Multiple dispersed phases in a high-strength low-carbon steel: An atom-probe tomographic and synchrotron X-ray diffraction study

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The co-precipitation of Cu, M₂C (where M is any combination of Cr, Mo or Ti) and austenite (face-centered cubic) is characterized for 5 h isochronal aging times by synchrotron X-ray diffraction and three-dimensional atom-probe tomography for a high-strength low-carbon steel, BlastAlloy 160. High number densities, \( \sim 10^{23} \text{ m}^{-3} \), of co-located Cu and M₂C precipitates were observed. Only small austenite volume percentages (<2.1%) were measured after aging at temperatures up to 625°C for 5 h.

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Strength and toughness generally have an inverse relationship in steels. It is therefore difficult to obtain steels that have both a high yield strength and a high impact toughness. Some demanding applications, such as pipelines and reactors, require just such a combination of properties. Naval applications also demand high-strength and excellent ductility and toughness for formability and explosion resistance. Additionally, naval steels must possess good weldability, which requires a high-strength low-carbon (HSLC) steel. HSLC steels have excellent weldability due to their low carbon content [1]. Such demanding mechanical properties are not met by normal steels. BlastAlloy (BA) 160 [2,3] is a HSLC steel that is designed to meet naval requirements. To achieve a 160 ksi (1103 MPa) yield strength, it employs Cu and M₂C (M is any combination of Cr, Mo, Ti and V) precipitation strengthening. Cu precipitation strengthening has been studied extensively in Fe–Cu alloys [4–6] and in HSLA steels [7–10] but not in BA160. M₂C precipitation occurs in quenched and tempered martensitic steels and also creates a toughness increment due to cementite dissolution by M₂C precipitation [11]. M₂C precipitation has been characterized in ternary Fe–Mo–C and Fe–W–C alloys [12], in high-performance, high Ni-Co alloy steels [13–17] and in high-speed steels [18] but not in BA160. Atom probe work on M₂C and other carbides is reviewed in Ref. [19].

To meet high toughness requirements, BA160 was designed to take advantage of transformation-induced plasticity (TRIP). TRIP is plastic deformation that is achieved by a phase transformation. Interaction of this transformation plasticity with fracture-controlling processes, such as shear localization, can delay shear instability and fracture to higher strains, resulting in enhanced toughness [20]. TRIP is usually accomplished through the transformation of austenite (face-centered cubic (fcc)) to martensite (body-centered tetragonal (bct)). Austenite or γ-Fe is the high temperature fcc Fe phase. The volume fraction and stability of γ-Fe are critical for determining the toughness increase due to TRIP [21]. Some γ-Fe is retained after thermomechanical processing, but more is needed for a toughness increment due to TRIP. Additional more stable dispersed γ-Fe can be precipitated in a controlled manner by reheating the steel into the γ + α (body-centered cubic (bcc)) two-phase field. Retained and precipitated γ-Fe morphologies have been studied in steels [22–24].

Although these different types of precipitates have received attention in other steels, the precipitation of all three phases in BA160 has been little studied [2,25]. The research presented herein characterizes precipitation of all three phases after isochronal aging using three-dimensional (3-D) local-electrode atom-probe (LEAP) tomography and synchrotron X-ray diffraction (XRD).

The composition of BA160 is given in Table 1. BA160 steel is formed into 8 in. (20.5 cm) ingots by vacuum induction melting and vacuum arc remelting. The ingots
are then homogenized at 1204 °C for 12 h and hot rolled to ~1.7 in. (4.3 cm) plates at 1093 °C. The plates are normalized at 910 °C for 1 h, annealed at 482 °C for 10 h, and then finished turned to 1.625 in. (4.128 cm) diam. rods. The rods are machined into Charpy V-notch blanks and then solutionized at 900 °C for 1 h and water quenched. The blanks are then submersed in a liquid nitrogen bath for 30 min to eliminate as much retained austenite as possible. The Charpy blanks are then finish-machined and aged at 475, 500, 525, 550, 575, 600 or 625 °C for 5 h.

Charpy tests were conducted at room temperature according to ASTM E23 standards. Three samples were tested for each aging condition and the values reported are average values. Samples for hardness testing and LEAP tomographic analyses were cut from the ends of the broken Charpy bars. Hardness samples were mounted and polished to 1 μm. The microhardness values presented are averages of 20 indentations per sample.

LEAP tomographic specimens were prepared from the broken Charpy samples by cutting them to 0.3 × 0.3 mm² rods and electropolishing using a dual-step process at room temperature. The electrolytes were the standard 10% perchloric in acetic and 2% perchloric in butoxyethanol solutions.

LEAP tomography was conducted employing either laser or voltage pulsing modes. Pulsed-laser LEAP tomography was performed using 0.75 nJ pulse⁻¹, and a pulse repetition rate of 250 kHz. Pulsed-voltage LEAP tomography was conducted using a pulse fraction (pulse voltage/steady-state DC voltage) of 20%, a pulse repetition rate of 200 kHz, and a specimen temperature of 60 ± 0.22 K.

