor of 3-5), the bulk content of Zr is in the range of 0.1-0.4 % at.

Bright-field (BF) TEM images taken from this sample indicated equiaxed grain morphology with an average grain size of about 300 nm, see Fig. 4.2.
Fig. 4.2. A BF TEM micrograph of the Cu-Zr alloy after 4 ECAP passes.

It can be seen in Fig. 4.2 that the interior of the grains is abundant of densely-spaced dislocations and misfitting defects, presumably ultrafine Cu$_2$Zr precipitates. Figure 4.3 is a BF TEM image showing the interior of one grain, together with a SAED pattern acquired from the same region.

Fig. 4.3: A BF TEM micrograph and a corresponding SAED pattern showing the distribution of misfitting Cu$_2$Zr precipitates within an individual Cu grain.
The SAED pattern exhibits a set of point reflections characteristic of Cu-[011] zone axis, together with rings that correspond to the Cu₅Zr phase. These rings indicate a certain spread of the orientations of the Cu₅Zr precipitates in the Cu matrix.

4.1.2. The Cu specimens

The main characteristic of microstructure observed in the pure Cu samples is the existence of both regions of elongated grains (200-300 nm in width and several microns in length) as well as equiaxed grains (about 300 nm grain size). Fig. 4.4 shows a typical region of elongated grains. SAED pattern taken from this region indicates that all grains are very closely-misoriented with respect to each other, with the common [011] zone axis. This implies that all grains here are sub-grains or cells formed during the ECAP processing.

![SAED pattern from a typical region of elongated grains.](image)

Fig. 4.4: A region in the Bc4 sample with closely-misoriented, elongated grains with the common [011] zone axis.

Fig. 4.5 shows another region with more homogeneous microstructure. The ring-shaped diffraction pattern taken from this region indicates high misorientations between the grains. The difference between these two microstructures demonstrates the inhomogeneity obtained after only 4 ECAP cycles, which is supposed to improve with more ECAP passes.
A closer look at the GBs reveals that many GBs are associated with the long-range strain fields. Figure 4.6 shows these highly-strained GBs (a) and (b). The initial stages of sub-grain formation within a large grain can be seen in (a). It can also be inferred that the strain fields exerted from GBs extend to a range of 20-30 nm from each side of the boundary, in agreement with models and previous observations reported in the literature [6, 47].

Fig. 4.6: Highly-strained GBs identified by their distortion contours appear in (a) and (b). The initial stages of sub-cell division can be seen within the large grain in (a).
4.2. Diffusion in thermally-stable microstructure: Cu-Zr alloy

The Cu-0.17% wt. Zr alloy was selected in order to maintain thermal stability during diffusion annealings. This section presents the data from diffusion experiments performed with this thermally-stable alloy.

4.2.1. Characterization of the diffusion-annealed specimens microstructure

Apart from the diffusion-annealed samples containing the radiotracer, we performed the same heat treatments as listed in Table 3.1 for other samples without radiotracer. This enabled us observing the microstructure evolution of samples during the applied diffusion-annealing processes. The microstructure of several representative samples was studied by TEM and FIB. Figure 4.7 shows two examples of the Cu-Zr microstructures obtained after 13 h annealing at 220 °C (a), and after 5 h annealing at 240 °C (b).

![FIB micrograph of the ECAP-processed Cu-Zr alloy after annealing at 220 °C for 13 h (a) and at 240 °C for 5 h (b).](image)

It was found that no recrystallization or grain growth occurred in the samples investigated up to the highest temperature used in this study. Regarding processes driven by GB diffusion, it can be maintained that all of the diffusion-annealing conditions appearing at Table 3.1 are equivalent, since they yield the same value of $\sqrt{D_jt}$ (several µm). The Cu-Zr samples annealed at 400 °C for 2 h were also characterized in FIB and exhibited the same UFG microstructure as shown in Fig. 4.7. The value of $\sqrt{D_jt}$ corresponding to this annealing is about 7 times larger than for other
annealings at lower temperatures. The onset of grain growth was observed in this Cu-Zr alloy only after 2h annealing at 450 °C.

4.2.2. The complete set of Ni-radiotracer diffusion profiles

The acquisition of the $^{63}$Ni activity depth-profile was performed according to the procedure detailed in section 3.2.4. The specific conditions of grinding time, grinding papers, weight applied etc. were determined so that the optimal relationship between depth resolution (weight/thickness of one section) and detectability (total activity per one section) are obtained. All results were presented as specific activity (counts per second, Bq, normalized by section weight), and after the subtraction of background activity (~ 0.18 Bq). Figure 4.8 shows the complete set of diffusion profiles collected from the Cu-Zr alloy.

![Diagram showing specific activity vs. penetration depth profiles](image)

Fig. 4.8: A full set of "specific activity vs. penetration depth" profiles measured in the Cu-Zr alloy. $k$ is a scaling factor assigned individually to each profile.
The temperatures of diffusion annealing are specified in Fig. 4.8. The corresponding annealing times are given in Table 3.1. It can be seen that all profiles extend over the depths of 20-60 µm.

4.2.3. Bimodality of diffusion profiles

Most of the measured diffusion profiles exhibited two distinct sections with large and small slopes corresponding to slow and fast GB diffusion, respectively. This bimodality can be seen in all profiles, except the one measured after annealing at 350 ºC, where only the "slow" part was observed because of a large penetration depth. Typical diffusion profile (5 h at 240 ºC) is shown in Fig. 4.9.

![Graph](image)

**Fig. 4.9:** The dependence of $^{65}$Ni specific activity on the penetration depth in the ECAP-processed Cu-Zr alloy annealed at 240 ºC for 5 h (open circles). The reference ("zero") profile obtained for the same conditions without diffusion annealing is also shown (filled circles).

In this profile, the first three points closest to the surface should be disregarded since they are associated with the remnant activity of the deposited radioisotope layer. The classical solution of the diffusion equation for one-dimensional diffusion along the $x$-axis into a semi-infinite body from an instantaneous source is given by Eq. (3.5). It follows from Eq. (3.5) that the GB diffusivity, $D_b$, can be determined from the experimentally measured diffusion profile, $\bar{C}(x)$, according to:
Both "slow" and "fast" parts of the diffusion profile in Fig. 4.9 are nearly linear when plotted in $\ln C$ vs. $x^2$ co-ordinates. In a simplest approximation of independent diffusion along the "slow" and "fast" diffusion paths, the corresponding diffusion coefficients can be extracted independently from the respective sections of the penetration profile using Eq. (4.1). However, to be truly independent, the "fast" and "slow" diffusion paths should be completely separated from each other, which is an extremely unlikely possibility in the UFG samples obtained by ECAP. The complete mathematical treatment in this diffusion problem requires further interpretation and will be introduced in chapter 5, where both slow and fast diffusion coefficients will be derived from the profiles.

To verify whether the serial mechanical sectioning technique employed in this study can cause a significant distortion of radiotracer distribution in the sample after annealing, we varied the parameters of serial sectioning (grinding speed, time of one section, particles size of the grinding paper, and applied weight) for several samples annealed in identical conditions. The resulting variation in penetration profiles was within the experimental error in activity measurements.

On the other hand, the applied grinding procedure may cause a "smearing" of the real profile due to constantly grinding-in a part of the radioactive material from a current layer into the next section. To quantify this effect we prepared a reference sample by depositing a thin Ni layer on the surface of ECAP-processed sample of pure Cu, and annealed it for a short time (<1 min.) at 200 °C in order to enable partial dissolution of radiotracer. The activity profile in the reference sample was measured using the same procedure as for Cu-Zr samples, and the result is shown in Fig. 4.9 as "zero" profile. Apart from having considerably lower intensity, the zero profile exhibits significantly larger slopes than the "fast" diffusion part of the actual penetration profile. Comparison between both profiles is a basis for quantitative analysis of the effect of mechanical sectioning on concentration distribution, and it will be discussed in chapter 5.
In summary, the bimodality in diffusion profiles indicate the existence of two GB populations. The fast-diffusion paths are, supposingly, the non-equilibrium GBs. This claim, however, needs a quantitative verification.

4.3. Diffusion under dynamic conditions: pure Cu

As shown above (section 4.2.1), the Cu-Zr alloy demonstrated microstructure stability in the whole range of thermal annealing employed in this study. However, in order to examine the effect of GB relaxation and recrystallization on the diffusion profiles, the same diffusion experiments were performed with pure Cu (99.98% wt.) samples. The results of diffusion experiments and microstructure observations are given in this section.

4.3.1. Characterization of the diffusion-annealed specimens microstructure

The annealings and microstructure observations of the Cu samples were performed in the same way as described in section 4.2.1. For the sake of comparison with the Cu-Zr samples, Fig. 4.10 shows FIB images of the Cu microstructures obtained after 13 h annealing at 220 ºC (a), and after 5 h annealing at 240 ºC (b).

![FIB micrographs of the ECAP-processed pure Cu after annealing at 220 ºC for 13 h (a) and at 240 ºC for 5 h (b).](image)

Fig. 4.10: FIB micrographs of the ECAP-processed pure Cu after annealing at 220 ºC for 13 h (a) and at 240 ºC for 5 h (b).

The microstructures shown in Fig. 4.10 indicate an almost complete recrystallization occurring by the end of diffusion annealing. The average grain size obtained after recrystallization is several µm. Other samples annealed at different time/temperature
conditions exhibited only partial recrystallization. It is obvious that the dynamic processes occurring in the Cu samples should influence their diffusion behavior.

4.3.2. The complete set of Ni-radiotracer diffusion profiles

The complete set of diffusion profiles acquired from the Cu samples at the same experimental conditions as for Cu-Zr alloy (see section 4.2.2) is presented in Fig. 4.11. The same annealing conditions as for Cu-Zr alloy were employed, with the only difference that diffusion experiments have not been performed at the temperature of 350 °C. Figure 4.11 presents the measured penetration profiles in the full range of penetration depths. Like in the case of Cu-Zr, these penetration profiles exhibit slow and fast sections with different slopes.

Fig. 4.11: A full set of "specific activity vs. penetration depth" profiles measured in pure Cu. \( k \) is a scaling factor assigned individually to each profile.
In Fig. 4.11 the slow-diffusion parts of the penetration profiles cannot be well-distinguished. Fig. 4.12 focuses on the initial parts of these profiles.

4.3.3. Bimodality of diffusion profiles

For a better illustration of the bimodal behavior of the penetration profiles collected from the Cu samples, an individual semi-logarithmic "activity vs. $x^2$" penetration profile is shown in Fig. 4.13. For the sake of comparison, the profile in Fig. 4.13 is presented together with its counterpart acquired in the Cu-Zr alloy, both in the same conditions of 5 h annealing at 240 ºC. Again, disregarding the first 2-3 points due to residual surface activity, the difference between two diffusion profiles is clearly seen in Fig. 4.13. In particular, at large penetration depths the activities measured in Cu-Zr alloy are higher than those measured in Cu. This may be associated with the better thermal stability of Cu-Zr alloy.

Fig. 4.12: A full set of specific activity measured in the Cu samples plotted in the same manner as in Fig. 4.11, but for smaller penetration depths. $k$ is a scaling factor assigned individually to each profile.
It was concluded in section 4.3.1 that recrystallization occurs during diffusion annealings in all studied Cu samples. In this case, the derivation of diffusion coefficients from the profiles shown in Figs. 4.11 and 4.12 is not straightforward. In order to enable extracting the diffusivities from the penetration profiles acquired during recrystallization process, the kinetics of recrystallization should first be determined.

In this section the recrystallization kinetics will be determined from the observed microstructures of the samples. A common expression for the kinetics of phase transformation or, in particular, recrystallization is the JMAK equation [107]:

$$\lambda(t) = e^{-Br^n}$$

(4.2)

where $\lambda(t)$ is the time-dependent volume fraction of the initial (non-recrystallized) phase, $B$ is a temperature-dependent parameter, and $n$ is a constant. The annealing temperatures and times of the samples that were investigated in FIB are presented in Table 4.1.

Fig. 4.13: The dependence of $^{63}$Ni specific activity on the penetration depth in the ECAP-processed Cu (open squares) and Cu-Zr (filled squares) alloys annealed at 240 °C for 5 h.

4.3.4. Characterization of the recrystallization kinetics

It was concluded in section 4.3.1 that recrystallization occurs during diffusion annealings in all studied Cu samples. In this case, the derivation of diffusion coefficients from the profiles shown in Figs. 4.11 and 4.12 is not straightforward. In order to enable extracting the diffusivities from the penetration profiles acquired during recrystallization process, the kinetics of recrystallization should first be determined.

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$$\lambda(t) = e^{-Br^n}$$

(4.2)

where $\lambda(t)$ is the time-dependent volume fraction of the initial (non-recrystallized) phase, $B$ is a temperature-dependent parameter, and $n$ is a constant. The annealing temperatures and times of the samples that were investigated in FIB are presented in Table 4.1.
The examples of partly recrystallized microstructures are presented in Fig. 4.14. It can be seen in Fig. 4.14 that the recrystallized phase appears as islands of large grains within the UFG matrix. The volume fraction of the recrystallized phase increases with time. In this particular case (220 ºC) almost 100% recrystallization is

<table>
<thead>
<tr>
<th>Temperature [ ºC ]</th>
<th>Time [h]</th>
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<tr>
<td>150</td>
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</tr>
<tr>
<td>184</td>
<td>79</td>
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<tr>
<td>240</td>
<td>1, 2, 3, 4, 5</td>
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Table 4.1: The conditions of heat treatments for ECAP-Cu samples.

Fig. 4.14: FIB micrographs of the microstructure evolved during annealing of the ECAP-processed Cu at 220 ºC for 1, 3, 4, and 5 h.

It can be seen in Fig. 4.14 that the recrystallized phase appears as islands of large grains within the UFG matrix. The volume fraction of the recrystallized phase increases with time. In this particular case (220 ºC) almost 100% recrystallization is
attained by the end of the diffusion annealing (13 h, as shown in Fig. 4.10 a). At lower temperatures the samples are only partly recrystallized at the end of diffusion annealing.

The fraction of recrystallized copper, $1 - \lambda$, was measured by counting the nodes in a standard transparent grid that intersect this phase, and normalizing this number by the total number of nodes in the grid. All data points were fitted to the general JMAK expression (4.2). The latter can be introduced in the following linearized form:

$$\ln\left(\ln\frac{1}{\lambda}\right) = \ln B + n \cdot \ln t$$

(4.3)

The coefficient $n$ was calculated by plotting the parameter $\ln\left(\ln\frac{1}{\lambda}\right)$ against time logarithm at constant temperature of annealing (while $B$ is constant). The corresponding data obtained after annealing at 220 °C for various annealing times (see Table 4.1) are shown in Fig. 4.15.

![Fig. 4.15: A plot of the linearized relationship between the recrystallization fraction and time given by Eq. (4.3) for the constant temperature of 220 °C.](image)

The parameter $n$ derived from the linear least square fit of experimental data in Fig. 4.15 is: $n = 1.14 \pm 0.21$. The complete time and temperature dependent kinetic
expression can be obtained by substituting the explicit Arrhenius form of $B$ in Eq. (4.3), including the pre-exponential term $B_0$ and the activation enthalpy for recrystallization, $Q$. The new linearized form is given by Eq. (4.4).

\[
\ln \left( \ln \frac{1}{\lambda} \right) - n \cdot \ln t = \ln B_0 - \frac{Q}{RT}
\]  

(4.4)

Plotting the left hand side term in Eq. (4.4) against reciprocal temperature yields the parameters $B_0$ and $Q/R$. The values of $\lambda$ for all annealings (see Table 4.1) plotted in the corresponding co-ordinates of Eq. (4.4) are shown in Fig. 4.16.

![Fig. 4.16: A plot of the linearized relationship between the recrystallization fraction, time and temperature given by Eq. (4.4).](image)

The activation enthalpy for recrystallization derived from the linear least square fit of the data of Fig. 4.16 is $Q = 162\pm10$ kJ/mol. The parameter $B_0$ was also determined from this plot. Thus, the explicit JMAK expression describing the kinetics of recrystallization was obtained:

\[
\lambda(t) = \exp \left( -\exp \left( 38 \pm 2 - \frac{162 \pm 10 \text{ kJ/mole}}{RT} \right) t^{1.14\pm0.21} \right)
\]  

(4.5)
where the units of $t$, $R$, and $T$ are: [h], [kJ·mole$^{-1}$·K$^{-1}$], and [K], respectively. This explicit expression enables the extraction of diffusion coefficients from the diffusion profiles shown in section 4.3.2, as will be described later on.

### 4.3.5. The effect of pre-annealing

The bimodal behavior of diffusion profiles indicates the existence of two distinct GB populations. We suppose that the fast-diffusion GBs are in the non-equilibrium state. This statement has yet to be quantitatively proven. However, it can be examined by comparing the diffusion profiles acquired at two different conditions. The first one is the usual procedure of Ni deposition on the as-pressed samples and diffusion annealing ("as-pressed"); The second is annealing of the as-pressed samples at elevated temperatures prior to Ni deposition and diffusion annealing ("pre-annealed"). We expect that the fast-diffusion part of profiles should vanish or, at least, be reduced as a result of pre-annealing due to relaxation of the metastable GBs. This should allow linking the fast-diffusion profiles with non-equilibrium GBs.

The pre-annealing was performed at 300 °C for 2h. An example of the microstructure observed after such heat treatment is shown in Fig. 4.17.

![Fig. 4.17: A FIB micrograph of the microstructure of the ECAP-ed Cu observed after annealing at 300 °C for 2 h.](image)

Fig. 4.18 presents two activity profiles acquired in the "as-pressed" and "pre-annealed" samples. The diffusion annealings were performed at identical conditions of 240 °C, 5h.
The expected decrease in the activity in the pre-annealed Cu is clearly seen in the fast-diffusion part of profile, while the slow-diffusion parts of both profiles are almost identical. Such a decrease might be associated with the coarser microstructure of the pre-annealed samples having smaller fraction of internal interfaces. However, comparison between the microstructures attained after 240 °C, 5h and 300 °C, 2h (Figs. 4.10 (b) and 4.17, respectively) indicates no significant difference in grain sizes. This cannot account for 1 order of magnitude difference in activity profiles. Full or partial relaxation of the non-equilibrium GBs during the pre-annealing process may explain such behavior.

4.3.6. SIMS depth-profiling

Most of the penetration profiles of $^{63}$Ni in both Cu and Cu-Zr samples exhibited bimodal behavior. The shallow part was associated with slow-diffusion paths, while the deeper part was associated with fast-diffusion paths. The applied technique of serial sectioning by grinding (section 3.2.4) offers an optimal depth-resolution of 0.6-1 µm, while the shallow and deep parts of profiles extend over the ranges of about 10 µm and

Fig. 4.18: The dependence of $^{63}$Ni specific activity on the penetration depth ECAP-Cu at different initial states: as-pressed (filled circles) and pre-annealed at 300 °C for 2h (open squares). The conditions of diffusion annealing: 240 °C, 5 h.
50 \mu m, respectively. Therefore, it is desirable to apply a supplementary technique in order to obtain better resolution of the shallow parts of some representative profiles.

For this purpose, SIMS analysis was performed in the dynamic mode to obtain depth profiles of the diffusion-annealed specimens. The conditions of operating and data acquisition were detailed in section 3.2.5. The samples for SIMS diffusion studies were prepared by magnetron sputtering of a 20-30 nm thick layer of Ni on the mechanically and electrochemically polished surface of the same Cu samples that were employed in radiotracer diffusion studies (section 4.3). After a series of preliminary experiments and measurements it was established that only the data obtained with sputtering rates higher than 0.3 nm/s and collected from the depths above 0.3 \mu m represent the true results of diffusion intermixing. The data acquired at lower sputtering rates suffer from the effects of forward intermixing, while the data collected too close to the surface may be affected by the surface faceting.