Cu precipitates were identified using the envelope method [26]. The parameters used were a maximum separation distance of 0.5 nm, a minimum of 30 solute atoms and a grid resolution of 0.12 nm. The precipitate radii were determined from the number of atoms in the precipitates, \( n \), employing:

\[
R = \left( \frac{3n}{4\pi\rho\xi} \right)^{\frac{1}{3}},
\]

where \( \rho \) is the atomic number density of the precipitate, 80 atoms nm⁻³, which is approximately the density of Fe, bcc Cu and \( \text{M}_2\text{C} \), and \( \xi \) is the detection efficiency, ~50%.

\( \text{M}_2\text{C} \) precipitates are first identified using 1 at.% C isoconcentration surfaces. \( \text{M}_2\text{C} \) precipitates are small (~2 nm in radius or less) and suffer from severe local magnification effects. Therefore, higher concentration isosurfaces will not identify them with reasonable statistics. The atomic contents interior to the isoconcentration surfaces are then analyzed similarly to the Cu precipitates. The average radii, \( \langle R_{\text{M}_2\text{C}} \rangle \), reported are also equivalent spherical radii calculated using Eq. (1).

Although the \( \text{M}_2\text{C} \) precipitates are not spherical, equivalent spherical radii allow for an easier comparison with the Cu precipitate data. Equivalent spherical radii also decrease sensitivity to field-evaporation artifacts, which affect Cu and especially \( \text{M}_2\text{C} \) precipitates. Volume fractions for both Cu and \( \text{M}_2\text{C} \) precipitates were determined by dividing the number of atoms in the precipitates by the total number of atoms in the analyzed volume, because all the involved phases have similar atomic number densities.

XRD characterization was performed utilizing synchrotron radiation at the Advanced Photon Source. Specimens were scanned for 3 s per data point using 0.01° 20 steps. Specimens were rotated about the specimen holder axis and rocked 0.75° in each direction step⁻¹ to obtain better averaging. The \( \gamma \)-volume fractions were determined using the direct comparison method [27] employing a NIST standard.

Figure 1 displays the evolution of the hardness and toughness of BA160 resulting from isochronal aging. The toughness increases and the hardness, which is related to yield strength, concomitantly decreases with increasing aging temperature. The maximum microhardness measured was 403 ± 12 VHN for the sample aged at 475 °C for 5 h. The samples aged at 525 or 550 °C for 5 h exhibit room temperature Charpy impact energies of 183 ± 8 and 205 ± 28 J, respectively, while maintaining microhardness values of 370 ± 10 and 348 ± 10 VHN, respectively. Atom probe tomography (APT) analyses were performed on samples aged at 525 and 550 °C because they exhibit desirable hardness–toughness combinations. Limited analyses were also performed on the sample aged at 625 °C for 5 h.

Figure 2 displays a 3D-APT reconstruction for the sample aged at 525 °C for 5 h. The blue dots represent Fe atoms, while the red and black surfaces represent 10 at.% Cu and 1 at.% C isoconcentration surfaces, respectively. The Cu precipitates are spheroidal, whereas

**Table 1. BA160 composition.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (wt.%)</td>
<td>Bal</td>
<td>6.76</td>
<td>3.33</td>
<td>1.89</td>
<td>0.63</td>
<td>0.06</td>
</tr>
<tr>
<td>Concentration (at.%)</td>
<td>Bal</td>
<td>6.42</td>
<td>2.85</td>
<td>1.98</td>
<td>0.36</td>
<td>0.26</td>
</tr>
</tbody>
</table>

![Figure 1. Charpy impact energy vs. Vickers microhardness (VHN) at different isochronal aging temperatures for 5 h, as indicated.](image)
the $\text{M}_2\text{C}$ precipitates have a rod-like morphology. Figure 2 shows that nearly all of the $\text{M}_2\text{C}$ precipitates are co-located with Cu precipitates. This is probably due to heterogeneous nucleation of $\text{M}_2\text{C}$ on Cu precipitates co-located with Cu precipitates. This is probably due to the smaller number densities of Cu and $\text{M}_2\text{C}$ [25]. Table 2 gives the precipitation parameters for the Cu and $\text{M}_2\text{C}$ precipitates. The error shown is 2 standard deviations. Both types of precipitates achieve high number densities, $\sim 10^{23} \text{ m}^{-3}$.

The value of $(R)$ of Cu or $\text{M}_2\text{C}$ precipitates increases and their number densities decrease with increasing aging temperature. These trends are due to the decreased Cu and C supersaturations at higher temperatures. The volume fraction of Cu precipitates after aging at 550 °C is larger than the value after aging at 525 °C, suggesting that Cu precipitation is incomplete after aging at 525 °C for 5 h. The Cu concentrations at the centers of the larger Cu precipitates are greater than 90 at.% Cu, which does not change significantly with aging temperature for this aging time, 5 h. The error for $(R_{\text{M}_2\text{C}})$ for $\text{M}_2\text{C}$ precipitates reflects the wide distribution of $\text{M}_2\text{C}$ radii. The smaller hardness value observed after 550 °C aging as compared to 525 °C aging is due to the smaller number densities of Cu and $\text{M}_2\text{C}$ precipitates and further tempering of the martensitic matrix.