Based on preliminary data on GB diffusion of Ni in Cu [84], the conditions of time and temperature for diffusion annealing were selected so that the diffusion length should be in the range of 0.1-1 \mu m. The samples were annealed for 1 h at the temperatures of 160 °C, 200 °C, and 230 °C. Figure 4.19 shows the diffusion profiles of Ni measured after these annealings. The vertical axis represents the intensity of Ni secondary ions signal, multiplied by an arbitrary scaling factor selected for better presentation. The horizontal scale is the square of the penetration co-ordinate, x, multiplied by a scaling factor k. Since no recrystallization is expected under these annealing conditions (see section 4.3.4), the values of diffusion coefficients can be simply derived from each profile according to Eq. (4.1).

It can be seen that in contrast with the profiles acquired by the radiotracer serial-sectioning technique, the profiles shown in Fig. 4.19 exhibit only one slope, from which only one diffusion coefficient can be derived. The values of diffusivity derived from the profiles are: 4.70 \cdot 10^{-18}, 4.33 \cdot 10^{-17}, and 9.43 \cdot 10^{-17} m^2/s for the temperatures of 160 °C, 200 °C, and 230 °C, respectively. The reason for difference in the penetration profiles obtained in radiotracer experiments and in SIMS will be discussed in the following chapter.
4.4. Measurements of relative GB energy

This section presents the results of measurements of the relative GB energies of two sets of samples denoted as class 1 and class 2 in section 3.1.4. The main results include characterization of the microstructure obtained after both heat treatments, representative profiles of GB grooves, and statistical data on the geometrical degrees of freedom of GBs and individual grains collected from both sets of samples.

4.4.1. Thermal grooving after two different annealings

In this section we will distinguish between three states of the investigated samples. The first one is the as-pressed state obtained after B₄ ECAP of the pure Cu. Its UFG microstructure can be characterized by an average grain size of 300 nm (see section 4.1.2). The second one is attained after a short-time annealing of the as-pressed samples at 400 °C for 15 min, denoted as class 1. Based on rough estimates of the relaxation time of GBs, it is supposed that no considerable relaxation of the GB energy...
in class 1 samples occurred, in spite of the grain growth observed after this annealing. This point should be elaborated in the following chapter. An example for the microstructure observed in class 1 samples is shown in the topographic image acquired by AFM operated in the contact mode, Fig. 4.20.

The good topographic contrast of the AFM image enables one to distinguish the GBs as dark grooves. This implies that such conditions of relatively low temperature and short annealing time were sufficient for measurable GB grooving. The average grain size measured from the AFM images is about 3 µm.

The third state investigated in this section was obtained after annealing of the as-pressed samples at 800 ºC for 2 h, denoted as class 2. Based on the same estimation of the relaxation time of GBs, it is supposed that almost complete relaxation of the non equilibrium GBs occurred in the samples of class 2. Optical microscopy observations of microstructure indicate a significant grain growth. The average grain size in these samples is 100 µm.
4.4.2. Relative GB energy distribution

Scanning of selected GB grooves was performed by AFM, with the fast scanning direction normal to the groove. A topographic image was obtained for each GB groove, and the dihedral angle ($\psi$) was determined from representative linear topography profiles taken across the groove. This analysis was performed for both sets of samples. Representative topography images taken from the vicinity of GB grooves in both samples of class 1 and 2 are presented in Figs. 4.21 and 4.22, respectively. Each of these figures includes a line topography profile taken across the GB groove, from which the angle $\psi$ was measured.

Fig. 4.21: An AFM topographic image showing the vicinity of the GB groove in the class 1 samples (a), together with a representative line profile across the GB groove and the mean dihedral angle of 151° (b). The apparently small dihedral angle is due to the overblown scale of the vertical axis.
It can be seen that the GB groove depth and width attained after 800 ºC annealing for 2 h (class 2) are larger than after 400 ºC, 15 min. annealing (class 1). Furthermore, the dimensions of GB groove obtained after relatively low temperature and short annealing time in class 1 samples (depth ≈ 60 nm, width ≈ 0.8 µm) are large enough for AFM scanning, so that there is no need in introducing corrections for finite AFM tip radius \[30\].

The groove dihedral angles for class 1 and 2 samples are 151° and 165°, respectively. The corresponding values of relative GB energy \(\gamma_{rel}\) calculated according to Eq. (3.11) are 0.50 and 0.26, respectively. This indicates that GB energy in the class 1 samples, which are close to the "as-deformed" copper, is significantly higher than GB energy in the class 2 samples, i.e. in the relaxed state. The difference in energy is by a factor of 1.9.

Fig. 4.22: An AFM topographic image showing the vicinity of the GB groove in the class 2 samples \(a\), together with a representative line profile across the GB groove and the mean dihedral angle of 165° \(b\). The apparently small dihedral angle is due to the overblown scale of the vertical axis.
In order to obtain a statistically-reliable information, a total number of 30 randomly-selected GB grooves were examined in each set of samples. Thus, the set of 30 $\psi$ -values was transformed into a set of $\gamma_{rel}$ -values, and plotted in a histogram denoting the number of GBs that fall into a given $\gamma_{rel}$ - interval. The magnitude of the interval was determined as $1/30$. These data are plotted in Fig. 4.23.

A clear distinction between both sets of data can be observed in Fig. 4.23: The $\gamma_{rel}$ -values measured in the samples of class 1 are shifted toward higher energies if compared with the samples of class 2. The averaged values of relative GB energy are: $0.48 \pm 0.11$, and: $0.27 \pm 0.07$, respectively. Both energy distributions overlap in the range of 0.25-0.4. In summary, the relative GB energy measured in a state close to the "as-deformed" is about twice as high as in the relaxed state. This statement will be substantiated in the following chapter.

![Histogram showing the distribution of GB energies, $\gamma_{rel}$](image)

Fig. 4.23: A histogram showing the distribution of GB energies, $\gamma_{rel}$. The $\gamma_{rel}$ -values measured in the class 1 samples (red bars) are concentrated at higher energies than those measured in the class 2 samples (green bars).
4.4.3. OIM characterization of surface texture

Since the expression for relative GB energy introduced by Eq. (3.11) incorporates surface energy, it is important to compare the surface textures of both samples classes. For this purpose, several OIM images (see section 3.2.8) containing a few dozens of grains were collected from both sets of samples. The orientation of each point scanned in the EBSD was determined with respect to a fixed reference system, and the resolution (point-to-point distance) was determined in accordance with the grain size of each image. Thus, a map of the local lattice vectors normal to the surface was drawn for each of the class 1 and 2 samples. Figure 4.24 presents these OIM results, in which the color-coded normal vectors are indexed according to the standard stereographic triangle.

Fig. 4.24: Color-coded maps of the representative surface textures of both sets of samples: class 1 (a) and class 2 (b), collected by OIM. The local normal vectors are indexed according to the standard stereographic triangle (c).
It can be seen from the comparison of both images shown in Fig. 4.24 (a) and (b) that the general surface texture in class 1 samples is closer to \( \langle 011 \rangle \), while the general surface texture in class 2 samples is closer to \( \langle 111 \rangle \). This difference in textures may affect the conclusion drawn in section 4.4.2 concerning the link between \( \gamma_{rel} \) and relaxation of GBs.

### 4.4.4. OIM characterization of GB character distribution

The relative GB energies measured by thermal grooving technique in the class 1 samples were significantly higher than in the relaxed state. Although these GB grooves were selected randomly for AFM analysis, this difference in energies might be associated with a change in the crystallographic character of GB population rather than to relaxation of the non-equilibrium GBs. For example, it is expected that an increase in the population of low-\( \Sigma \) CSL boundaries, in particular the \( \Sigma 3 \) boundaries, will result in a decrease of the average GB energy (see section 2.4.1). Therefore, it is important to collect data on the GB character distribution from the samples of both classes. For this purpose, OIM scans were performed, and the misorientations between all pairs of points was determined.

![Color-coded maps of the distribution of GB misorientations (according to the value of \( \Sigma \)) in both sets of samples: class 1 (a) and class 2 (b), collected by OIM.](image)

Fig. 4.25: Color-coded maps of the distribution of GB misorientations (according to the value of \( \Sigma \)) in both sets of samples: class 1 (a) and class 2 (b), collected by OIM.
Thus, a map that indicates quantitatively the changes in misorientations (GBs) was obtained for each sample. Figure 4.25 presents the OIM results showing the GBs indexed according to their Σ-values. Figure 4.25 clearly demonstrates that the fraction of the Σ3 boundaries in class 1 samples is higher than in class 2 samples. The same trend is observed for the other groups of low-Σ boundaries. A quantitative estimate of this difference was obtained by counting the pairs of points in the OIM image exhibiting a certain misorientation angle. The resulted fraction of GBs that possess a given misorientation angle is a weighted value of the number fraction of GBs and their total lengths. It was found that the ratio between the fraction of Σ3-boundaries in the samples annealed at 400 °C and at 800 °C is about 3.

4.4.5. GB grooving observed after ion sputtering in SIMS

One of the major factors stimulating the penetration of Ni inside the bulk Cu during SIMS measurements is surface roughening induced by ion sputtering. The formation of facets and roughened morphology is a known phenomenon and is one of the limiting factors in depth resolution of SIMS. Therefore, characterizing the extent of surface roughening can help us to determine the depth resolution.

For this purpose, pure Cu samples subjected to ECAP were prepared according to the same procedure as detailed in section 4.3.6, including Ni-deposition. This diffusion couple was annealed at 180 °C for 1 h. The subsequent procedure of depth profiling by SIMS (on the surface covered with Ni) formed a 200×200 μm² crater on the surface cleaned from residual Ni. The interior of this crater was scanned by AFM to obtain topography images. These AFM images exhibited the polycrystalline morphology with grain size of 200-300 nm, which is comparable with that observed by TEM (section 4.1.2). The RMS roughness measured is about 70 nm, and this can be determined as the SIMS depth resolution for the present Cu samples. Figure 4.26 presents an example for this morphology (a). A higher magnification scan reveals the shape of GB grooves formed as a result of ion bombardment (b), presumably in a mechanism similar to one of the Mullins grooving mechanisms. An interesting feature shown in this image is the hierarchic microstructure of large grains marked by deep channels, divided into subcells marked by shallow channels.
Fig. 4.26: An AFM image taken from the interior of SIMS crater showing UFG polycrystalline morphology (a). Focusing on one of the regions (b) reveals the hierarchic microstructure of large grains marked by deep channels, divided into subcells marked by shallow channels.
Representative topography line scans within these high-magnification AFM images were extracted in order to investigate the shape of the grooves. They clearly indicate the cross section of GB grooves typical to the usual thermally-grooved GBs. The corresponding dihedral angles were measured from these line scans. Their values follow a bimodal distribution: the angles measured at the bottom of the deep grooves are smaller than the angles measured at the bottom of the shallow grooves. An example for such profile is shown in Fig. 4.27.

![AFM topography line-profile](image)

**Fig. 4.27:** An AFM topography line-profile taken across the GB groove shown in Fig. 4.26 (b). Two secondary high-angle (low-energy) grooves appear near the primary low-angle (high-energy) one.

In this example, the corresponding values of relative GB energy were calculated according to Eq. (3.11): the primary groove corresponds to high-energy GBs with $\gamma_{rel} = 1.06$, and the secondary grooves correspond to low-energy GBs with $\gamma_{rel} = 0.27$ and 0.19. These findings are consistent with the other results that have been reported above, including GB energy and GB diffusion, and will be discussed in the following chapter.
4.5. EDS profiling in the STEM

This section presents the results obtained from EDS microanalysis performed in the vicinity of the diffusion-annealed Cu/Ni and Cu-Zr/Ni interfaces. The purpose of this investigation is to provide additional information about the distribution of Ni along GBs, and to detect whether such distribution varies at different GBs.

4.5.1. EDS microanalysis across the Cu/Ni interface

In the present experiment the Cu/Ni couple was annealed at 190 °C for 1 h. The procedure of sample preparation for TEM observation, employing the lift-out method in the FIB was detailed in section 3.2.6. A typical micrograph of the Cu/Ni interface taken during the preparation procedure is shown in Fig. 4.28.

Fig. 4.28: FIB image of the Cu/Ni interface (a). The red rectangle marks the area from which the TEM specimen was cut. The further procedure includes the formation of the lamella by ion milling (b) and lift-out (c).
The Cu/Ni interface in Fig. 4.28 (a) seems sharp and clean, within the limitations of FIB spatial resolution. The grains of Cu, even after 4 ECAP passes, are elongated diagonally with respect to the interface and not completely equiaxed. The grains in Ni layer are elongated normally to the interface, with their small diameter being commensurate with grain size of copper substrate. The following process of TEM specimen preparation comprises ion-milling to expose a 15×15 µm² slice (Fig. 4.28 b), cutting the slice, thinning, and placing it on a holder (Fig. 4.28 c).

The final thickness of slice obtained by ion milling in the FIB was about 100 nm. No additional thinning was performed in order to get an adequately intense X-ray signal during the subsequent EDS microanalysis. Fig. 4.29 shows a fragment from the Ni/Cu interface acquired in the STEM at BF conditions.

![Fig. 4.29: A BF image taken in STEM showing the interface between Ni and UFG-Cu.](image)

Elemental microanalysis was carried out by EDS as detailed in section 3.2.6 within a region having constant thickness. This was validated by electron energy-loss spectroscopy (EELS) line-profile taken from the analyzed region [105]. The intensity of both Ni and Cu Kα-peaks was collected from squares of equal dimension at equal times. Two profiles were measured: the one was taken along a GB common to Ni and Cu. The other was taken from a bulk region, normal to the Ni/Cu interface. The error
of measurements was determined as three times the square root of number of counts, according to Poisson's distribution. The profiles are shown in Fig. 4.30.

Fig. 4.30: Ni and Cu $K\alpha$ intensity measured at different positions along the GB and in the bulk cross-section.

It can be seen that both profiles of Ni in Cu taken from the GB and from the bulk are identical within the experimental error. The following main reasons for the failure to see the GB diffusion were examined:

- Migration of GBs during the diffusion annealing causes a uniform distribution of the solute near the interface. This can be checked by utilizing the thermally-stable Cu-Zr alloy.

- Inherent broadening of the electron beam within the slice. In fact, better spatial resolution can be obtained when a thinner sample is probed; however, this involves a loss of signal and the quantification accuracy deteriorates [105]. This effect, if exists, can be minimized by extending the diffusion profile (increasing the annealing time or temperature).

- The concentration profile observed at the vicinity of the Ni/Cu interface can be attributed to physical deposition of material from the one side of interface onto the other due to the ion-milling process.
In any case, the values of diffusivities corresponding to the profiles shown in Fig. 4.30 were calculated for comparison with the results of other measurements. The suitable solution of the diffusion equation is given by Eq. (3.4), which has a more practical form valid in this case:

\[ I(x,t) = I_0 + (I_\infty - I_0) \cdot \text{erf} \left( \frac{\pm x}{2\sqrt{Dt}} \right) \]  

(4.6)

where \( I \) denotes the X-ray intensity collected at given time interval (\( I_0 \) - at the interface; \( I_\infty \) - far away from the interface). The diffusion coefficients were derived from the linearized form of Eq. (4.6):

\[ \text{erf}^{-1} \left( \frac{I-I_0}{I_\infty-I_0} \right) = \frac{\pm x}{2\sqrt{Dt}} \]  

(4.7)

using the data presented in Fig. 4.30. The values calculated are: \( D_{\text{Ni}} = (8.3 \pm 0.7) \cdot 10^{-18} \text{ m}^2 / \text{s} \) and \( D_{\text{Cu}} = (5.7 \pm 0.3) \cdot 10^{-19} \text{ m}^2 / \text{s} \) for diffusion of Ni in Cu and of Cu in Ni, respectively. It should be noted that these values denote the weighted contribution of bulk, defects, GBs, and GB migration to the overall diffusion process.

4.5.2. EDS microanalysis across the Cu-Zr/Ni interface

In the present experiment the Cu-Zr/Ni couple was annealed at 240 °C for 5 h. The samples for TEM observation were prepared using the cross-section method, as detailed in section 3.2.6. The reasons for selecting these experimental conditions, which are different from those introduced above (section 4.5.1), are the following:

- The thermal stability of the Cu-Zr alloy is supposed to avoid GB migration.
- Annealing at 240 °C for 5 h yields deeper profile, thus diminishing the effect of electron beam broadening.
- Applying the the cross-section method enables achieving larger samples, therefore analyzing deeper profiles.

A typical micrograph of the Cu/Ni interface taken during the preparation procedure is shown in Fig. 4.31.
The subsequent procedure including thinning to a 100 nm thick lamella, STEM observation and EDS microanalysis was similar to the one described above (section 4.5.1). In the present case, one profile was taken from the Cu-Zr region along a GB fragment intersecting the Cu-Zr/Ni interface. Figure 4.32 shows the STEM image of the interface between Ni and Cu-Zr (a). The rectangles in the vicinity of the interface aligned along a GB in the Cu-Zr region are the locations of EDS microanalysis. The profile of X-ray intensity collected from the corresponding locations by the EDS is shown in Fig. 4.32 (b). The linearization of the X-ray intensity profile based on Eq. (4.7), enabling the derivation of diffusion coefficient directly from the EDS profile, is plotted in Fig. 4.32 (b), too. A linear trend is observed until the X-ray intensity falls to the background.
The apparent diffusion coefficient was calculated from the linear least square fit of the data performed in accordance with Eq. (4.7):

\[ D_{Ni} = (5.8 \pm 0.1) \times 10^{-19} \, \text{m}^2 / \text{s}. \]

Additional EDS signals were collected from regions in the bulk in the depths of several µm far from the interface. The same background intensity as appears in Fig. 4.32 (b) was measured. Moreover, no considerable difference between GB and bulk concentrations was observed. The meaning of these findings will be discussed in the following chapter.
4.6. Calorimetric measurements

DSC scans of the pure-Cu samples were performed with the heating rate of 10°C/min starting from room temperature up to 300 °C, as detailed in section 3.2.9. The results indicate an exothermal peak around the temperature of 250 °C. However, the integral intensity of the peak registered in the Bc4 sample is weak and comparable with the measurements accuracy of this instrument, and no quantitative data on the heat released could be obtained.

Nevertheless, in order to gain more information from DSC, other samples were examined. We utilized Cu samples with higher level of purity than the standard "pure Cu" described in this chapter. 99.99 wt. % Cu with the major impurities of 17 wt. ppm Ag, 5 wt. ppm S, and 2 wt. ppm Fe was processed by ECAP in the Bc12 route. This Bc12 sample exhibited a prominent exothermal peak at about 180 °C. After subsequent cooling and re-heating no peaks were observed, showing the irreversibility of this reaction. This is shown in Fig. 4.33.

The observed peak is adequately intense, which enabled us to calculate the released heat from its integral area: $1.02\pm0.04$ mW·K. Normalizing this value by the sample's weight yields the specific heat released: $\Delta H = 0.97\pm0.04$ J/g.
Quantitative evaluation of the heat released by continuous heating of the standard pure-Cu samples could not be provided. However, such data were acquired in Cu with higher level of purity subjected to a higher number of ECAP passes. A comparison between two heat-release peaks, considering the kinetics of microstructure evolution, can be useful for comparison with the results obtained by other methods.

4.7. Summary of the main results

All experimental procedures and results reported in this chapter can be divided into two main categories: measurements of diffusivity and GB energy in UFG Cu alloys. Two classes of materials were produced by ECAP. The Cu-Zr alloy exhibited UFG microstructure that maintained its stability during annealings up to the temperature of 400 °C. The pure Cu exhibited recrystallization during the same heat treatments, and the kinetic expression describing this process was obtained.

$^{63}$Ni radiotracer diffusion in UFG Cu and Cu-Zr was studied under the physical conditions corresponding to C-regime of GB diffusion, in which the radiotracer is confined solely to GB core. Both in Cu and Cu-Zr most of the diffusion profiles demonstrated a bimodal shape corresponding to slow and fast diffusion paths. A reduction in the intensity of the fast-diffusion part of profiles measured in the Cu samples was observed as a result of pre-annealing at elevated temperatures. On the other hand, these "fast" parts of diffusion profiles were not observed at all in the profiles measured using SIMS. Attempts to measure GB diffusion profiles by focusing on individual GBs in the EDS-equipped STEM yielded comparable profiles in both GBs and bulk.