Two Cu precipitates were observed in the 3-D APT reconstructions of samples aged at 625 °C for 5 h due to a smaller Cu precipitate number density. Both precipitates were plate-shaped rather than spheroidal, indicating that they transformed to fcc Cu and grew anisotropically. The Cu precipitate number density after aging at 625 °C for 5 h is $\sim 10^{21} \text{ m}^{-3}$.

Figure 3 displays the γ-phase volume percentage as a function of aging temperature. Very little austenite precipitation occurs below 600 °C. The maximum austenite volume percentage measured is 2.1 ± 0.4% after aging for 5 h at 625 °C. It is possible that preferred orientation effects could skew these results, but regardless of these effects, the amount of austenite measured is still ~2% even after 5 h at 625 °C. This contrasts strongly with the 10% equilibrium prediction determined [3] using the ThermoCalc [28] SGTE/SSOL database at 490 °C due to the high Ni content (6.42 at.%) of the steel. This indicates that (i) the kinetics of austenite precipitation is relatively slow even at 625 °C, and/or (ii) ThermoCalc is inaccurate at predicting austenite phase fractions at low temperatures for the available databases.

XRD does not provide any morphological information on the austenite. Figure 4 shows, however, a possible austenite precipitate found by 3-D APT. Figure 4 also presents compositional analysis of the precipitate employing the proximity histogram method [29]. The distance from the interface on the ordinate refers to distance from a 12 at.% Ni isoconcentration surface, which was chosen because it is approximately the inflection point of the Ni concentration, as seen in the proximity histogram. The strongly enhanced Ni concentration (16.4 ± 0.2 at.% in the precipitate vs. 5.42 ± 0.1 at.% in the matrix) suggests, but does not prove, that the precipitate is austenite since Ni is an austenite stabilizer. The elements Ni, C and Cu partition strongly to the austenite, with partitioning ratios of 3.04 ± 0.05, 5.08 ± 0.54 and 3.95 ± 0.28, respectively. The Ni, C and Cu concentrations in the austenite are 16.44 ± 0.2, 0.25 ± 0.02 and 1.35 ± 0.04 at.%, respectively. The partitioning ratios of Cr and Mo are 1.21 ± 0.04 and 1.1 ± 0.1, respectively, showing insignificant partitioning of these elements. The exact $R$ value of the austenite precipitate is unknown because it is not fully contained in the analysis volume, but the precipitate is at least $52 \times 29 \times 15 \text{ nm}^3$. It does not prove or disprove the existence of smaller austenite precipitates, but it does prove the existence of larger austenite precipitates after aging at 625 °C for 5 h.

In summary, the precipitation of three different phases was characterized in BA160 steel after isochronal aging. The average radii, number densities and volume

Table 2. Cu and $\text{M}_2\text{C}$ precipitation parameters.

<table>
<thead>
<tr>
<th>Aging condition</th>
<th>525 °C for 5 h</th>
<th>550 °C for 5 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu precipitate average radius (nm)</td>
<td>3.2 ± 2.5</td>
<td>4.1 ± 3.3</td>
</tr>
<tr>
<td>Cu precipitate volume percent</td>
<td>2.3 ± 0.5</td>
<td>3.4 ± 0.6</td>
</tr>
<tr>
<td>Cu precipitate number density ($\times 10^{23} \text{ m}^{-3}$)</td>
<td>1.1 ± 0.3</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>$\text{M}_2\text{C}$ precipitate average radius (nm)</td>
<td>1.27 ± 1.25</td>
<td>1.5 ± 1.8</td>
</tr>
<tr>
<td>$\text{M}_2\text{C}$ precipitate volume percent</td>
<td>0.26 ± 0.06</td>
<td>0.26 ± 0.06</td>
</tr>
<tr>
<td>$\text{M}_2\text{C}$ precipitate number density ($\times 10^{23} \text{ m}^{-3}$)</td>
<td>1.67 ± 0.38</td>
<td>0.85 ± 0.17</td>
</tr>
</tbody>
</table>
fractures of Cu and M2C precipitates were measured after aging at 525 or 550 °C for 5 h. High number densities, ~10^23 m^-3 of both Cu and M2C precipitates, were measured and account for maintaining the microhardness after aging. Nearly all of the M2C precipitates are co-located with Cu precipitates, suggesting heterogeneous nucleation. Limited austenite precipitation is observed below 600 °C, and even after aging at 625 °C for 5 h the measured austenite volume percent is only 2.1 ± 0.4%. This contrasts strongly with equilibrium thermodynamic predictions [3]. A study of the concentration of an austenite particle revealed strong partitioning of Ni, Cu and C to austenite.

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References