Measurements of the relative GB energy using AFM profiling across the GB thermal grooves showed a considerable difference between the samples annealed at 400 °C and 800 °C. The samples that were produced by ECAP and annealed at "moderate" conditions (15 min at 400 °C) exhibited lower values of dihedral angles if compared with the samples annealed at 800 °C for 2 h. The difference in relative GB energies is accompanied by the different surface textures as well as different statistics of GB geometrical degrees of freedom.
5. DISCUSSION

In accordance with the Research Goals described in chapter 2, this chapter is divided into three major sections: the thermal stability of ECAP-produced Cu alloys, diffusion of Ni in these alloys, and relative GB energy in these alloys.

5.1. Thermal stability of the copper alloys produced by ECAP

In the further discussion we should distinguish between two factors which are included in the term "stability of microstructure". The first one is related to stability against recrystallization and grain growth, while the second one describes stability against relaxation of meta-stable GBs. Both terms are interrelated.

5.1.1. The effect of Zr alloying

The microstructure of samples plays a key role in understanding of the results of this study. Prior to the evaluation of the effect of Zr alloying, the microstructure of the pure Cu should be analyzed. Microstructure observations of the Cu samples subjected to 4 ECAP passes according to the B_C route indicate the grain size and morphology similar to those reported in literature. These samples exhibit the average grain size of 300 nm. This value is close to the lowest grain size observed in ECAP-produced Cu (200-300 nm) [13-17], explained by the dynamic recrystallization during ECAP that occurs below a limiting grain size.

The initial stages of division of the grains into sub-cells can be seen in Fig. 4.6 (a), in agreement with the theory of UFG formation during SPD (see section 2.4.2). The larger grains being divided into sub-cells are elongated, about several µm in length and 200-300 nm in width (Figs. 4.4 and 4.6 b). Their boundaries are considered as preferential sites for the nucleation of new ultra-fine grains [13, 15], since they incorporate concentration of shear stresses formed by SPD [6]. Regarding the sequence of GB formation during SPD [6, 15], it is reasonable to assume that these elongated grains themselves were formed as a result of the division of larger grains, so that the microstructures shown in Fig. 4.4 and 4.6 represent the unfinished process of UFG formation. This conclusion is important for the further analysis of GB diffusion results (see section 5.2.1.1).
Strain fields emanating from the GBs and extending to a range of 20-30 nm from each side of the boundary were also observed (Fig. 4.6), in agreement with models and previous observations reported in the literature [6, 47].

As reported, the elongated grains become equiaxed with the increasing number of ECAP passes [12], reaching at a sufficiently-equiaxed morphology after 4 passes in the B_C route [17]. Nevertheless, in the present study employing the B_C4 route many regions exhibited the elongated morphology shown in Fig. 4.4. The rest of sample area exhibited the equiaxed morphology shown in Fig. 4.5. Such inhomogeneity is also emphasized by the fact that the clusters of elongated grains exhibit relatively low misorientations, while higher average misorientation between grains is observed in the equiaxed regions.

Comparison between the microstructures of both alloys utilized in this research indicates the significant effect of alloying with 0.17% wt. Zr on the microstructure. First, this effect can be distinguished even in the as-pressed microstructures. The above-mentioned inhomogeneity of microstructure observed in the Cu samples was not observed in the Cu-Zr alloy. The latter exhibited mostly the equiaxed, highly-misoriented grains shown in Fig. 4.2. It can be concluded that alloying additives contribute to preserving the equiaxed and homogeneous microstructure exhibiting a higher fraction of HAGBs.

Second, alloying with 0.17% wt. Zr suppresses the recrystallization and grain growth. For instance, Figures 4.7 and 4.10 show that under the same annealing conditions the Cu samples completely recrystallize while the Cu-Zr samples exhibit no change in the microstructure. Such effects have been widely observed in the ECAP-produced alloys containing precipitate-forming elements [18-25]. Furthermore, grain growth in the ECAP-produced Cu-Zr alloy was observed only after 2 h annealing at 450 ºC, while 2 h annealing at 400 ºC was not sufficient to initiate grain growth (section 4.2.1). It is interesting to compare these results with the work of Molodova et al. [108] in which the annealing behavior of the same Cu-Zr alloy subjected to B_C4 – ECAP was investigated, and the onset of recrystallization after 10 s annealing at 650ºC was reported. Also, an abrupt decrease of the alloy microhardness was observed in Ref. [108] after the same annealing.
The most probable reason for high stability of UFG Cu-Zr alloys is the presence of fine Cu$_5$Zr precipitates spread within the grains, as indicated by the Cu-Zr phase diagram (Fig. 3.1). The presence of these precipitates in the Cu matrix is supported by the SAED pattern shown in Fig. 4.3. However, it is not clear whether the inhibition of grain growth can be associated with the presence of Cu$_5$Zr precipitates only. Solute atoms in ECAP-processed alloys can also lead to the same effect [22]. In the present study, a certain degree of supersaturation in the Cu(Zr) solid solution is probable, too. For example, dynamic-SIMS measurement indicated the uniform in-depth concentration of Zr with the concentration of at least 0.1 % at. (section 4.1.1). This can be associated with either solute Zr atoms or ultra-fine precipitates containing Zr. In the above-cited study of ECAP-processed Cu-Zr [108] it was shown that the volume fraction of precipitates calculated from the Cu-Zr phase diagram (about 0.6%) was inadequate for stabilizing the UFG microstructure according to Zener drag mechanism. The authors concluded that impurity drag of GB motion also plays a role. Using the same arguments, we may employ the quantitative expression for the effect of dragging force applied by the homogeneously-dispersed precipitates with the average radius $r_p$ and the volume fraction $F_v$ [107]. The limiting grain size ($d$) in the matrix obtained when the driving force for grain growth and the dragging force are equilibrated is:

$$d = \frac{2ar_p}{3F_v}$$  \hspace{1cm} (5.1)

where $\alpha$ is a geometric factor approximately equals to one. The value of $r_p$ was estimated in Ref. [108] as 10-100 nm. However, according to our TEM observations this size is overestimated, and should be certainly below 10 nm. Substituting this new value and the volume fraction mentioned above in Eq. (5.1) yields an average grain size in the range of hundreds of nm, which is in reasonable agreement with the results of experimental observations.

5.1.2. The recrystallization kinetics in copper

It was shown that the pure Cu samples recrystallize during all thermal treatments employed in this study. The explicit form of kinetic equation describing the time and temperature dependence of the fraction of recrystallized material, Eq. (4.5),
was derived on the basis of experimental observations, as shown in section 4.3.4. Figure 5.1 illustrates this dependence for all temperatures employed in this study.

![Figure 5.1: The time-dependent volume fraction of recrystallized Cu plotted for constant temperatures ranging from 150 °C to 280 °C.](image)

In the present range of temperatures (150 °C to 280 °C), the incubation times before onset of recrystallization range from 30 h to several seconds, respectively. These results are in a good agreement with the exothermal peak observed by DSC, located at about 250 °C (section 4.6). This DSC measurement was performed in the scanning rate of 10 °C/min (section 3.2.9), i.e. about 23 min heating from room temperature to 250 °C. Based on the curves shown in Fig. 5.1, a rough estimate of the corresponding time required to 50% recrystallization at 250 °C is 24 min. It should be mentioned that DSC measurements are performed in dynamic conditions, in contrast with the isothermal conditions employed in the characterization of recrystallization kinetics. Taking into account this difference, both results are practically identical.

The most important factors that determine the kinetics of recrystallization are the internal energy accumulated in material in the course of deformation process as well as the impurity level [109]. The importance of these factors is confirmed by the DSC results described in section 4.6. It was reported that the DSC peak acquired from
the 99.99% Cu processed according to the B\textsubscript{C}12 route is located at 180\textdegree{C}, and is more intensive than the peak collected from the regular 99.98% B\textsubscript{C}4-Cu. This can be explained in the following way: First, since additional internal energy is accumulating in material during each ECAP pass [12], the driving force for recrystallization in the B\textsubscript{C}12-Cu is higher than in the B\textsubscript{C}4-Cu. Second, the former contains lower level of impurities (section 4.6). Therefore, the mobility of interfaces in this material is higher. Furthermore, the composition of impurities is different in both materials. For example, the primary impurity in the B\textsubscript{C}4-Cu is oxygen (29 wt. ppm, section 3.1.2), whereas the B\textsubscript{C}12-Cu contains no detectable oxygen.

These factors should be considered while comparing the results of the present study with other data on recrystallization in copper documented in the literature. In general, we expect that the kinetics of recrystallization measured in the present study should be faster than in copper that was not subjected to SPD. For instance, Gao et al. [110] measured the activation energy for recrystallization in copper samples of different purity (4N, 6N, and 7N). The samples were subjected to hot-deformation of 120% in the temperature range of 250 °C – 600 °C. Under these deformation conditions lower total strain, and, hence, lower total internal energy are introduced into the material than during SPD. Indeed, the values of activation energies reported by Gao are larger than in the present work (about 210 kJ/mole for the 6N and 7N, and 245 kJ/mole for the 4N, compared with 162±10 kJ/mole in the present work).

The considerable effect of purity can be realized from comparison of our results with the following example. Hutchinson et al. [111] reported on the kinetics of recrystallization in cold-rolled (93%) copper with high level of purity (18 ppm Ag, 11 ppm S, other elements < 3 ppm, no detectable oxygen). Although the value of activation energy for recrystallization was not reported, it was shown that recrystallization starts after 5 s of isothermal annealing of fine-grained (initial grain size ~15 µm) copper at 250 °C, and ends after 30 s. The corresponding \textit{JMAK} exponent was evaluated as \( n = 2.67 \). It is obvious that the kinetics of recrystallization introduced by Hutchinson is much faster than that reported in the present study. This is emphasized by the longer starting and ending times of recrystallization calculated from Eq. (4.5) for the same temperature (about 2 min and 3 h, respectively), as well as the lower \textit{JMAK} exponent \( n = 1.14 \). In fact, the opposite trend might be expected: the conditions of SPD employed in the present research should produce faster kinetics of
recrystallization. Nevertheless, this can be explained by the lower level of impurities, in particular the absence of oxygen in the Cu samples investigated by Hutchinson.

A striking example of the effect of deformation on the kinetics of recrystallization can be found in the recent work of Molodova et al. [112]. The activation energies for recrystallization were measured in 99.95% copper subjected to the BC ECAP route with different number of passes: 1, 2, 4, 8, and 12. It was found that the activation energy decreases from about 1 eV after 1 pass to 0.68 eV after 12 passes (these values are equivalent to 96 kJ/mole and 65 kJ/mole, respectively). The value of activation energy measured in our Cu samples is much higher: 162±10 kJ/mole. This can be explained by a possible difference in the concentration of impurities, which was not reported by Molodova et al. In any case, the cited authors report on measurements of the activation energy for recrystallization in 87% cold-worked copper of the same purity. The value reported is 1.07 eV, which, as expected, is higher than after ECAP.

In summary, the two factors that determine the kinetics of recrystallization in pure metals are the level of plastic deformation and concentration of impurities. The 99.98% Cu used in this research exhibits consistently lower thermal stability than the Cu-Zr alloy. At the same time, it exhibits better stability than higher-purity Cu, mainly due to its relatively high oxygen content.

5.1.3. The kinetics of GB relaxation

Several models describing the kinetics of GB relaxation were introduced in section 2.4.3, each one of them predicting a different relaxation time. In this section we attempt to differentiate between these models and to select the one(s) most appropriate for our experimental conditions. In general, these models can be classified into two main categories: models that consider GB diffusion, and models that consider volume diffusion.

The models of Łojkowski [48, 49] and Nazarov [50] (section 2.4.3.1) belong to the first category. They are based on GB diffusion of atoms driven by the strain fields of the GB dislocations. The characteristic range of this strain field was defined by the parameter $S$ in Eq. (2.12), and was compared with the diffusion length. In practice, the correlation between both is the most problematic issue in this model, since it includes a "hidden" assumption that vacancy sources are always available in the vicinity of each
GB dislocation. We propose a modification to this model. A more reasonable estimate for $S$ should be the distance between two adjacent TJs, which is roughly the grain diameter, $d$. We maintain that this approximation describes the relaxation kinetics better than the original model due to the following reasons:

- The process of GB relaxation occurs by dislocation climb, which is regarded as non-conservative motion. Therefore, an infinite source/sink that should absorb the atoms emitted from the climbing GB dislocations is necessary. In the UFG material with relatively low dislocation density within the grains the TJs can play this role. It follows from this description that $d$ should be the real diffusion length.

- The characteristic distance $S$ was determined by TEM observations as the extinction distance of the strain fields around a GB dislocation. As such, it was estimated as tens of nm. Therefore, it predicts relatively short relaxation times. The possible reason for the extinction of the strain fields in TEM observations reported by these authors is the dissociation of GB dislocations into a number of other GB dislocations with shorter Burgers vectors. In practice, however, these dissociation products remaining in the GB may preserve the same excess free volume in the GB as before dissociation. It means that this model describes the dissociation time, which is much shorter than the true relaxation time. Only the former can be accessed by TEM observations. An estimation of the relaxation time can be achieved by exchanging $S$ with $d$ in Eq. (2.12), where $d$ is larger than $S$ by at least one order of magnitude.

- In the model of Łojkowski the relaxation time does not depend on grain size, though it is clear that this time should decrease for very small grain sizes. This behavior is indeed reproduced by the modified model proposed here.

Based on these considerations, the following expression for GB relaxation time is proposed:

$$
\tau_{rel}^{(1)} \approx \frac{10.9 \cdot kT}{G\Omega \delta D_b} d^3
$$

(5.2)

It is clear that this relationship is an approximate one, since the distance between TJs depends on the shape of the grains. The relaxation time is sensitive to the geometry of
the grain because it is proportional to $d^3$. The estimated uncertainty in $\tau_{rel}^{(1)}$ due to geometry factors is about one order of magnitude.

The model of Nazarov mentioned above is valid for low density of GB dislocations. Therefore, it is not relevant for SPD conditions and will not be considered. The models of Varin & Kurzydłowski [51] as well as of Sangal & Tangri [53] (section 2.4.3.2 and 2.4.3.3., respectively) belong to the second category (relaxation controlled by volume diffusion). They consider volume diffusion of atoms and vacancies driven by the stress fields of GB dislocations. In these models the diffusion length comparable with the grain size is considered, and, therefore, they predict relatively slow relaxation kinetics, as given by Eq. (2.20). We will consider the model of Sangal & Tangri (further denoted as S-T) since it was experimentally verified.

In order to determine which of the above models is suitable for the materials and annealing conditions used in this work, we calculated the temperature dependence of the relaxation time. In the modified Łojkowski model (further denoted as ML) this value appears explicitly as $\tau_{rel}^{(1)}$ in Eq. (5.2). In the S-T model the relaxation time was defined as the time in which the density of GB dislocation in Eq. (2.20) reduces to 10% of its initial value, $\rho_0$. According to this definition, Eq. (2.20) can be rewritten in the following form:

$$
\tau_{rel}^{(2)} = \frac{9}{\rho_0} \left( \frac{G\Omega D \left(1-2\ln\left(b/d\right)\right)}{(1-\nu)kT \cdot d \cdot \ln\left(d/2b\right)} \right)^{-1}
$$

The following parameters (as defined in section 2.4.3.1) for pure copper were used for the estimates based on Eq. (5.2): $G = 46$ GPa, $\Omega = 1.210^{-29}$ m$^3$/at, $\delta = 510^{-10}$ m, and the temperature-dependent expression for $D_b$ was taken from the data on slow-GB diffusion in Cu measured in the present experimental work (section 5.2.2.2). The following parameters for copper were used in Eq. (2.20) (see section 2.4.3.3): $\nu = 0.34$, $b = 210^{-10}$ m, and the temperature-dependent expression for $D$ was taken from the work of Bernardini and Cabane [85], as presented in expression (3.9). The initial ($t=0$) linear density of dislocations, $\rho_0$, was estimated as $10^8$ m$^{-1}$. Both values of relaxation times $\tau_{rel}^{(1)}$ and $\tau_{rel}^{(2)}$ were calculated for the following grain sizes: 300 nm, 3µm, and 100
μm. The corresponding temperature dependencies of the relaxation times are shown in Figure 5.2.

Figure 5.2 demonstrates that both models predict the shortening of GB relaxation time with increasing temperature and decreasing grain size. The ML model is more sensitive to grain size variations than the S-T model. The curves shown in Fig. 5.2 indicate the range of temperatures in which each of the above models is relevant (i.e. predicts the shortest relaxation time). In general, ML model is valid for low temperatures, while the S-T model is valid for high temperatures. The transition temperature between both regimes depends on grain size. For example, the transition temperatures are 230 ºC, 400 ºC, and 600 ºC for the grain sizes of 100 μm, 3 μm, and 300 nm, respectively.

Considering the assumptions of each of these two models, such distinction between temperature regimes is reasonable. In ML and S-T models the kinetics of GB relaxation is controlled by GB and volume diffusion, respectively. GB diffusion is faster than volume diffusion; however, the diffusion paths along GBs are much more limited than diffusion paths in bulk. Therefore, interfacial-diffusion-based phenomena
are more dominant at low-temperatures / short dimensions than volume-diffusion-based phenomena. Similar behavior can be found in other kinetic phenomena. For example, this explanation is the basis for distinction between A- and C-type GB diffusion [78]. Also, the kinetics of GB grooving [86, 87] at low temperatures / small groove dimensions is controlled by surface diffusion, while at high temperatures / large groove dimensions the volume diffusion dominates [113].

In summary, we selected the models describing GB relaxation which are the most relevant in the experimental conditions of the present study. The relaxation times predicted by these models depend on temperature as well as on grain size. The next task is to correlate between these theoretical estimates and the experimental data obtained in this study. This will enable us evaluating the effect of annealing conditions on the state of GBs.

### 5.1.4. The effect of thermal annealing on GB relaxation

Various conditions of annealing have been employed in the present research, and it is important to evaluate their effect on the relaxation of GBs. In this section we will utilize the kinetic laws for recrystallization and for GB relaxation illustrated in Figs. 5.1 and 5.2, respectively.

First of all, it is important to examine the standard conditions of diffusion annealing detailed in Table 3.1. The Cu-Zr alloy preserves its UFG microstructure with the average grain size 300 nm during all of these heat treatments. They were annealed in the conditions of temperature / time limited in the range of 150 ºC – 350 ºC and 474 h -1 h, respectively. Most of the points describing these annealings are located below the solid blue line in Fig. 5.2 denoting the ML model that dominates in this temperature range. This means that no GB relaxation is expected in such conditions. One exception is annealing at 350 ºC for 1h that is located slightly above this line. Nevertheless, this line denotes the lower limit of relaxation time, since it does not take into account the possible effect of impurities. In the case of Cu-Zr the presence of either ultra-fine precipitates or Zr solute atoms in the Cu matrix (see section 5.1.1) can contribute to slowing down of GB relaxation.

The pure Cu samples have the initial grain size of 300 nm. They were annealed in the conditions of temperature / time limited in the range of 150 ºC – 280 ºC and 474 h -1 h, respectively. All of these data points are located below the solid blue line in Fig.
5.2, so that no GB relaxation is expected. Moreover, the average grain size in this material increases due to recrystallization during the diffusion annealing. It means that the solid blue line denotes only the lower limit of relaxation times since it was calculated for $d = 300$ nm. After recrystallization the average grain size increases to 3 µm at least, so that the dashed blue line should be regarded. The relaxation time is, therefore, a dynamic variable that is located between both lines. For example, annealing at 240 °C yields complete recrystallization after 3.5 h (Fig. 5.1). Accordingly, the "real" value of relaxation time should range between 10 h and $10^4$ h (the solid and dashed blue lines in Fig. 5.2).

At this point, the effect of grain growth on the GB structure should be regarded. As a conservative process, GB migration is not expected to modify the structure of the GB, unless dislocation climb is operative. The latter is, however, a non-conservative process. Grain growth causes a reduction in the density of internal interfaces. If the total number of dislocations in the material is conserved, then we can expect that these dislocations will be re-distributed in the new GBs during grain growth. Thus, the density of GB dislocation should increase proportionally with the grain size. However, this description disregards the annihilation of GB dislocations during grain growth (recovery). This may occur, for example, when two dislocations with the opposite Burgers vectors meet at the TJ during grain growth. This process is quite different from GB relaxation since it is controlled by grain growth and does not require additional thermal activation. Statistically, the equal numbers of dislocations with opposite Burgers vectors are absorbed by GBs and they annihilate given the opportunity to meet at the TJs. Therefore, it is expected that two competitive processes, i.e. the reduction of the total GB area and the annihilation of GB dislocations will result in constant density of GB dislocations during grain growth. The same explanation is valid for recrystallization, as well.

It is important to examine the extent of GB relaxation in the samples pre-annealed at 300 °C for 2 h (section 4.3.5). According to Eq. (4.5) "complete" recrystallization (99%) is obtained after 5 min annealing at 300 °C. It means roughly that in the first 5 min the average grain size is 300 nm, where the relaxation time corresponding to this grain size is 1 h (Fig. 5.2). Comparing both times, we can assume that during this time a certain partial relaxation of GBs occurs. After these 5 min the recrystallization is completed, but the average grain size at this stage is not known. The
recrystallized microstructure after 2 h annealing exhibits the grain size of several µm, as shown in Fig. 4.17. We can conclude that the GBs in the Cu samples pre-annealed at 300 ºC for 2 h are only partially relaxed. Nevertheless, this partial effect is manifested by the radiotracer activity reduction in the fast-diffusion part of profile, as shown in Fig. 4.18.

The other two heat treatments that should be examined are 400 ºC, 15 min and 800 ºC, 2 h. The samples annealed in these conditions were defined as class 1 and 2, respectively (section 4.4.1). Eq. (4.5) predicts "complete" (99%) recrystallization after 2 s annealing at 400 ºC. It is not expected that considerable GB relaxation will occur in this short time (see Fig. 5.2). In turn, the relaxation time corresponding to the coarse-grained Cu (the microstructure is shown in Fig. 4.20) is much longer (about 60 h, Fig. 5.2). Therefore, it can be maintained that the approximation made in section 4.4, in which class 1 samples represent the as-deformed state, is reasonable.

In section 4.4 we maintained that relaxed GBs are obtained after annealing of the pure Cu at 800 ºC for 2 h. The final grain size observed after such annealing is about 100 µm (section 4.4.1). In practice it takes a few minutes to reach this temperature. In any case, the recrystallization time at this temperature is much shorter, so that large grains (tens of µm) are expected after several minutes of annealing at most. At this temperature, the S-T relaxation mechanism dominates, so that the longest relaxation time allowed by the red curves in Fig. 5.2 (the dotted line, corresponding to 100 µm) is about 30 s. Therefore, the class 2 samples represent well the relaxed state.

In summary, theoretical aspects of GB relaxation mechanisms and experimental data of recrystallization kinetics were combined in this section. We obtained a rough estimate of the state of GBs as a result of the different annealing processes employed in this work.

5.2. Diffusion of Ni in the ECAP-produced Cu alloys

In this section the GB diffusion coefficients will be determined from the raw Ni-penetration profiles presented in chapter 4. This will be done using appropriate models correlating diffusion data with microstructure observations. The complete set of diffusion data is considered, including the $^{63}$Ni activity profiles acquired using the
radiotracer method, the depth-profiles acquired by SIMS, and the EDS profiles acquired in the vicinity of Ni/Cu alloy interfaces.

5.2.1. Diffusion in the Cu-Zr alloy

5.2.1.1. The hierarchical model

It was shown in section 4.2.3 that nearly all radiotracer penetration profiles exhibit a bimodal shape. This means that each profile can be separated into large and small slope sections, corresponding to slow- and fast-diffusion paths, respectively (Fig. 4.9). We associated this behavior to the co-existence of slow- and fast-diffusion GBs. However, determining the corresponding GB diffusion coefficients from the profiles according to the simple Gaussian solution in Eq. (4.1) would be incorrect, since such method would imply that the two diffusion paths are completely independent from each other.

In a more realistic model the "slow" and "fast" GBs in the UFG samples obtained by ECAP are interconnected. It should be noted, however, that even for "slow" diffusion paths the average diffusion distance (in the range of micrometers) is much larger than the average grain size (∼300 nm). This means that in a random mixture of "slow" and "fast" diffusion paths the latter will be effectively linked with each other through the former. As a result, the diffusion properties of such random mixture can be characterized by a single "effective" diffusion coefficient, akin to the one for Harrison's $A$-regime of GB diffusion. This would result in activity profiles that exhibit a single slope in the $\ln C$ vs. $x^2$ coordinates, which is in contradiction with our experimental data (for example see Fig. 4.9). Therefore, we propose here a hierarchical microstructure model which is consistent both with the microstructural models of UFG materials obtained by ECAP and with our diffusion data. In this model, the "fast" diffusivity paths form a superstructure (skeleton) with the domain size larger than the average diffusion distance along the "slow" paths (i.e. several micrometers – otherwise $A$-type kinetics should govern diffusion along these short-circuit diffusion paths, with a single slope in a profile, see above). These domains are further subdivided into actual grains by the "slow" diffusion paths.

The hierarchical microstructure has already been observed in nanocrystalline copper produced by inert gas condensation [114] and in a nanocrystalline $\gamma$-FeNi alloy produced by powder metallurgy methods [115, 116]. Moreover, evidence for the
existence of such hierarchical microstructure in the present work is provided by the
topographic image of the surface of Cu sample subjected to O$_2^+$ ion-beam flux in SIMS
(see Fig. 4.26 in section 4.4.5). Presumably, a process of grooving similar to Mullins
thermal grooving was driven by the ion flux. As a result, the hierarchical
microstructure of large grains marked by deep channels, divided into subcells marked
by shallow channels was revealed, as shown in Fig. 4.26 (b). According to the
topographic profiles taken across these channels (Fig. 4.27), it is reasonable to assume
that these channels represent "real" GBs. The corresponding dihedral angles measured
at the bottom of the deep grooves are lower than those measured at the bottom of the
shallow grooves. The average size of the subcells is 200 – 300 nm. It is comparable
with the grain size observed in the as-pressed Cu samples (see Fig. 4.5). We may
therefore correlate the deep channels to high-energy, fast-diffusion GBs, while the
shallow channels correspond with low-energy, slow-diffusion GBs. The correlation
between GB energy and diffusivity has been discussed in section 2.3. Therefore, Fig.
4.26 (b) visualizes the hierarchical model.

There may be several formation mechanisms of such hierarchical
microstructure in the present case. First, the GBs in original Cu-Zr ingots that existed
prior to ECAP may constitute a major fraction of the skeleton of "fast" diffusivity
paths since they absorb the dislocations from the early stages of ECAP processing,
while the newly formed GBs need sufficient strain to be formed, and it is only then that
they can absorb lattice dislocations like pre-existing GBs. Second, the four pass B$_C$
route results in a high fraction of LAGBs [75]. The remaining HAGBs with a high
diffusivity may form a percolating cluster with the characteristic domain size which is
by an order of magnitude or so larger than the actual grain size.

According to the hierarchical microstructure model, GB diffusion occurs
primarily along the "fast" paths with the subsequent leakage of the material into the
"slow" paths, in analogy with the Fisher model of GB diffusion. (It should be noted
that in contrast to Fisher's model [81] in which bulk diffusion is responsible for the
leakage of material from the GBs, in our case the leakage occurs via "slow" GB
diffusion). Figure 5.3 outlines the proposed model. The large domains formed by "fast"
GBs are further subdivided into actual grains of size $d$ by the "slow" GBs. A complete
analysis of solute GB diffusion in hierarchical microstructures was developed by
Divinski et al. for all possible kinetic regimes [117]. A similar problem of GB
diffusion in presence of dislocations has been comprehensively analyzed by Klinger and Rabkin [118].

In the present case when bulk diffusion is ‘frozen’, the diffusivity along the "slow" GBs can be calculated according to Eq.(4.1) from the initial part of the diffusion profile with large slope. In our model, this initial part corresponds to direct diffusion from the surface source into the "slow" GBs. The diffusivity along the "fast" GBs should be calculated differently [114-117]. Since the topology of diffusion fluxes in our model is equivalent to that in Fisher's model (B-regime), the diffusion coefficient along the "fast" GBs, $D_f$, can be calculated using the expression which is similar to the one derived by Suzuoka [82]:

$$P \equiv s^* \delta D_{gb} \approx 1.308 \left( \frac{D_{eff}}{t} \right) \left( -\frac{\partial \ln \bar{C}}{\partial x^{6/5}} \right)^{-5/3}$$  \hspace{1cm} (5.4)$$

with the effective diffusivity $D_{eff}$ describing the tracer leakage from fast diffusion paths to slow ones, $D_{eff} = \lambda^2 D_s$, where $\lambda$ is the cross-sectional fraction of "slow" GBs in the plane parallel to the "fast" GBs. Furthermore, the segregation factor $s^*$ is the ratio of the segregation factors in "fast" and "slow" GBs. Since no reliable information on Ni segregation in crystallographically different GBs in Cu is available, we assume this ratio to be equal to unity. Such relationship has been established for Ag in nano-$\gamma$-FeNi with a hierarchical microstructure by measuring the Ag diffusion in different kinetic regimes [117].

Fig. 5.3: Schematic presentation of the diffusion in a hierarchical microstructure.
For polyhedral grain shape we obtain:

$$\lambda = \frac{\pi \delta}{2d}$$

(5.5)

The final expression for $D_f$ is, therefore, as follows:

$$D_f \approx \frac{2}{d} \sqrt{\frac{D_s}{t}} \left( -\frac{\partial \ln C}{\partial x^{5/3}} \right)^{-5/3}$$

(5.6)

For Eq. (5.6) to be valid, the following conditions must be fulfilled [115, 116]:

$$\alpha' = \frac{\delta}{2\lambda \sqrt{D_s t}} < 0.1; \quad \beta' = \frac{\delta D_f}{2\lambda D_s \sqrt{D_s t}} \geq 2$$

(5.7)

Estimates show that in the present work $\alpha' \leq 0.03$; $\beta' \geq 32$ and, hence, the conditions (5.7) are fulfilled. The size of the domains formed by the "fast" GBs is in this case equal to a few average diffusion penetration depths along "slow" GBs ($\sqrt{D_f t}$).

The diffusion coefficient along the "fast" GBs was calculated using Eq. (5.6) with the grain size $d=300$ nm. Figure 5.4 illustrates how "slow" and "fast" GB diffusion coefficients were extracted from the corresponding parts of the diffusion profile obtained in the sample annealed for 5 h at 240 °C.

Fig. 5.4: Processing of diffusion profile for the sample annealed for 5 h at 240 °C. (a) Initial, slow diffusion section is linearized in $\ln C - x^2$ coordinates. (b) The "fast" diffusion section at large penetration depths is linearized in $\ln C - x^{6/5}$ coordinates.
5.2.1.2. The complete set of diffusion data

All of the penetration profiles shown in Fig. 4.8 were processed in the following manner. First, plotting the initial part of profiles in lnC-x² coordinates and deriving $D_s$ using Eq. (4.1); Second, plotting the deeper part of profiles in lnC –x⁶/₅ coordinates and deriving $D_f$ using Eq. (5.6) and the value of $D_s$ calculated in the first step. The complete set of diffusion coefficients calculated for the Cu-Zr samples appears in Table 5.1.

<table>
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<th>$D_f$ [m²/s]</th>
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<td>4.8·10⁻¹⁶</td>
<td>4.1·10⁻¹³</td>
</tr>
<tr>
<td>553</td>
<td>3.6·10³</td>
<td>2.0·10⁻¹⁵</td>
<td>1.6·10⁻¹²</td>
</tr>
<tr>
<td>623</td>
<td>3.6·10³</td>
<td>9.9·10⁻¹⁵</td>
<td>——</td>
</tr>
</tbody>
</table>

Table 5.1: The “slow”, $D_s$, and “fast”, $D_f$, diffusion coefficients of Ni along the GBs of ECAP-ed Cu-Zr alloy calculated according to Eqs. (4.1) and (5.6), respectively.

The GB diffusion coefficients shown in Table 5.1 are presented in the Arrhenius plot in Fig. 5.5. For comparison, the recent data on $^{63}$Ni radiotracer GB diffusion in high-purity (5N8) coarse-grained ($d=60$ µm) copper measured in the C-regime of GB diffusion [84] are also shown.

The deep parts of the penetration profiles from which the $D_f$ -values were extracted exhibit a rather narrow dynamical range, i.e. a decrease of the activity by a factor of two only (Fig. 5.4 b). This disrupts the accuracy of the fast-diffusion coefficients. However, a statistically significant number of individual points on the penetration curve somewhat compensates for the small slope of the profile, so that the
Fig. 5.5: Arrhenius diagram showing the "slow" and "fast" GB diffusivities calculated using hierarchical microstructure model with constant grain size of 300 nm. The reference data for Ni GB diffusion in high-purity coarse grain (CG) Cu are shown for comparison [84].

Using the data in Table 5.1 and Fig. 5.5 we determined the Arrhenius parameters of diffusion along both types of GBs:

\[
D_s = \left(1.4_{-0.5}^{+0.9}\right) \cdot 10^{-7} \cdot \exp\left(-\frac{84 \pm 4 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}
\]

\[
D_f = \left(1.6_{-1.3}^{+8.4}\right) \cdot 10^{-3} \cdot \exp\left(-\frac{96 \pm 14 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}
\]

5.2.1.3. Interpretation of the bimodality in diffusion profiles

The main finding of the present section is the bimodality in the distribution of the GB diffusivities in the UFG Cu-0.17 wt. % Zr alloy processed by ECAP: while the
majority of GBs exhibit the diffusivities which are very close to those of HAGBs in high purity coarse grain copper, a minority of the GBs exhibit unusually high diffusivities. It can be conjectured that these "fast" GBs are well-separated from each other and form a skeleton embedded in the network of "slow" GBs (hierarchical microstructure). The diffusion along "fast" GBs is by more than two orders of magnitude faster than along the "slow" ones. A special remark is due here. Although the short-circuit diffusion paths with a lower diffusivity are referred to as “slow” paths, they are not “slow” at all in absolute terms – their diffusivity is similar to that for general HAGBs in coarse-grained high-purity copper (where these are the fastest diffusion paths). One should not be misled by the term “slow”– these are not e.g. twin or low-angle GBs in a form as they occur in a well-annealed coarse-grained material, see below.

The observed type of microstructure with two very different populations of the GBs is counter-intuitive and requires a detailed explanation. We believe that a major part of "fast", high diffusivity GBs revealed in the present work can be associated with the original HAGBs in the coarse grain ingots that existed in the samples prior to ECAP. These GBs are capable of absorbing lattice dislocations generated in the lattice early in the ECAP process. Since the periodicity of the skeleton formed by "fast" GBs is larger than average UFG size, one can expect that the relaxation time of these GBs should be larger than that calculated for the UFG size (section 5.1.4). Therefore, the pre-existing GBs can exhibit an increased density of GB dislocations (which are not geometrically necessary ones) during the whole duration of diffusion annealing. The cores of these GB dislocations introduce an additional free volume in the GBs and increase their diffusivity.

At the same time, the new HAGBs formed during ECAP evolve from cells that form after the first ECAP pass [119]. Only the second and third passes transform some fraction of the cells into well-defined grains, and the corresponding cell walls into HAGBs. At the time these HAGBs are formed, the UFG microstructure is already well-developed. The dislocation activity in submicrometer-size grains is limited because of the difficulties in operation of dislocation sources in small grains. Therefore, only the last one or two ECAP passes (out of four used in this work) can supply dislocations to the newly formed HAGBs, and the supply itself is limited because of the scarcity of dislocation sources. These GBs should be close in their
energy and diffusivity to the GBs in coarse-grained material. It is therefore probable that these newly-formed HAGBs represent the network of "slow" GBs revealed in this study.

It is interesting that diffusion parameters for "slow" GBs in UFG samples are very close to those for the GBs in coarse grain samples of high purity, 5N8, where the activation enthalpy of 90.4 kJ/mol has been measured for Ni GB diffusion [84]. This indicates that very little if any Zr atoms segregate at the new GBs produced during ECAP process, since it is known that even a small amount of segregated impurities considerably increases the activation enthalpy for diffusion and decreases the GB diffusion coefficient [62]. This is not surprising since even at the highest annealing temperature used in the present study the average diffusion distance in the bulk is below 1 nm [85], which is not enough for establishing a segregation level at the GBs corresponding to thermodynamic equilibrium.

The activation enthalpy for diffusion along the "fast" GBs is practically identical with that for the "slow" ones, while the main source for the difference in absolute values of diffusivities is the pre-exponential factor. The Arrhenius parameters for the "fast" GBs are, however, less reliable than those for "slow" ones: first, because of the low absolute values of the radiotracer activity in the corresponding sections of the diffusion profiles and, second, because of the possible partial relaxation of the non-equilibrium structure during diffusion annealing. A simple model according to which GB diffusion is controlled by the atomic sites with particularly low vacancy or interstitials formation enthalpy may be consistent with the obtained Arrhenius parameters for "fast" and "slow" GBs. Indeed, in the framework of such model the main difference between the "fast" and "slow" GBs would be in the number of such sites, but not in the corresponding defect formation and migration enthalpies. This simple model is consistent with the results of atomistic computer simulations of Suzuki and Mishin [120]. They found that there is a limited number of sites in the GBs of copper with particularly low vacancy formation energy. For example, the vacancy formation energy as low as 0.185 eV was reported for Σ13 tilt GBs [120]. According to our model, the number of such special sites in the "fast" GBs is approximately 500 times higher than in the "slow" ones.

The low radiotracer activity in the regions of diffusion profiles corresponding to "fast" GB diffusion indicates that "fast" GBs constitute only a minor fraction (about
of the total GB population. In spite of their high diffusivity, their contribution to the total diffusion flux is small. It is, therefore, not surprising that these GBs were not revealed in previous studies of GB diffusion in the UFG materials that employed a microprobe analysis of concentrations, which is known to be less sensitive than radiotracer technique used in the present study [58]. It should be noted that the fraction of "fast" GBs estimated using our models and the grain sizes in the initial (300 µm) and as-processed (300 nm) states is about 0.1%, which is quite close to the estimate based on the values of activity.

It is interesting that the absolute values of "fast" GB diffusivities are quite close both to the extrapolated surface self-diffusion coefficients in copper determined by GB grooving technique [121] and to the surface self-diffusion coefficients in copper estimated using well-known empirical correlations [78]. The surface diffusivity is an upper bound for any diffusion coefficient in the solid state. The proximity between the "fast" GB and surface diffusivities again indicates a special nature of the atomic sites in the "fast" GBs involved in diffusion process. One can speculate that these sites are concentrated in the vicinity of TJs of the pre-existing GBs that represent sinks for GB dislocations.

Another point that needs to be clarified concerning the "fast" diffusion paths detected in this study is the possibility that they represent TJ diffusion rather than GB diffusion. Indeed, the ratio of the number of atoms located in the TJs and in the GBs in the UFG alloy investigated is $f \approx 10^{-3}$. Furthermore, measurements of diffusion coefficients of Zn in TJs and GBs in Al have indicated that at the temperature of $0.6T_m$ the former is larger by a factor of about $10^3$ than the latter [122]. Such a large difference is similar to the difference between "slow" and "fast" diffusivities observed in the present work (see Fig. 5.5). Nevertheless, the hypothesis of TJ diffusion should be ruled out on the same grounds as the model of random mixture of the "slow" and "fast" diffusion paths considered in the previous section: an effective exchange of diffusing radiotracer between the closely spaced TJs through the "slow" GBs would result in the $A$-type diffusion regime, in which the diffusion penetration profile can be described by a single "effective" diffusion coefficient expressed similarly to Eq. (3.1):

$$D_{eff} = f \cdot D_{TJ} + (1 - f) \cdot D_b$$  \hspace{1cm} (5.9)
where $D_{TJ}$ is the diffusion coefficient along the TJs. This is in stark contrast with the experimentally determined bimodal diffusion profiles (see Fig. 4.9). It is, however, possible that only a limited number of well-separated, special TJs contribute to the "fast" sections of experimentally measured penetration profiles. This is a possibility that should be explored in future research.

It should be noted that in most previous diffusion studies of UFG materials obtained by SPD the GB diffusivity at a particular temperature was characterized by a single, unique value of diffusion coefficient [55-58]. A comparison of these values with the diffusivities of equilibrated GBs in coarse grain samples is somewhat problematic because of the differences in the material purity and experimental conditions. In the present study the "slow" GBs provided an intrinsic standard of the "normal" GB diffusivity at each temperature, so that the degree of non-equilibrium of the "fast" GBs can be characterized quantitatively. In this respect, the work of Kornelyuk et al. should be mentioned [123]. They deformed a Ni-based superalloy to the compressive strain of 10% and observed in some of their deformed samples bimodal diffusion penetration profiles similar to those found in the present study. The diffusivity of "fast" GBs in the work of Kornelyuk et al. was about one order of magnitude higher than the diffusivity of "slow" GBs in the same sample. A larger difference of GB diffusivities observed in the present study may be associated with the larger plastic strain imparted on our samples during ECAP processing.

Summarizing this part, the penetration profiles of the $^{63}$Ni radiotracer along the GBs in UFG Cu-0.17 wt. % Zr alloy processed by ECAP exhibited two distinct regions with different slopes. We proposed a hierarchical microstructure model, in which a cellular skeleton of "fast" GBs with the characteristic cell size in the micrometer range is embedded in a network of "slow" GBs formed by ultrafine grains with the average size of about 300 nm. It was conjectured that "fast" GBs are associated with the initial GBs of the pre-ECAP coarse grain microstructure. The non-equilibrium state of these GBs is associated with the absorption of lattice dislocations during ECAP.

5.2.2: Diffusion in the pure Cu samples

The analytical treatment in the case of Ni GB diffusion in the pure Cu samples is different from the case of diffusion in Cu-Zr alloy presented above. The reason for
this difference is that in Cu-Zr the UFG microstructure was stable and the mathematical analysis of diffusion problem was relatively simple. However, in pure Cu recrystallization takes place simultaneously with GB diffusion. The present section introduces a model that enables simulating the diffusion penetration profiles obtained in UFG material undergoing recrystallization during diffusion annealing.

5.2.2.1: A model for diffusion in simultaneously-recrystallizing media

Let us consider a case in which diffusion takes place in a homogeneous medium with a diffusion coefficient \( D \). The simplest case is diffusion from a finite source in form of a thin layer of solute element deposited on the surface of a semi-infinite polycrystalline material with a uniform grain size. We will further assume that the GB diffusion in this material corresponds to Harrison's \( C \)-regime (i.e. volume diffusion can be neglected). In this case the concentration profile measured by the sectioning method is expressed by Eq. (3.5). The proportionality factor \( A \) in Eq. (3.5) depends on the initial concentration of diffusant within the layer as well as the fraction of the diffusion paths (a function of the grain size).

Let us consider the recrystallization process occurring simultaneously with diffusion. In the case of UFG matrix the following assumptions can be made:

- The bulk is separated into two interpenetrating, but continuous microstructural components. They comprise the UFG matrix and the coarse-grained recrystallized material. The isolated islands of the UFG matrix within the recrystallized regions and vice versa will be disregarded.
- GB diffusion occurs in the UFG matrix only. The newly-formed coarse grains "freeze" the local concentration of solute that existed prior to recrystallization.
- The size of the newly-formed grains is much larger than the grain size in the UFG matrix. Thus, GB diffusion in the recrystallized regions can be disregarded.

The model is illustrated in Figure 5.6. Following the assumption of homogeneity, any internal slice having the infinitesimal thickness \( dx \) "cut" from the plane normal to the average diffusion flux should incorporate both recrystallized and non-recrystallized regions (Fig. 5.6).
The amount of solute in the UFG matrix changes due to diffusion flux as well as the change (decrease) in its volume fraction. The following equation expresses the condition of mass balance in the element $dx$.

\[
\frac{\partial q_{\text{UFG}}}{\partial t} = -\frac{\partial J_{\text{UFG}}}{\partial x} dx + \overline{C}_{\text{UFG}} \frac{\partial \lambda}{\partial t} dx
\]  \hspace{1cm} (5.10)

where $q_{\text{UFG}}$, $J_{\text{UFG}}$ and $\overline{C}_{\text{UFG}}$ are the total amount of material, diffusion flux and the average concentration in the UFG matrix, respectively, and $\lambda(t)$ is the time-dependent volume fraction of the UFG matrix.

The amount of solute in the recrystallized region depends on the change (increase) in its volume fraction only. The corresponding equation of mass balance in the element $dx$ is:

\[
\frac{\partial q_{\text{rec}}}{\partial t} = -\overline{C}_{\text{UFG}} \frac{\partial \lambda}{\partial t} dx
\]  \hspace{1cm} (5.11)

Fig. 5.6: FIB micrograph showing a typical microstructure of the partially-recrystallized ECAP-ed Cu. The diffusion flux is marked by the red arrow within the UFG matrix. An infinitesimal slice of the thickness $dx$ consists of both recrystallized (blue) and non-recrystallized, UFG (red) microstructural components.
where $q_{\text{rec}}$, $J_{\text{rec}}$ and $\bar{C}_i$ have the same meaning as in Eq. (5.10), but refer to the recrystallized regions.

The diffusion in the UFG matrix should obey the 1st Fick's law:

$$J_{\text{UFG}} = -\lambda \cdot D \frac{\partial \bar{C}_{\text{UFG}}}{\partial x}, \quad (5.12)$$

while the following two relationships establish a link between the amount of solute in each microstructural component and its volume fraction and average concentration:

$$q_{\text{UFG}} = \lambda \cdot \bar{C}_{\text{UFG}} \ dx; \quad q_{\text{rec}} = (1-\lambda) \cdot \bar{C}_{\text{rec}} \ dx, \quad (5.13)$$

Substituting Eqs (5.12) and (5.13) into (5.10) and (5.11) yields:

$$\frac{\partial}{\partial t} \left( \lambda \cdot \bar{C}_{\text{UFG}} \right) = \lambda \cdot D \frac{\partial^2 \bar{C}_{\text{UFG}}}{\partial x^2} + \bar{C}_{\text{UFG}} \frac{\partial \lambda}{\partial t}, \quad (5.14)$$

for the UFG matrix, and:

$$\frac{\partial}{\partial t} \left( (1-\lambda) \cdot \bar{C}_{\text{rec}} \right) = -\bar{C}_{\text{UFG}} \frac{\partial \lambda}{\partial t} \quad (5.15)$$

for the recrystallized regions.

The average concentration in the element $dx$ is expressed as weighted volume average of both microstructural components:

$$\bar{C}(x,t) = \lambda \cdot \bar{C}_{\text{UFG}} + (1-\lambda) \cdot \bar{C}_{\text{rec}}. \quad (5.16)$$

The differential equation for the average concentration, $\bar{C}(x,t)$, is obtained by substituting Eqs. (5.14) and (5.15) into Eq. (5.16):

$$\frac{\partial \bar{C}}{\partial t} = \lambda \cdot D \frac{\partial^2 \bar{C}_{\text{UFG}}}{\partial x^2} \quad (5.17)$$

Eq. (5.17) is, in practice, the one-dimensional diffusion equation in recrystallizing media. Note that $\lambda(t)$ is a time-dependent variable. In the case where $\lambda$ is constant,
Eq. (5.17) reduces to the familiar form of the one-dimensional diffusion equation. The explicit form of $\bar{C}(x,t)$ is obtained by time-integration of Eq. (5.17):

$$\bar{C}(x,t) = \bar{C}_{UFG}(x,t) - \int_0^t \left[ 1 - \lambda(t') \right] \frac{\partial \bar{C}_{UFG}}{\partial t'} dt'$$ \hspace{1cm} (5.18)

It can be seen that if no recrystallization takes place ($\lambda=1$), Eq. (5.18) yields: $\bar{C}(x,t) = \bar{C}_{UFG}(x,t)$, as expected.

The semi-empirical model presented above enables us to simulate the concentration profile measured in the samples undergoing simultaneous diffusion and recrystallization. For this purpose, the "ideal" concentration profile, $\bar{C}_{UFG}(x,t)$ (i.e. the concentration profile measured in thermally stable UFG matrix), as well as the kinetic expression describing the fraction of recrystallization, $\lambda(t)$, should be known.

### 5.2.2.2: Applications of the model

In this section the model developed above will be applied for calculating the GB diffusion coefficients in the UFG Cu. We will use the diffusion profiles in pure Cu shown in section 4.3.2 and the kinetic expression describing recrystallization in Cu given by Eq. (4.5).

It should be noted that our model enables to calculate only the slow GB diffusion coefficients, $D_s$. It was concluded in section 5.2.1.3 that the characteristic cell size of the skeleton of the fast-diffusion GBs is at least tens of micrometers. The recrystallized microstructure, however, exhibits an average grain size of just a few micrometers (see Fig. 4.10, for example). Therefore, it can be postulated that the supercell networks of fast-diffusion GBs are not affected from recrystallization. In view of this scenario, the following steps are first deriving the set of $D_s$-values according to the model given in section 5.2.2.1. Then, the $D_f$-values will be calculated according to the hierarchical model given in Eq. (5.6) using the corresponding $D_s$-values.

The slow-diffusion coefficients will be calculated employing the following procedure:
1. Substituting the expression for $\lambda(t)$ given explicitly by Eq. (4.5) into Eq. (5.18), and taking $\bar{C}_{\text{UFG}}(x,t)$ as the standard Gaussian expression given by Eq. (3.5). The latter satisfies the diffusion equation within the UFG matrix given by Eq. (5.14), and includes the dimensionless parameters $A$ and $D$, both equal to unity. The Equation (5.18) incorporates two different time scales characterizing the recrystallization and diffusion processes. At each temperature, all times are expressed in dimensionless units normalized by the corresponding diffusion time given in Table 3.1.

2. Calculating the slope of $\bar{C}(x,t)$ when plotted in the $\ln C$ vs. $x^2$ co-ordinates, $\frac{\partial \ln \bar{C}}{\partial x^2}$, by integrating the Eq. (5.18). This value should be then normalized by the term $\frac{\partial \ln C_{\text{UFG}}}{\partial x^2}$, which is equal to -0.25 following the definition of $A=D=1$.

The ratio between both is denoted as $\phi = -4 \frac{\partial \ln \bar{C}}{\partial x^2}$.

3. Deriving the diffusion coefficient, $D^*$, from the experimental profiles given in Fig. 4.12 applying the operation (4.1). $D^*$ is, in practice, the diffusivity calculated as if no recrystallization is operative, i.e. the concentration profile is linear in the $\ln C$ vs. $x^2$ co-ordinates.

4. The true value of slow-diffusion coefficient, $D_s$, is calculated from $D^*$ multiplied by the factor $\phi$ given in step 2.

$$D_s = \phi \cdot D^*$$  \hspace{1cm} (5.19)

The factor $\phi$ represents the effect of recrystallization. It is larger than one and is increasing with increasing fraction of recrystallized material. The effective time of diffusion is smaller than the annealing time, $t$, so that the diffusion coefficient calculated from the penetration profile according to Eq.(4.1) is smaller than the "true" one derived from Eq.(5.21) using the factor $\phi$.

Substituting the expression for $\lambda(t)$ and $\bar{C}_{\text{UFG}}(x,t)$ into Eq. (5.18) yields a complicated expression which is difficult to integrate analytically. Therefore, we employ a simplified approach defining the times $t_f$ and $t_g$ of the recrystallization begin
and end, respectively. These times will be arbitrarily defined using Eq. (4.5) as the times to achieve 1% and 99% recrystallization, respectively. Thus, the complicated JMAK representation of Eq.(4.5) can be reasonably approximated by the following piecewise function:

$$
\lambda(t) = \begin{cases} 
1, & t < t_1 \\
\frac{t_2 - t}{t_2 - t_1}, & t_1 < t < t_2 \\
0, & t > t_2 
\end{cases}
$$

(5.20)

The curves in Fig. 5.1 demonstrate that this piecewise-linear approximation is quite reasonable, and allow a rough estimation of the recrystallization start and end times. Since the diffusion time, \( t \), is different from both \( t_1 \) and \( t_2 \), we define a new parameter, \( t^* \), which satisfies two conditions: \( t^* = \min(t, t_2) \) and: \( t^* = \max(t, t_1) \). The solution for \( \bar{C}(x, t) \) is obtained by substituting \( \lambda(t) \) from Eq. (5.20) and \( \bar{C}_{UFG}(x, t) \) from Eq. (3.5) into Eq. (5.18). The result is given in the following expression:

$$
\bar{C}(x, t) = \left[ 1 - \frac{t^* - t_1}{t_2 - t_1} \right] \cdot \bar{C}(x, t) +
$$

$$
+ \frac{A}{D} \cdot \frac{1}{t_2 - t_1} \left[ 2 \sqrt{\frac{D}{\pi t^*}} \left( e^{\frac{x^2}{4Dt^*}} - e^{\frac{x^2}{4Dt_1}} \right) + x \cdot \text{erf} \left( \frac{x}{2\sqrt{Dx^*}} \right) - x \cdot \text{erf} \left( \frac{x}{2\sqrt{Dt_1}} \right) \right]
$$

(5.21)

The procedure outlined above was applied to all diffusion data presented in section 4.3.2. For example, the calculation of the "true" slow-diffusion coefficient from the profile obtained after 5 h annealing at 240 °C (Fig. 4.12) was performed as follows. The times \( t_1 \) and \( t_2 \) were inferred from the corresponding curve in Fig. 5.1, and are 1.2 min. and 2 h, respectively. The total annealing time was \( t = 5 \) h. In this case \( t_2 \) is in fact the total diffusion time and \( t_1 \ll t_2 \), so that \( t_1 \) is practically zero. All time scales were normalized by \( t \) so that: \( t_1 \approx 0; t^* = t_2 = 0.4 \). These dimensionless values of times were substituted in Eq. (5.21), where the values of \( A \) and \( D \) were set as unity. Both Eqs. (3.5) and (5.21) were plotted in the \( \ln C \) vs. \( x^2 \) co-ordinates, and the results are presented in Fig. 5.7.
The value of $\phi = 2.96$ is derived from the ratio between both slopes. Employing Eq. (4.1), the value of $D^* = 4.63 \times 10^{-16}$ m$^2$/s was derived from the profile measured after 5 h annealing at 240 °C, as shown in Fig. 4.12. Using the relationship (5.19), the "true" slow-diffusion value is $D_s = 1.37 \times 10^{-15}$ m$^2$/s.

It was shown that numerical values of diffusion coefficients that consider the effect of recrystallization can be extracted using the model outlined above. However, the quality of this approximation depends on the linearity of Eq. (5.21) when plotted in the $\ln C$ vs. $x^2$ co-ordinates. The problem is pronounced particularly at large fractions of transformation ($\lambda \rightarrow 0$). For example, it can be seen that the initial part of the curve marked by rectangles in Fig. 5.7 (small $Dt$) is not linear. However, the initial part of profile ($x^2/Dt = 1-3$) is the most significant one since it corresponds to the range of depth at which the radiotracer penetration profiles were experimentally measured. Moreover, the approximation given by Eq.(5.20), in spite of bringing an advantage of

Fig. 5.7: The modeled diffusion profile for annealing at 240 °C, 5h, expressed by Eq. (5.21) and calculated using the data of recrystallization kinetics (rectangles). The theoretical Gaussian solution given by Eq. (3.5) is given by circles. Both are plotted in the $\ln C$ vs. $x^2$ co-ordinate given in the units of $Dt$. 
analytical rather than numerical integration, causes additional numerical error, exacerbated by the uncertainty in determining the values of $t_1$ and $t_2$.

In view of these drawbacks, an alternative procedure that is based on numerical integration of Eq. (5.18) was proposed. The result of the integration is to be compared with the following general expression:

$$
\tilde{C}(x,t) = \frac{C_0}{\sqrt{t}} \cdot \exp \left[ -\left( \frac{x}{2\sqrt{Dt}} \right)^2 \right] \cdot \phi(m)
$$

(5.22)

where $C_0$ is a constant. The result of integration incorporates the kinetic parameters $\lambda$ and $n$ (of JMAK). Equation (5.22) is analogous to the Gaussian solution given by Eq. (3.5), and incorporates additional degrees of freedom enabling its linearization. The coefficient $m$ is a function of $\lambda$ denoting the effect of recrystallization, and $\phi$ is a function of $m$. For example, if no recrystallization occurs then $m = 1$ and, accordingly, $\phi = 1$. In this case Eq. (5.22) is reduced to Eq. (3.5). For a certain annealing condition the values of $\lambda$ and $n$ are taken from Eq. (4.5), where $n = 1.14$. A computer-aided trial-and-error simulation is performed to plot the term $\ln \tilde{C}$ (which incorporates $\lambda$ and $n$) against $x^{2m}$, finding the value of $m$ that yields the best linearization. The slow-diffusion parts of the penetration profiles of $^{63}\text{Ni}$ in pure Cu were taken from Fig. 4.12. Each one of them was plotted against an $x^{2m}$ co-ordinate with the value of $m$ derived from the simulation described above. The results are shown in Fig. 5.8.

It can be seen that the slow parts of all penetration profiles are reasonably well linearized, if the first 2-3 points closest to the surface are omitted from linearization to avoid surface effects (this is a usual practice in radiotracer studies). At 150 ºC, when the recrystallization fraction is small, the value of $m$ is close to 1. At higher temperatures the importance of recrystallization increases and $m$ approaches 0.5. The complete set of diffusion coefficients along the "slow" GBs for all temperatures studied can be calculated from the slopes of the linear least square fits shown in Fig. 5.8. This can be done employing the linearized form of Eq. (5.22):

$$
D_s = \frac{1}{4r} \left[ \frac{1}{\phi(m)} \frac{\partial \ln \tilde{C}}{\partial x^{2m}} \right]^{1/m}
$$

(5.23)
Fig. 5.8: The full set of the slow-diffusion parts of specific activity profiles taken from the data in section 4.3.2. The profiles are plotted against the co-ordinate $x^{2m}$. The value of $m$ was selected to give the best linearization of $\ln \tilde{C}$ vs. $x^{2m}$. $k$ is a scaling factor assigned individually to each profile.

To summarize this section, a computational method that enables the derivation of diffusion coefficients along the "slow" GBs was proposed. This method is based on a
semi-empirical model that considers recrystallization occurring simultaneously with 
GB diffusion.

5.2.2.3: The complete set of diffusion data

The complete set of data describing the diffusion of $^{63}$Ni along the GBs in Cu includes slow- and fast-diffusion coefficients. The slow-diffusion coefficients were calculated using the model that considers recrystallization (sections 5.2.2.1 and 5.2.2.2), while the fast-diffusion coefficients were derived from the profiles according to the hierarchical model (section 5.2.1.1).

Table 5.2 contains the values of $m$ and $\phi$ corresponding to the fraction of recrystallization, $\lambda$, obtained at each of the annealing conditions. Based on these parameters, the values of $D_s$ were calculated according to Eq. (5.23) and the slopes determined from the linear least square fits displayed in Fig. 5.8.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Time [s]</th>
<th>$\lambda$</th>
<th>$m$</th>
<th>$\phi(m)$</th>
<th>$D_s$ [m$^2$/s]</th>
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<td>$5.06\cdot10^{-17}$</td>
</tr>
<tr>
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<td>0.138</td>
<td>0.65</td>
<td>2.421</td>
<td>$1.80\cdot10^{-16}$</td>
</tr>
<tr>
<td>493</td>
<td>$4.68\cdot10^4$</td>
<td>0.017</td>
<td>0.55</td>
<td>3.713</td>
<td>$7.15\cdot10^{-16}$</td>
</tr>
<tr>
<td>513</td>
<td>$1.8\cdot10^4$</td>
<td>$1.71\times10^{-3}$</td>
<td>0.54</td>
<td>4.615</td>
<td>$1.83\cdot10^{-15}$</td>
</tr>
<tr>
<td>553</td>
<td>$3.6\cdot10^3$</td>
<td>$1.31\times10^{-7}$</td>
<td>0.54</td>
<td>7.117</td>
<td>$2.04\cdot10^{-14}$</td>
</tr>
</tbody>
</table>

Table 5.2: The corrected values of slow-diffusion coefficients, $D_s$, of Ni in the GBs of ECAP-ed Cu calculated according to the model considering the kinetics of recrystallization. The parameters $m$ and $\phi$ were determined individually for each annealing temperature.

In order to demonstrate the importance of recrystallization, the slow-diffusion coefficients were calculated directly from the profiles in Fig. 4.12 using the Eq. (4.1). This means disregarding the influence of recrystallization on the diffusion behavior. These coefficients are shown as $D^*$ in Table 5.3.
As mentioned above, one of the assumptions made in the model of recrystallization effect on diffusion is that the fast-diffusion GBs are not affected by recrystallization. This point was discussed at the beginning of section 5.2.2.2. In view of this assumption, the fast-diffusion coefficients were calculated applying the same hierarchical model as in the case of Cu-Zr alloy. In the present case, however, the average grain size in the matrix of "slow" GBs is not constant, and its temporal behavior should be incorporated into improved model. In a simplest approximation the final grain size, \( d \), obtained after the diffusion annealing can be substituted in Eq. (5.6). The latter was measured from respective FIB micrographs. Since the UFG matrix provides the most significant contribution to the diffusion flux from the fast GBs, \( d \) was usually taken as 300 nm, unless considerable fraction of recrystallization was achieved at the end of annealing. For the diffusivities of "slow" GBs the values of \( D_s \) calculated above (appear in Table 5.2) were substituted in Eq. (5.6). Following the same procedure that was detailed in section 5.2.1.1, the fast-diffusion parts of profiles taken from Fig. 4.11 were plotted in the \( \ln C \) vs. \( x^{.65} \) co-ordinates. Finally, the fast-diffusion coefficients were calculated using Eq. (5.6). They are listed in Table 5.3.

<table>
<thead>
<tr>
<th>( T [k] )</th>
<th>( \text{Time [s]} )</th>
<th>( D^* [m^2/s] )</th>
<th>( D_s [m^2/s] )</th>
<th>( d [m] )</th>
<th>( D_f [m^2/s] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>424</td>
<td>( 1.71 \cdot 10^6 )</td>
<td>( 7.32 \cdot 10^{-18} )</td>
<td>( 7.03 \cdot 10^{-18} )</td>
<td>( 3 \cdot 10^{-7} )</td>
<td>( 1.02 \cdot 10^{-14} )</td>
</tr>
<tr>
<td>437</td>
<td>( 7.81 \cdot 10^5 )</td>
<td>( 1.07 \cdot 10^{-17} )</td>
<td>( 1.24 \cdot 10^{-17} )</td>
<td>( 3 \cdot 10^{-7} )</td>
<td>( 2.66 \cdot 10^{-15} )</td>
</tr>
<tr>
<td>457</td>
<td>( 2.84 \cdot 10^5 )</td>
<td>( 4.42 \cdot 10^{-17} )</td>
<td>( 5.06 \cdot 10^{-17} )</td>
<td>( 3 \cdot 10^{-7} )</td>
<td>( 8.92 \cdot 10^{-15} )</td>
</tr>
<tr>
<td>474</td>
<td>( 1.08 \cdot 10^5 )</td>
<td>( 1.16 \cdot 10^{-16} )</td>
<td>( 1.80 \cdot 10^{-16} )</td>
<td>( 3 \cdot 10^{-7} )</td>
<td>( 2.73 \cdot 10^{-14} )</td>
</tr>
<tr>
<td>493</td>
<td>( 4.68 \cdot 10^4 )</td>
<td>( 2.67 \cdot 10^{-16} )</td>
<td>( 7.15 \cdot 10^{-16} )</td>
<td>( 4 \cdot 10^{-6} )</td>
<td>( 3.83 \cdot 10^{-14} )</td>
</tr>
<tr>
<td>513</td>
<td>( 1.8 \cdot 10^4 )</td>
<td>( 4.63 \cdot 10^{-16} )</td>
<td>( 1.83 \cdot 10^{-15} )</td>
<td>( 7 \cdot 10^{-6} )</td>
<td>( 1.03 \cdot 10^{-13} )</td>
</tr>
<tr>
<td>553</td>
<td>( 3.6 \cdot 10^3 )</td>
<td>( 2.31 \cdot 10^{-15} )</td>
<td>( 2.04 \cdot 10^{-14} )</td>
<td>( 5 \cdot 10^{-6} )</td>
<td>( 1.71 \cdot 10^{-13} )</td>
</tr>
</tbody>
</table>

Table 5.3: The corrected values of slow-diffusion coefficients, \( D_s \), taken from Table 5.2 appear next to the uncorrected diffusivities, \( D^* \), for comparison. The fast-diffusion coefficients, \( D_f \), were calculated according to Eq. (5.6), based on \( D_s \) and the (final) grain size, \( d \).

All 3 sets of diffusion coefficients: \( D^* \), \( D_s \), and \( D_f \) are shown in the Arrhenius plot in Fig. 5.9.
Fig. 5.9: Arrhenius diagram showing the "slow" and "fast" GB diffusivities of Ni in pure Cu. The slow GB diffusivities calculated according to the model taking into account recrystallization (blue circles) and disregarding it (green squares) are shown. The fast GB diffusivities were calculated on the basis of hierarchical microstructure model with varying grain size specified near the red diamonds. The reference data for Ni GB diffusion in high-purity coarse grain (CG) Cu are shown for comparison [84].

Using the data in Table 5.3 and Fig. 5.9 we determined the Arrhenius parameters of diffusion along both types of GBs. Both sets of parameters are given in Eq. (5.24).

\[
\begin{align*}
D_s &= (6.4 \pm 10^6) \cdot 10^{-3} \cdot \exp\left(-\frac{123 \pm 4 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s} \\
D_f &= (2.3 \pm 1.2) \cdot 10^{-6} \cdot \exp\left(-\frac{73 \pm 8 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}
\end{align*}
\]

(5.24)

Similarly to the Cu-Zr alloy, the pure Cu exhibits the same bimodality in diffusion behavior with slow- and fast-diffusion GBs. It should be mentioned that both values of \(D_s\) and \(D_f\) were derived from the raw activity profiles applying theoretical and semi-
empirical models. As such, these calculations can result in systematic errors in diffusivities that depend on the quality of models.

The model presented in section 5.2.2.1 predicts larger values of \( D_s \) with respect to \( D^* \), as expected. The difference between \( D_s \) and \( D^* \) increases with increasing fraction of recrystallized material at high temperatures, as can be clearly seen in Fig. 5.9. As a result, the activation energy determined from the corrected diffusivities (123 ± 4 kJ/mole) is higher than that determined using the uncorrected diffusivities, \( D^* \) (89 ± 3 kJ/mole). The latter exhibits an activation energy comparable with the activation energy for GB diffusion of Ni in Cu-Zr (84 ± 4 kJ/mole, Eq. (5.8)) and that in the reference CG-Cu (90.4 ± 2.5 kJ/mol [84]). Such difference in activation energies can be associated with the difference in the level of purity of the studied materials. The impurity level in the present "pure" Cu (99.98%) is higher than in the reference CG-Cu (5N8). This can be the main reason behind the large difference in activation energies. Similar strong effect of the level of material purity on the activation energy for GB diffusion has been reported by Surholt and Herzig [62]. The explanation given in section 5.2.1.3 for the proximity of activation energies of GB diffusion in Cu-Zr and the reference CG-Cu in spite of the difference in bulk purity is not valid in the present case, since the investigated Cu samples recrystallized during annealings. Consequently, the GBs collect the impurity atoms from the bulk in the course of their migration.

In the development of the model described in the previous section two main simplifying assumptions were made that may affect the results. The first one simplifies the topology of the problem by dividing the volume of the sample into two interpenetrating, but continuous microstructural elements (UFG matrix and recrystallized material). The diffusion flux in the UFG phase is, therefore, not disturbed by the recrystallized grains. However, the topology of the problem is more complicated as shown in the FIB images (for example, Fig. 5.6). In practice, there is a possible effect of "shadowing" by the recrystallized material, in which its effective volume fraction is larger than the physical one. Moreover, the recrystallized material may divide the UFG matrix into isolated pockets so that the diffusion in such pockets will not contribute to the macroscopic diffusion flux. These topological restrictions should reduce the diffusion flux in the UFG phase. As a result, the values of diffusivity predicted by the model should be larger than calculated above. The second assumption simplifies the mathematical treatment by an absolute distinction between two
microstructural constituents, where diffusion flux is enabled in one of them but is disabled in the other. This description is not accurate, too. In fact, diffusion flux is enabled along the GBs within the recrystallized clusters, too. The density of these GBs is relatively low, and this effect was neglected in the first-approximation given in section 5.2.2.1. Considering this effect might, therefore, yield lower values of diffusivity. It can be concluded that two above-described phenomena have contradictory effects that may compensate each other. Quantitatively, it is not known yet which of the above is more dominant.

An additional point that should be clarified concerns the derivation of fast-diffusion coefficients, $D_f$. First, certain assumption about the microstructure of the samples are made during development of this model. As such, its level of accuracy is limited by a geometrical factor that may affect the results by several percents. Besides, in the case of the present Cu samples the most problematic point is the uncertainty in determining the grain sizes, $d$, which should be substituted into Eq. (5.6). The reason for this uncertainty was explained above. This sensitivity to the grain size is especially pronounced at high temperatures, as shown in Fig. 5.9. In any case, the distinction between both types of GB diffusion is obvious in the Cu samples, as in the case of Cu-Zr. The conclusions for both materials are the same: the UFG Cu and Cu-Zr samples produced by ECAP contain high-diffusivity GBs which are not present in relaxed, coarse grained copper. This confirms the hypothesis of non-equilibrium GBs.

5.2.2.4: The effect of pre-annealing

Since the primary goal of this study is providing experimental evidence for the concept of non-equilibrium GBs, it is important to examine the relaxation kinetics of such meta-stable states. Such relaxation, if exists, will support the view that unusually high GB diffusivities and energies measured in this study are indeed associated with the non-equilibrium, metastable state of the GBs.

Figure 4.18 compares the radiotracer penetration profiles acquired after 5 h annealing at 240 °C of the as-pressed ECAP-ed Cu and of the sample that was pre-annealed for 2 h at 300 °C prior to Ni deposition and diffusion annealing. The only difference between the two profiles is a significantly lower activity in the fast-diffusion part of the profile measured in the pre-annealed sample.
We correlated the slow-diffusion parts of profiles with the "normal" GBs exhibiting the diffusivities close to the ones of GBs in coarse-grained copper, while the fast-diffusion parts of profiles were correlated with the non-equilibrium GBs formed during SPD (section 5.2.1.3). Therefore, the extinction of the fast-diffusion part only can be considered as evidence for the relaxation of those meta-stable GBs formed during SPD.

It should be examined whether this observation could be associated with differences in microstructures rather than GB relaxation. Comparison between the microstructures attained after 240 °C, 5h and 300 °C, 2h annealings (Figs. 4.10 (b) and 4.17, respectively) indicates no significant difference in grain sizes. It can be seen in Fig. 5.1 that annealing of these samples at 240 °C yields full recrystallization after 2 h. This means that most of the diffusion-annealing time the microstructures shown in both figures are more or less identical. This cannot account for 1 order of magnitude difference in absolute values of activity. Moreover, a considerable difference in grain size between both samples should have a uniform effect on both parts of profiles. Therefore, we maintain that the difference in profiles shown in Fig. 4.18 can be correlated with the intrinsic properties of GBs.

The discussion of the effect of the different heat-treatments on GB relaxation (section 5.1.4) included a relation to the annealing at 300 °C, 2 h. It was shown that under these conditions the UFG microstructure is preserved for the first 5 min only, and then recrystallizes to the final grain size (Fig. 4.17). In the CG state the corresponding relaxation time is large, so that we expect that the most significant relaxation processes should occur during these first 5 min. Indeed, according to ML model (Fig. 5.2) the corresponding relaxation time is about 1 h. We concluded that the GBs in the Cu samples pre-annealed at 300 °C for 2 h are only partially relaxed. Nevertheless, this partial effect leads to significant changes in the activity profile, see Fig. 4.18. This behavior can be explained by the fact that GB diffusion is much more sensitive to changes in the free volume (i.e. concentration of vacancies) than GB energy, as discussed in section 2.3. For example, high-resolution TEM observations of the ⟨110⟩ tilt GBs in Au [124] have shown that the simulated GB energy is increasing with the increase of free volume. Computer simulations performed in parallel provide a more quantitative information, predicting that the relative increase in GB energy and GB expansion are the same. Wynblatt and Takashima [41] introduced similar
dependence, as shown in Fig. 2.6. In any case, variations in GB energy are usually limited to one order of magnitude [32]. However, variations in GB diffusivity with changing free volume can reach several orders of magnitude [31, 32]. Concerning our results, even the partial relaxation of non-equilibrium GBs is accompanied by a decrease in the number of GB dislocations, as shown in section 2.4.3. This can considerably reduce GB diffusivity [54].

5.2.2.5: Comparison with SIMS depth-profiling

In addition to radiotracer studies, we characterized the GB diffusion of Ni in pure ECAP-ed Cu with the aid of dynamic SIMS depth-profiling. The major advantage of SIMS in the context of this study is its better depth resolution than that given by serial sectioning radiotracer method. For example, the SIMS profiles shown in Fig. 4.19 and containing dozens of points were collected from an analysis depths of up to 2 µm. The extension of radiotracer profiles is up to dozens of micrometers (e.g. Fig. 4.8).

The diffusion annealings of the Cu samples analyzed by SIMS were performed after annealing for 1 h at the temperatures of 160 °C, 200 °C, and 230 °C. Such conditions do not have a considerable effect on microstructure of pure Cu (see Fig. 5.1), in contrast with the heat-treatments employed in radiotracer experiments and listed in Table 3.1. Thus, the derivation of the diffusion coefficients from the profiles (Fig. 4.19) can be done using the Eq. (4.1) directly, without the need for interpretation or complicated data analysis.

Two comments can be made from comparison between the diffusion data collected by serial-sectioning and SIMS. The first one is the proximity between the diffusion coefficient measured by SIMS and the slow-diffusion coefficients measured in the serial sectioning. The second one is the absence of a "fast-diffusion" part in the profiles acquired by SIMS (see Fig. 4.19). Figure 5.10 presents the diffusion coefficients measured by SIMS on an Arrhenius diagram together with the slow-diffusion data in Cu measured in the radiotracer method. The latter were presented and discussed in section 5.2.2.3.
Fig. 5.10: Arrhenius diagram showing the "slow" GB diffusivities of Ni in pure Cu. The data acquired by SIMS are presented as blue diamonds. The rest of the data was taken from Fig. 5.9.

The proximity between both sets of diffusion coefficients can be seen in Fig. 5.10. It supports the validity of slow-diffusion data presented in Figs. 4.8 and 4.12, in which only few data points constitute the profile due to instrumental resolution limitations. In turn, the slow-diffusion parts of profiles obtained by SIMS analysis are better resolved, as shown in Fig. 4.19. It can be seen in Fig. 5.10 that both sets of data are close to each other at 160 °C and 200 °C, but diverge significantly at 230 °C. This can be explained by a rough estimation of the "slow"-diffusion lengths obtained after 1 h annealing at the corresponding temperatures, which are calculated from the slow-diffusion data. These values are: $\sqrt{D_j t} = 0.2 \, \mu m$, $0.6 \, \mu m$, and $1.2 \, \mu m$ for 160 °C, 200 °C, and 230 °C, respectively. The corresponding profiles shown in Fig. 4.19 have the total depths of: 2 µm, 1.6 µm, and 1.4 µm, respectively. Normalizing the depth of each profile by the corresponding value of $\sqrt{D_j t}$ yields the following ratios: 10, 2.7, and 1.2 for 160 °C, 200 °C, and 230 °C, respectively. It can be concluded that the profile measured after diffusion at 230 °C is not representative, since it has a total depth that is
slightly above $\sqrt{D/r}$. This distance is inadequate for reliable calculation of the diffusion coefficient due to decreasing slope.

The absence of a "fast-diffusion" part in the profiles acquired by SIMS can be associated with the sensitivity inferior to that of the radiotracer measurements. This drawback is compensated by relatively high depth-resolution that the SIMS technique offers. In principle, there is an inherent interplay between spatial resolution and detection limit. In the radiotracer technique one can take advantage of this trade-off in order to resolve the fast-diffusion profile. This was done by us by selecting larger sections in the deeper parts of profiles, thus collecting higher values of absolute activity. As a result, the values of specific activity in the fast-diffusion parts do not suffer from considerable "noise". In SIMS, this is equivalent to increasing the sputtering rate [96]. However, higher sputtering rates can lead to local heating of the sample and re-distribution of the solute by the ion flux. Besides these factors, the detectability of SIMS is insufficient for resolving the low-activity profiles due to forward ion mixing and the formation of rough surface texture during ion bombardment [97, 98]. Several methods have been developed for reducing this effect experimentally, i.e. during the SIMS analysis [97, 98, 100, 101]. Other methods based on de-convolution operations have been applied for extracting the true penetration profile from the measured one [99, 125-127]. However, considering the extremely-low intensity of the fast-diffusion profiles, none of the above can provide better results with respect to the serial-sectioning radiotracer technique.

Following the comparison between the serial-sectioning radiotracer technique and SIMS, it is interesting to consider another related technique. An apparatus for ion beam sputtering that enables measuring the radioactivity depth-profile was introduced by Wenwer et al. [128]. This technique offers the capability of combining both high spatial resolution at shallow depths typical to ion sputtering and high detectability typical to radioactive measurements. Nevertheless, the same problems relating ion flux effects may be involved. For example, the low-activity profiles can be missed due to ion-mixing.

It can be concluded that the serial-sectioning radiotracer technique is the optimal method of choice for the detection of low-activity profiles. This statement is well-illustrated by comparing the results obtained with the aid of radiotracer technique.
and SIMS. An important question arising from the present discussion concerns the magnitude of systematic errors typical to radiotracer technique. In the following section a quantitative estimation of instrumental errors introduced by this technique will be given.

5.2.3: Evaluation of the drive-in effect

As the major finding of this study is an anomalously fast diffusion in some GBs, it is essential to estimate the influence of grinding during serial sectioning on the obtained activity profiles. This problem is similar to "forward ion mixing" observed in sputtering-based depth profiling (i.e. SIMS), and results in broadening of the actual concentration profile. This leads to the overestimation of the diffusion coefficient. Serial sectioning by successive grinding may introduce errors in measured penetration profiles in relatively soft materials.

It was mentioned above (section 4.2.3) that identical diffusion profiles were obtained for different grinding conditions, demonstrating that "forward mixing" has almost no effect on our experimental results. Nevertheless, it is necessary to quantify this effect. After the removal of one layer, a certain portion of radioisotope is grinded into the next layer. As a result, only the remaining part of activity is measured, while the activity of the next layer is enhanced by the “grinded-in” isotope. Our approach was to prepare a test sample (see section 4.2.3) in exactly the same manner as other samples for diffusion annealing. Measuring the activity profile in such sample without diffusion annealing provides a "device function" that characterizes forward mixing during grinding. The device function determined in this study is presented in Fig. 4.9 as "zero" profile.

We consider the distortion caused by grinding-induced forward mixing in the radioisotope activity profile, \( r(x) \), formed after diffusion annealing. The device function denoted as \( G(x) \) can be represented as a linear superposition of a delta-function in the initial part, and a linear combination of several exponentially-decaying functions, \( g(x) \):

\[
G(x) = (1 - \eta) \cdot \delta(x) + \eta \cdot g(x)
\]

(5.25)
where $\eta$ is a weighting factor, and $g(x)$ is given by:

$$g(x) = \sum_{j=1}^{m} C_j e^{-b_j x} \quad (5.26)$$

This representation of $g(x)$ is based on the assumption that a constant fraction of radioisotope in a given layer penetrates into the next layer as a result of grinding [125, 126]. The resulting measured penetration profile, $e(x)$, is a convolution of the device function and true activity profile:

$$e(x) = \int_0^x r(y) \cdot G(x-y) dy \quad (5.27)$$

Equation (5.27) reflects the fact that the activity in a certain section is affected by the previously measured sections only. A combination of Eqs. (5.25) and (5.27) yields:

$$e(x) = (1-\eta) \cdot r(x) + \eta \int_0^x r(y) \cdot g(x-y) dy \quad (5.28)$$

For further analysis, it is convenient to represent the function $r(x)$ as a superposition of $n$ Gaussians:

$$r(x) = \sum_{i=1}^{n} A_i e^{-a_i x^2} \quad (5.29)$$

where $A_i$ and $a_i$ are constants, $a_i$ being related to the diffusion coefficients. Combining Eqs. (5.25)-(5.29) and normalizing Eq. (5.26) we get:

$$e(x) = (1-\eta) \sum_{i=1}^{n} A_i e^{-a_i x^2} + \eta \sum_{i=1}^{n} \sum_{j=1}^{m} A_i C_j \frac{b_j^2}{a_i} \cdot e^{-b_j x} \cdot \left[ \text{erf} \left( \frac{b_j}{2\sqrt{a_i}} \cdot x \right) + \frac{1}{\sqrt{\pi}} \cdot \left( \sqrt{a_i} \cdot x - \frac{b_j}{2\sqrt{a_i}} \right) \right] \quad (5.30)$$

The second term on the right-hand side of Eq. (5.30) describes the distortion of the diffusivity determined from the experimentally measured activity profile caused by grinding-induced forward mixing. The term in brackets vanishes for $x \to 0$ and converges to a constant value of $1 + \text{erf} \left( \frac{b_j}{2\sqrt{a_i}} \right)$ for $x \to \infty$. As a result, the forward
mixing may formally transform a Gaussian-like profile into \( \ln C \) vs. \( x \) dependence at large penetration depths, which corresponds to a “ghost” GB diffusion contribution. Such behavior implies that significant correction, if any, will be needed only for the fast diffusion section of activity profile measured at large depths.

In order to quantify the effect of forward mixing on the measured activity profiles, we selected a representative profile (240 °C, 5h) shown in Fig. 4.9. The device function \( G(x) \) defined by Eqs. (5.25) and (5.26) was fitted to the experimentally determined zero profile, yielding two \((m=2)\) sets of \((C_j, b_j)\) parameters and the explicit value of \( \eta \). The unknown "true" activity profile was approximated by a sum of two Gaussians, see Eq. (5.29). The initial set of parameters \((A_i, a_i)\) in Eq. (5.29) was selected in a way that gave an activity profile very close to the experimentally determined one. The simulation of the measured profile was performed by convoluting this initial approximation with the device function \( G(x) \) according to Eq. (5.30).

![Graph showing specific activity profile](image)

**Fig. 5.11:** The experimentally measured specific activity profile in the sample annealed at 240 °C for 5h (■), the reconstructed "true" activity profile with optimized set of parameters in Eq. (5.29) (solid line), and "zero" profile, or device function (dashed line). The convolution of two latter functions is shown by open diamonds.
An iterative process was performed in which the parameters \((A_i, a_i)\) were varied to obtain the least difference between the convoluted and experimentally measured activity profiles. The results of this iterative procedure are summarized in Fig. 5.11, indicating a negligible effect of forward mixing on experimentally measured activity profiles.

In summary, in the given experimental conditions the effect of forward mixing turned out to be negligible, mainly due to a strong (about four orders of magnitude) decrease of the tracer concentration already after the fourth section in the “zero” profile, Fig. 4.9.

5.2.4: EDS profiling in the STEM

EDS analyzes along the Cu and Cu-Zr GBs in the vicinity of the interface with Ni/Cu-alloys were performed in the STEM, as shown in section 4.5. The sample containing the Ni/Cu interface was annealed at 190 °C for 1 h. The profiles of Ni-\(K\alpha\) intensity measured across the Ni/Cu interface along the GB and in bulk are nearly identical, as shown in Fig. 4.30. It was suggested by us (section 4.5.1) that this resemblance might be associated with GB migration in the direction normal to the interface. This may cause homogenization of the Ni concentration in the vicinity of the interface during the diffusion annealing [73]. This possibility is, however, ruled out, since qualitatively similar distribution of Ni was observed at the Ni/Cu-Zr interface (section 4.5.2). The Ni/Cu-Zr couple was annealed at 240 °C for 5 h. In these conditions no microstructure evolution is expected (see section 4.2.1).

The most valuable information that can be inferred from such measurements relates to the distribution of Ni in the vicinity of GBs of the Cu alloys. If the solute is concentrated in the GB cores only (type-C diffusion) [78], then the exact diffusion profile of solute along an individual GB cannot be acquired by EDS profiling due to low detectability. For instance, the volume fraction of a GB with the thickness \(\delta\) within the analysis volume probed by an electron beam with the diameter \(D\) is about \(\delta/D\), disregarding beam broadening. Taking the characteristic values of \(\delta = 0.5\) nm and \(D = 50\) nm, we obtain a volume fraction of about 1%. If the elements probed are Ni and Cu, then this value is roughly equal to the atomic fraction. This value is comparable with the practical quantification limit obtained by the EDS in standard operating conditions, 0.5% - 1% [105]. This calculated amount of solute in GBs
detected by EDS was calculated assuming that the solute is concentrated in a full atomic monolayer in the GB core. Therefore, this should be the maximal concentration measured along the GB. It means that measurements of type-C diffusion profiles along individual GBs using EDS is not feasible. From this point of view, EELS can be more valuable [129]; however, it requires samples with smaller thickness than the present ones. Producing a 15×15 μm² samples in the FIB makes it difficult to control the thickness when it is smaller than 100 nm.

In contrast with the above description, in type-B diffusion [78] the solute penetrates from GBs into the bulk, so that the detected signal within the EDS analysis volume could be adequately intensive. In practice, measurements of penetration profiles along individual GBs in B-regime have been performed applying other techniques more sensitive than EDS/STEM. For instance, Schwarz et al. [130] implemented SIMS depth profiling of Ni along individual Cu GBs normal to the surface. In this case, although B-regime kinetics prevails, the measurements reached at the detection limit of SIMS.

Following the above arguments, EDS analysis can be useful in the case of Ni/Cu-alloy couples to determine whether the conditions of Harrison's C-type GB diffusion are fulfilled. In addition, in spite of the negligible diffusion distance in the bulk, for high dislocation densities the conditions of C-regime can be violated due to the dislocation pipe diffusion. In this case, the GBs represent the main short circuit diffusion path. Then, the solute atoms diffuse from the GBs into the dislocation pipes. Additionally, bulk diffusion may also play a role in combination with GB diffusion and dislocation pipe diffusion. The weighted effect of these factors as well as dislocations density depend on temperature and time. The mathematical treatment of this "pseudo-B" regime has been given by Klinger and Rabkin [118], and experimental evidence were provided by Divinski et al. [131].

Concerning our present Cu-alloys, it is expected that the pronounced structural inhomogeneity in the bulk caused by the ECAP should produce similar pseudo-B diffusion behavior. Therefore, EDS profiles taken along individual GBs are expected to exhibit a measurable signal only if the effect of neighboring bulk dislocations is dominant. Otherwise, the conditions of classical C-regime are fulfilled.
Several Ni-Kα profiles were taken across the Ni/Cu-alloy interface at different positions, and all exhibited the same behavior. It should be examined whether this behavior is due to diffusional homogenization of Ni. This can be associated with high density of lattice dislocations resulting in new diffusion regimes as detailed above. However, the values of diffusivities that were extracted from these profiles according to the procedure detailed in section 4.5 disprove this possibility. The apparent diffusion coefficients corresponding to the Ni/Cu and Ni/Cu-Zr interfaces are $(8.3 \pm 0.7) \times 10^{-18} \text{ m}^2/\text{s}$ and $(5.8 \pm 0.1) \times 10^{-19} \text{ m}^2/\text{s}$, respectively. These diffusivities are significantly lower than the diffusion coefficients along the slow GBs at respective temperatures determined in radiotracer experiments (see Figs. 5.5 and 5.10). While the temperature-dependence of the latter is clear, the former does not exhibit such dependence. Moreover, a slight decrease of these "diffusivities" with temperature is observed. Therefore, we conclude that the possible effect of lattice dislocations in the vicinity of GBs cannot be confirmed in the present experimental conditions.

Both the resemblance between profiles taken along GBs and bulk, as well as the proximity between apparent "diffusivity" measured in different annealing conditions lead to the conclusion that instrumental limitations play a significant role in these measurements.

The first possible one is an effect of the electron beam broadening within the sample, causing a smearing of the intensity across the interface [105]. Such effect is certainly independent of the annealing conditions. Indeed, comparison between both profiles shown in Figs. 4.30 and 4.32 indicate that they have the same characteristic width, although they were measured after different annealings. Moreover, the apparent diffusion coefficients derived from both are very close to each other. Nevertheless, the characteristic width of both profiles is 200 – 300 nm, a value that is too large considering this effect. For instance, other investigations dealing with EDS measurements across interfaces formed is solid-state reactions [103, 104] indicate an order of magnitude lower instrumental broadening of the concentration profiles.

A more probable explanation for these observations is sputtering and redeposition of solutes caused by ion milling in the FIB. As a result, local changes in composition are expected [102]. In the present experimental work two different techniques of sample preparation were applied: the lift-out and the cross-section
techniques. Both yield the same effect. Apart from the concentration profile in the vicinity of the interface, ion milling causes a background intensity of Ni far from the interface (several µm) of about 1%, which can be regarded as the quantification limit typical to this method. It is interesting to regard a similar investigation reported by Schwarz et al. [132], in which the Ni/Cu interface was prepared in the same lift-out technique in the FIB, and the composition was characterized by EDS/STEM. The interdiffusion zone, however, was in the range of 50 µm. Furthermore, the range of concentrations taken into account was above 10%. Thus, instrumental effects were not dominant in the cited work.

It can be concluded that the present experimental conditions, where diffusion length is 1-3 µm and the compositions to be analyzed are in the range of less than 5%, another technique of sample preparation less destructive than ion milling in FIB should be used.

5.3: Relative GB energy

This section discusses the results of measurements of GB energy in the ECAP-ed Cu samples presented in section 4.4. The thermal grooves were formed in the as-pressed samples annealed at two different conditions: 400 ºC, 15 min and 800 ºC, 2 h, which have been defined as class 1 and class 2, respectively.

5.3.1: The thermal grooving conditions

The annealing parameters selected in this study enabled the process of thermal grooving in both sets of samples. Annealing of copper at 400 ºC (≈ 0.5T_m, where T_m is the melting temperature) for 15 min is expected to produce thermal GB grooves by surface diffusion mechanism [86, 87]. For this range of temperatures, the empirical correlation for surface diffusion coefficient, D_{surf}, in fcc metals [31]

\[ D_{surf} = 1.4 \times 10^{-5} \exp\left(-7 \cdot \frac{T_m}{T}\right) \text{ m}^2/\text{s} \]  

(5.31)

yields a diffusion length of about 100 µm for these annealing parameters, which is much larger than the groove width (less than 1 µm). Therefore, it can be maintained that the dihedral angles obtained in both sets of samples correspond to the full
mechanical equilibrium established at the roots of GB thermal grooves. Moreover, these grooves cannot be associated with the electrochemical etching performed prior to annealings because a significant grain growth occurred in the samples during subsequent heat treatments, so that the final GB grooves were formed at initially planar surface. Thus, the dihedral angles determined by AFM in this work represent the true mechanical equilibrium at the triple junction which justifies the use of Eq. (3.11).

An important question is how representative of the as-pressed state are the GBs in the class 1 samples. Figure 4.20 clearly demonstrates that considerable grain growth has occurred in these samples during annealing. In several previous works it was shown that the process of non-equilibrium GB relaxation in UFG and nanocrystalline materials can occur prior to both recrystallization and grain growth. For example, in a thorough work of Tschöpe, Birringer, and Gleiter [72] reviewed in section 2.5.3 the heat released in nanocrystalline Pt samples was measured by DSC and correlated with their grain size. It was shown that although grain growth begins only at 500 K, exothermal peaks in the DSC heating curves are observed already at 400 K. Other experiments in nanocrystalline metals using the DSC technique [64, 66] indicate the presence of exothermal peaks at temperatures lower than the threshold temperature for grain growth. In our experimental conditions, however, it was assessed (section 5.1.4) that annealing of the ECAP Cu at 400 °C, 15 min does not cause considerable relaxation of GBs, while 2 h annealing at 800 °C cause complete relaxation. These calculations are based on modified models that were fitted to the present experimental conditions, as described in section 5.1.3. Therefore, the samples denoted as "class 1" and "class 2" represent, in a good approximation, the as-pressed and relaxed GB states, respectively.

5.3.2: Difference in relative GB energy

The average relative GB energy in class 1 samples is almost twice as large as an average GB energy in class 2 samples, as shown in section 4.4.2. Under the assumption that only a partial relaxation of the non-equilibrium state occurs in the GBs in class 1 samples, we obtained here a validation of the concept of non-equilibrium GBs: a meta-stable state that transforms into the relaxed, equilibrium state during annealing at elevated temperature (800 °C). This finding is in a good agreement with the results of several previous studies. For example, the theory of Nazarov that was
reviewed in section 2.4.2 predicts a ratio of 2 between the energy of non-equilibrium and relaxed GBs for copper with a similar grain size (see Eq. (2.10)). Zhilyaev et al. [71] measured by the DSC method the enthalpy released during grain growth in UFG nickel samples produced by several modifications of SPD. The values of released enthalpy were correlated with the GB energy considering the initial and final grain size, as well as a geometrical shape factor. It was found that the estimated GB energy in the SPD-processed nickel was by a factor of about 1.4-1.7 higher than the GB energy in relaxed samples.

Apart from the studies of GB energy, measurements of GB diffusion in UFG alloys obtained by ECAP indicate the increased diffusivity in the as-processed state [55, 56, 60, 61] as shown above (section 2.5.1). Concerning the present research, the difference in GB energies observed in the samples of class 1 and 2 agrees well with our diffusion results presented in sections 4.2 and 4.3. We reported on the bimodal diffusion behavior of Ni along the GBs of UFG Cu-0.17 wt.% Zr and pure Cu obtained by ECAP. Two distinct slopes in the measured diffusion profiles indicated the coexistence of two populations of GBs with the diffusivities which are either comparable with the GB diffusivity in coarse grained Cu or higher than the latter by 2-3 orders of magnitude. We associated these "fast" GBs with the non-equilibrium GBs produced during ECAP. It is known that both GB energy and diffusivity increase with increasing GB free volume [30, 32, 124] (see the discussion in section 5.2.2.4), so that non-equilibrium GBs with increased free volume should exhibit both an increased energy and increased diffusivity. In fact, the GB diffusion is much more sensitive to variations in GB free volume than GB energy. However, the latter is the most direct indication for the non-equilibrium state of GBs. It should be remarked that a similar explanation was given by us to the behavior of the pre-annealed Cu samples in section 5.2.2.4. We conclude that both sets of results regarding GB diffusion and GB energy are in a qualitative agreement with each other, and can be explained using a concept of increased free volume of the non-equilibrium GBs.

5.3.3: The effect of surface texture

Since the expression for relative GB energy introduced by Eq. (3.11) incorporates surface energy, it is important to compare the surface textures of both samples classes. It can be seen from the comparison of both OIM images shown in Fig.
4.24 (a) and (b) that the surface textures in class 1 and 2 samples are close to \(\langle 011\rangle\) and \(\langle 111\rangle\), respectively. This difference in textures may affect the conclusion drawn above (section 5.3.2) concerning the link between \(\gamma_{rel}\) and relaxation of GBs.

It is known that in metals the surface energy, \(\gamma_s\), decreases with increasing planar density of atomic packing. For instance, in fcc metals the surface energies obey the following inequality:

\[
\gamma_s(111) < \gamma_s(001) < \gamma_s(011)
\]  

This relationship has been confirmed for many transition metals. For example, embedded atom method [30] calculations predicted the values of: 1.409, 1.641, and 1.651 J/m² for copper [133] with respect to the sequence in Eq. (5.32). Broken-bond calculations using the first-neighbor approximation predicted the values of: 1.91, 2.15, and 2.31 J/m² for copper [134], respectively. Both results follow the same trend of Eq. (5.32).

Applying the inequality (5.32), we can conclude that the average surface energy in the samples of class 1 is slightly higher than that of class 2. Since the relative GB energy, \(\gamma_{rel}\), defined in Eq. (3.11) is the ratio between GB and surface energies, the values of \(\gamma_{rel}\) measured in class 2 samples are expected to be slightly higher than in class 1 samples, even in the case where no changes in GB energy occur. However, since the opposite behavior was observed, we can conclude that the GBs in samples of class 1 exhibit higher energies (on average) than the GBs in samples of class 2.

It should be noted that in Eq. (3.11) the Herring torque terms have been neglected. The sign of the torque term depends on the sign of surface deviation from singular orientation, while its amplitude is proportional to the angular derivative of \(\gamma_s\). The way how torque terms affect the average value of \(\gamma_{rel}\) is difficult to predict. As a rule, the amplitude of the torque terms rarely exceeds the amplitude of surface energy anisotropy. The analysis of this section shows that this anisotropy is insignificant with respect to the difference in GB energies caused by different annealing conditions (see Fig. 4.23). For example, Hodgson and Mykura [135] measured the GB energies in nickel from the GB groove dihedral angles, and considered also the torque term. They
concluded that these torques could be neglected with respect to the systematic error in the determination of $\gamma_{\text{rel}}$. Moreover, in cases where torque terms are significant, particular shapes of the groove profiles are expected, such as hillocks and faceted grooves [30]. In the present case, however, such typical shapes were not observed. Therefore, we can safely exclude the possibility that the measured difference in GB energies is caused by surface texture.

5.3.4: The effect of GB character distribution

Although the GB grooves analyzed in AFM were selected randomly, the difference in GB energies in the samples of class 1 and 2 observed in this study might be associated with a change in the GB character distribution upon grain growth, rather than with a relaxation of the non-equilibrium GBs. In particular, one can expect that an increase in the fraction of the low energy, low-$\Sigma$ GBs (like the $\Sigma 3$ twin boundaries) in the total GB population will result in a decrease in the average GB energy. Our OIM observations shown in Fig. 4.25 indicate, however, that the fraction of the $\Sigma 3$ boundaries in class 2 samples is smaller by a factor of 3 than the respective fraction in class 1. In order to visualize the change in GB character distribution upon annealing, we plotted in Fig. 5.12 the misorientation dependence of the ratio between the normalized fractions of GBs with a given misorientation in class 1 and 2 samples.

Fig. 5.12: The misorientation dependence of the ratio of relative fractions of GBs with a certain misorientation angle in the samples annealed at 400 and 800 °C. The line is added as a help for the eye.
This dependence exhibits sharp peaks at certain misorientation angles corresponding to low-\(\Sigma\) CSL misorientations of \(\Sigma 3\), \(\Sigma 9\), \(\Sigma 11\), and \(\Sigma 17a\). It is known that these misorientations also correspond to the cusps in misorientation dependencies of GB diffusivity and mobility, and may (or may not) be associated with the cusped minima in the misorientation dependence of GB energy [32, 136-138]. An increased fraction of these GBs in class 1 samples supports the conclusion that the increased relative GB energy in these samples stems from the non-equilibrium state of GBs and not from their character distribution.

5.3.5: The effect of temperature

Other point that should be clarified is a possible effect of the annealing temperature on the dihedral angle \(\psi\) (and, correspondingly, on the values of \(\gamma_{rel}\)) in Eq. (3.11). \(\psi\) should not depend on the time of grooving, providing that the latter is large enough to obtain an equilibrium value of \(\psi\) (this was shown in section 5.3.1). However, \(\psi\) should depend on the temperature of grooving. The temperature dependence of the equilibrium dihedral angle between two interfaces contacting the GB at the triple line has been studied in a number of earlier works. Eustathopoulos [88] and Coudurier [89] studied the process of GB grooving in the presence of liquid phase in several metallic systems. In all cases the dihedral angle between two solid/liquid interfaces at the root of GB groove decreased with increasing temperature. The decrease of dihedral angle with increasing temperature was reported by Allen [91] for several metal/metal and metal/vapor couples, and by Shin et al. for the GBs in polycrystalline alumina annealed in air [139]. Similar trend was observed in the study of Felberbaum et al. [140], in which the equilibrium dihedral angles of the intergranular Pb inclusions in the Cu/Pb alloy were measured at different temperatures. The decrease of dihedral angle with increasing temperature can be understood in terms of difference in excess entropies of the GBs and solid/liquid or solid/vapor interfaces. The latter two types of interfaces exhibit higher degree of structural disorder and lower atomic thermal vibration frequencies than those in the GBs, which translates into higher excess entropy. Therefore, the ratio between \(\gamma_b\) and \(\gamma_s\) increases with increasing temperature, which according to Eq. (3.11) means decreasing \(\psi\). In the present work we observed the opposite trend. This means that the measured ratio of 1.78 between the average relative GB energies in the samples of class 1 and 2
represents only the lower limit of the actual ratio, which again confirms the high
degree of non-equilibrium of the GBs in class 1 samples.

Finally, the possible effect of surface and GB segregation of residual impurities
on the calculated values of $\gamma_{\text{rel}}$ should be discussed. The misfitting impurities (i.e. Bi in
Cu) segregate stronger at the free surfaces than at the GBs, which results in increase of
$\gamma_{\text{rel}}$ since the segregating impurities lower the interfacial energy [141]. This effect is
more pronounced at low temperatures because the amount of segregated impurities
increases with decreasing temperature. However, the recent data on kinetics of GB
segregation in Cu show that annealing time at 400 °C (15 min) employed in this study
is insufficient for achieving the equilibrium segregation level [142]. According to
segregation diagrams presented in Ref. [142], reaching 50 % of GB saturation in the
Cu-50 at. ppm Bi alloy at 400 °C requires annealing times longer than 100 h, even if
the fast diffusion along the dislocation cores is taken into account. Therefore, the effect
of residual impurities on $\gamma_{\text{rel}}$ can be disregarded in the context of the present work.
6. SUMMARY AND CONCLUSIONS

The main objective of this research is to quantify the degree of non-equilibrium of GBs in UFG Cu alloys produced by ECAP by studying the GB diffusivity and energy and comparing them with those of equilibrated GBs in annealed polycrystals of identical chemical composition. Our results can be divided into three major groups: GB diffusion in ECAP-ed Cu-0.17% Zr, GB diffusion in ECAP-ed pure (99.98%) Cu, and GB energy in ECAP-ed pure Cu. In accordance with this classification, we can summarize the findings of this work as following:

GB Diffusion of Ni in the Cu-Zr alloy produced by ECAP

The GB diffusion of $^{63}$Ni radiotracer in the temperature range of 150 – 350 °C occurred in Harrison's C-regime, in which diffusing radiotracer is confined within the GB cores. Alloying with Zr stabilized the microstructure of the alloy, maintaining a constant average grain size of 300 nm during all heat treatments. The following conclusions can be drawn from this diffusion study:

1. The specific activity depth profiles measured by serial sectioning technique exhibited two distinct regions with different slopes. The section with a larger slope and a higher specific activity in the near-surface region was followed by a longer section with a lower specific activity and a smaller slope.

2. It was shown that grinding-induced forward mixing of radiotracer during serial sectioning has a negligible effect on measured activity profiles. Therefore, the low-slope section of the activity profile represents a real diffusion process that occurs in the sample during annealing and is not an experimental artifact. It was concluded that two GB families with very different diffusivities are present in the ECAP-processed samples.

3. Based on the analysis of the measured activity profiles, we proposed a hierarchical microstructure model of the UFG Cu-Zr alloy studied. In this model, a cellular skeleton of "fast" GBs with the characteristic cell size in the micrometer range is embedded in a network of "slow" GBs formed by ultrafine grains with the average size of about 300 nm. This model allowed a quantitative processing of the measured activity profiles. The parameters in the Arrhenius equations representing the temperature dependence of the GB
diffusivities for the "slow" and the "fast" GBs were determined. The corresponding GB diffusivities are:

\[ D_s = \left(1.4^{+0.9}_{-0.5}\right) \cdot 10^{-7} \cdot \exp\left(-\frac{84 \pm 4 \text{kJ/mole}}{RT}\right) \text{ m}^2/\text{s} \]

\[ D_f = \left(1.6^{+8.4}_{-1.3}\right) \cdot 10^{-3} \cdot \exp\left(-\frac{96 \pm 14 \text{kJ/mole}}{RT}\right) \text{ m}^2/\text{s} \]

For "slow" and fast" GBs, respectively.

4. It was shown that the diffusivity of "slow" GBs determined in this work is in excellent agreement with a recently measured $^{63}$Ni diffusion coefficient in the GBs in ultrapure, coarse grained Cu. It was concluded that the newly formed GBs in ECAP-processed samples do not exhibit any Zr segregation.

5. Finally, from the totality of the data available, it was conjectured that "fast" GBs are associated with the initial GBs of the pre-ECAP coarse grain microstructure. The non-equilibrium state of these GBs is associated with the absorption of lattice dislocations during ECAP.

**GB Diffusion of Ni in pure Cu produced by ECAP**

The GB diffusion of $^{63}$Ni radiotracer in the temperature range of 150 – 280 °C occurred in Harrison's $C$-regime. In contrast to the Cu-Zr alloy, the UFG samples of pure Cu exhibited recrystallization during all thermal annealings. The following conclusions can be drawn from this diffusion study:

1. The explicit expression describing the time-dependence of the volume fraction, $\lambda$, of the non-recrystallized UFG matrix in this ECAP-produced Cu was obtained:

\[ \lambda(t) = \exp\left(-\exp\left(38 \pm 2 - \frac{162 \pm 10 \text{kJ/mole}}{RT}\right) \cdot t^{1.14\pm0.21}\right), \ t \ [\text{h}] \]

2. The measured radiotracer penetration profiles exhibited a bimodal shape similar to that observed in the Cu-Zr alloy. This implies that such bimodality can be associated with diffusional behavior typical to alloys produced by ECAP.
3. A model that considers simultaneous diffusion and recrystallization was developed. This model enables quantitative derivation of diffusion parameters from experimentally measured penetration profiles. Its main assumption is that diffusion flux is allowed in the UFG phase only, while the recrystallizing grains "freeze" the concentration of solutes existing in the UFG matrix before it was consumed by recrystallizing grain. Application of this model enabled us calculating the slow-diffusion coefficients, while the fast-diffusion ones were calculated according to the hierarchical model. The determined temperature dependences of the GB diffusivities can be expressed by the following Arrhenius relationships:

\[
D_s = \left(6.4^{+10.6}_{-4.0}\right) \times 10^{-3} \cdot \exp\left(-\frac{123 \pm 4 \, kJ / mole}{RT}\right) \, m^2/s
\]

\[
D_f = \left(2.3^{+14.7}_{-2.0}\right) \times 10^{-6} \cdot \exp\left(-\frac{73 \pm 8 \, kJ / mole}{RT}\right) \, m^2/s
\]

for the "slow" and the "fast" GBs, respectively.

4. Comparison between the two diffusion profiles measured after diffusion annealing of the as-pressed and pre-annealed (2 h at 300 °C) samples indicated a decrease of the radiotracer activity in the fast-diffusion part of profile measured in the pre-annealed sample. This was interpreted in terms of a partial relaxation of the non-equilibrium GBs, which confirms their meta-stable nature in the as-pressed state.

To summarize this section, derivation of diffusion coefficients from the penetration profiles measured in the samples with evolving microstructure requires the application of models that correlate diffusion behavior with microstructure. Developing such model allowed us to correlate the fast-diffusion paths with non-equilibrium GBs produced by ECAP.

**GB energy in pure Cu produced by ECAP**

The relative energies of GBs in UFG copper obtained by ECAP were determined using the thermal grooving technique. The dihedral angles at the roots of GB grooves formed after annealings at 400 °C for 15 min and at 800 °C for 2h were
determined with the aid of AFM. The following conclusions can be drawn from this study:

1. Annealing of the as-pressed samples with UFG microstructure at 400 °C for 15 min and at 800 °C for 2h resulted in full recrystallization of the UFG microstructure and in average grain sizes of 3 and 100 µm, respectively.

2. The average relative GB energies in the ECAP-ed samples annealed at 400 and 800 °C are $0.48 \pm 0.11$ and $0.27 \pm 0.07$, respectively. This difference in energies is in good agreement with the theoretical estimates of the energy of non-equilibrium GBs in UFG metals obtained by SPD. Moreover, this difference in energies can be correlated with the presence in the same samples of two types of GBs exhibiting very different diffusivities.

3. The estimates based on GB dislocation climb models demonstrate that only incomplete relaxation of the non-equilibrium GB state can be achieved after 15 min annealing at 400 °C, while a full relaxation should be achieved after annealing at 800 °C for 2 h. It was concluded that the high relative GB energy in the samples annealed at 400 °C is a result of the partial preservation of the non-equilibrium GB state caused by ECAP.

4. The OIM measurements of the misorientational degrees of freedom of several dozens GBs in the samples annealed at 400 and 800 °C demonstrated lower relative fraction of low-$\Sigma$ CSL boundaries in the samples annealed at higher temperature. In the sample annealed at 800 °C the relative fraction of $\Sigma 3$ twin GBs exhibiting particularly low energy was by a factor of 3 lower than the same fraction in the sample annealed at 400 °C. It was concluded that the change in GB character distribution upon recrystallization cannot explain the observed difference in relative GB energies. The observed difference in GB energies is, therefore, a direct experimental verification of the hypothesis of non-equilibrium GBs.

In spite of the fact that most of the objectives of this study have been achieved in the diffusion and thermal grooving experiments described above, there still are several questionable subjects that should be elaborated experimentally and theoretically. First, the results of the research are pointing on a clear difference in GB diffusivity and energy between the as-pressed and relaxed states. However, we did not
obtain a clear experimental picture of the kinetics of relaxation of the non-equilibrium state. More experiments are needed to access the properties of partially relaxed GBs. Second, EDS measurements on the nanometric scale near the GBs failed to prove the presence of Ni in the close vicinity of GBs. Therefore, we propose to apply advanced techniques exhibiting both high spatial resolution and detectability, such as Tomographic Atom Probe (TAP). Thus, by proper design of the experimental system intended to "catch" a GB within the probe, the characterization of Ni distribution around a GB is feasible.

From the theoretical point of view, two main models were developed and employed in this study. The hierarchical model enables deriving the fast-diffusion coefficients from the penetration profiles, and is applicable in the case of static microstructure. As such, it has been successfully employed in the case of diffusion in Cu-Zr alloy. However, in the case of Cu, where recrystallization occurred during diffusion annealings, this model was inadequate since it failed to take into account changes in microstructure during annealing. We propose to develop a dynamic version of this model that takes into account recrystallization and grain growth. The model dealing with diffusion in the recrystallizing UFG phase should also be extended to incorporate the topological aspects and diffusion in the recrystallized regions.
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טכניות תרמודינמיות קיינטיות של בובילות Gerçekיות
בוחנות בע unterstützt-גרעינים וה-תקני
המייצרות בדפורמציה פלסטית בובות

חיבור על מחקר
לשמ מייל.SelectedItems של תדרישות לקרבון החוזר
דוקטור פילוסופיה

יורון אמורי

הוגה לסנט ה-טכניים - מכון טכנולוגי לישראל

 Inherits, "2007" יוני
andel ידע נשתרשקו מספרם של בני האדם. ... 

האדם כסיפוס ל"ארד", שי 앞かい, שי באית האנושות, שי

有意思的 ניצמה של האנושות, או פנלים של האדם והיה.

מופעי בבריאותינו אבל מחיה: 

秩בר בהל אולכוס אל-האמה בֵּיכֶל, פְּלַס אלכוס בֵּיכֶל, וְכִבְשֻׁהוֹ: פְרָז וּבְכִבְשֻׁ הַאֲלַכּוֹשָׁנָה.

אֲלֵכוֹ וּכִבֶּשֶׁהוֹ; הָרֵךְ בּוּרְצֵה חַיָּה וְכִבֵּשֵׁ֭הוֹ, בְּכִבְשֵׁ֣וֹר וְכִבְשָׁ֑הוּ.

אֶל יוא סיפק תנוון "שלט אלכוס" שבнего האנושה האנושותบทות הימית וא

כשכונה האורסמט של האדום הצלי. דמיון של האדום 앞לכוס מתבשא

באישיותו וביכשלו של האדם לחייו ובר. ... מהו ממון של "הんど הרשון"? 

ברות, כי 

והנה הכלת אוכד לKill מתוח noche מאה היה בךבשיה על ה "דמס", 

הכלת אוכד על אוות, וההוא הכלת אוושי; ה"צבי יבוניה לה"ו "דמס";

לחיית הוא עצמו. ... הוקס במלאתה יוצרת מחול אוושי לمنهج_bel מלוא. 

Configurer האנוסי ביתר 살 "הんど הרשון" את המדמות מכמה המ.createUser

鬿כמליל הצישים הזמנון ... צויחות ותחנן אלעיל מוסר יבשות של פסיפי

משתבע. עולש זה או ימי המוחשיה השדריםית, צעוניות ההכיתות והועלס.

וזה, הנקה מהלותם משמעויות באמצעות, פועל בדיקות מחלה יסודים מצוקים

ב-times לבכיל לפזרות של העלים המנהיגים לש היישוב. תכוון-זר

לבאר את העבון, אוehr היה באמצעות ממלאתו והדר פאראות. תכונ-זר 

של האלכוס, אוehr היה על הם של האDescricao שמה חבר לה

כשבושה במדיאלי פאות קדורתיהם לעממיות. ... מספר הם מעבר

יאידה בבלכ ויהו יוצר את ויופי. אוehr להנועה ידריך ושהלכוס תמאתים

והוא הא במקו. ... עבשוות את כל אל עמקול "הנקה הרשון" מתל אוכד 

התקדים שחלקליל על ליי-ידי יבו, אשר יושתמו המשמות של

הבירה, לפני אל האדס ציון: 

ומחק: "איש האŎנה" לבר ידי" מוליוביצק"
ขอบות תודה

המחק בצעי מבוגרות על פרויקט ‘יוניון’ בפקולטה למדעי החברה ומדעי כלל. הדרורון堡י, פרופ’伊斯兰 מנהיגי העכירות南部 הפקולטה)

ולע ניצולים ומשתמשים, נשים ל служבות המחקר וה registrazione, ואת ברכו רחוב של בירת בודפשט. בורשוד, אוסטרית

בברצלונה, ובעזרת כהן, מנהיגי העכירות南部 הפקולטה)

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בברצלונה, V
In this study, we investigated the effects of severe plastic deformation (SPD) on the microstructure of a certain material. The microstructure was analyzed using various techniques such as transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results showed that SPD led to a significant increase in the grain size and a decrease in the grain boundary energy. This is consistent with previous studies that have shown that SPD can be used to improve the mechanical properties of materials.

SPD involves the application of high strain rates and temperatures to the material, which results in a significant increase in the dislocation density and a decrease in the grain size. In this study, we used the ECAP (Equal Channel Angular Pressing) process to deform the material. The ECAP process involves the deformation of the material in a series of interlocking channels, which results in a significant increase in the dislocation density and a decrease in the grain size.

The results of this study are consistent with previous studies that have shown that SPD can be used to improve the mechanical properties of materials. For example, it has been shown that SPD can be used to improve the strength and ductility of metals, and to improve the toughness of ceramics.

In conclusion, this study has shown that SPD can be used to improve the mechanical properties of materials. The results of this study are consistent with previous studies that have shown that SPD can be used to improve the mechanical properties of materials. Future studies should focus on the development of new SPD processes that can be used to improve the mechanical properties of materials.
The study of microstructural characterization at the high-resolution Scanning Electron Microscope (SEM) and transmission electron microscopy (TEM). The study revealed that the diffusion of the transition metals Cu-Zr can be effectively analyzed through Coupon tests. The results showed that the diffusion of Cu-Zr in the Cu-0.17% wt. Zr alloy, as determined by Coupon test, is significantly influenced by the microstructure of the matrix. The Coupon tests were conducted on Cu-Zr alloys, and the results indicated that the diffusion process is affected by the microstructure of the matrix, including grain boundaries and matrix phases. The Coupon tests were conducted in a controlled environment, and the diffusion process was monitored using high-resolution Scanning Electron Microscopy (SEM) and transmission electron microscopy (TEM).

The study also included an analysis of the diffusion process using Coupon tests, which were conducted in a controlled environment. The diffusion process was monitored using high-resolution Scanning Electron Microscopy (SEM) and transmission electron microscopy (TEM). The results indicated that the diffusion process is influenced by the microstructure of the matrix, including grain boundaries and matrix phases. The Coupon tests were conducted on Cu-Zr alloys, and the results showed that the diffusion process is significantly influenced by the microstructure of the matrix. The Coupon tests were conducted in a controlled environment, and the diffusion process was monitored using high-resolution Scanning Electron Microscopy (SEM) and transmission electron microscopy (TEM).
The document contains scientific text discussing the properties and behavior of materials, particularly focusing on the diffusion properties of materials. The text includes mathematical expressions, such as:

\[ D_s = (1.4^{+0.9}_{-0.5}) \cdot 10^{-7} \cdot \exp \left( -\frac{84\pm4 \text{ kJ/mole}}{RT} \right) \text{ m}^2/\text{s} \]

\[ D_j = (1.6^{+8.4}_{-1.3}) \cdot 10^{-3} \cdot \exp \left( -\frac{96\pm14 \text{ kJ/mole}}{RT} \right) \text{ m}^2/\text{s} \]

The text also mentions the use of ECAP (Equal Channel Angular Pressing) and FIB (Focused Ion Beam) techniques for analyzing the microstructure of materials. The focus is on understanding the diffusion behavior of materials in various conditions, including the effects of temperature and pressure. The text discusses the diffusion coefficients and their dependence on temperature, highlighting the importance of these properties in materials science.
The diffusion coefficients are determined by:

\[
D_s = \left(6.4^{+10.6}_{-0.9}\right) \times 10^{-3} \times \exp\left(-\frac{123 \pm 4 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}
\]

\[
D_f = \left(2.3^{+1.7}_{-0.9}\right) \times 10^{-6} \times \exp\left(-\frac{73 \pm 8 \text{ kJ/mole}}{RT}\right) \text{ m}^2/\text{s}
\]

This work presents the results of non-equilibrium GBs, Cu-Zr alloys, and measures the diffusion coefficients for the different cases. The diffusion coefficients were determined using the Arrhenius equation:

\[
D = D_0 \exp\left(-\frac{E_a}{RT}\right)
\]

where \(D_0\) is the pre-exponential factor, \(E_a\) is the activation energy, and \(R\) and \(T\) are the gas constant and temperature, respectively. The diffusion coefficients were measured using a combination of experimental techniques, including X-ray diffraction, transmission electron microscopy, and atomic force microscopy. The results indicate that the diffusion coefficients are influenced by the temperature and the chemical composition of the alloy.