Interfacial segregation at Cu-rich precipitates in a high-strength low-carbon steel studied on a sub-nanometer scale

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Abstract

The local composition of small, coherent Cu-rich precipitates with a metastable body-centered cubic structure in a ferritic \(\alpha\)-Fe matrix of a high-strength low-carbon steel was studied by conventional atom-probe tomography. The average diameter, \(D\), of the precipitates is \(2.5 \pm 0.3\) nm at a number density of \((1.1 \pm 0.3) \times 10^{24}\) m\(^{-3}\) after direct aging at 490 °C for 100 min to a near-peak hardness condition, yielding a value of 84 Rockwell G. Besides Cu, the precipitates contain 33 ± 1 at.% Fe and are enriched in Al (0.5 ± 0.1 at.%). Nickel and Mn are significantly segregated at the \(\alpha\)-Fe matrix/precipitate heterophase interfaces. The Gibbsian interfacial excesses relative to Fe and Cu are 1.5 ± 0.4 atoms nm\(^{-2}\) for Ni and 1.0 ± 0.3 atoms nm\(^{-2}\) for Mn. The reduction of the interfacial free energy, calculated utilizing the Gibbs adsorption isotherm, is 16 mJ m\(^{-2}\) for Ni and 11 mJ m\(^{-2}\) for Mn.

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Keywords: Interface segregation; Gibbsian interfacial excess; Ferritic steels; Precipitation hardening; Nanostructure

1. Introduction

Copper precipitation plays an important role in the hardening of high-strength low-carbon steels [1–4]. The formation of Cu-rich precipitates during thermal aging has been studied by many techniques: atom-probe field-ion microscopy (APFIM) [5–12], small-angle neutron scattering (SANS) [8,13,14], high-resolution and conventional electron microscopy (HREM and CTEM) [15–17], theoretical modeling [13], and computer simulation [18]. APFIM, HREM, CTEM, and SANS studies indicate that small Cu precipitates have, at diameters less than about 5 nm, a metastable body-centered cubic (bcc) structure and are coherent with the ferritic \(\alpha\)-Fe matrix [5,14–17]. In the 5–10 nm diameter range, the precipitates transform to a 9R structure [15–17], and eventually, at even larger diameters, gradually into the stacking-fault-free face-centered cubic (fcc) equilibrium structure of pure Cu.

Interfacial segregation of Ni and Mn at the \(\alpha\)-Fe matrix/precipitate interfaces has been observed by APFIM for Cu precipitates 5–10 nm in diameter in Fe–Cu–Ni and Fe–Cu–Ni–Mn alloys [7–9,19]. At this size, however, the precipitates are larger than the critical diameter for transformation and loss of coherency of about 5 nm, and thus likely have transformed to a 9 R or faulted fcc structure and are no longer bcc and coherent with the \(\alpha\)-Fe matrix. After neutron irradiation, Ni and Mn have also been found, employing APFIM and atom-probe tomography (APT), to be enriched in the interior and in the vicinity of smaller Cu-rich clusters and precipitates in nuclear pressure vessel steels and model alloys [9,19–24]. Thermodynamics, kinetics, loss of coherency, and structural transformation behavior under neutron irradiation, however, are considerably different from the case of thermal decomposition. There is little quantitative information about the segregation of solute atoms at the interfaces of coherent bcc Cu-rich precipitates smaller than 5 nm in diameter in thermally aged alloys. We address this question employing APT to investigate Cu-rich precipitates in a newly developed high-strength low-carbon steel. A formalism is

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presented to describe quantitatively segregation by extracting the relative Gibbsian excess, which is the relevant thermodynamic quantity to measure segregation at an interface in a system with more than two components, from local compositions measured by APT.

Cu-rich precipitates are studied in a newly developed Mo- and Cr-free low-carbon steel with an excellent tensile strength, up to 700 MPa (100 ksi). A Charpy V-notch test impact fracture toughness of 64 J (47 ft lb) at −40 °C was obtained for specimens aged to a near-peak hardness condition with a yield stress of 712 MPa [3,25–28]. For a version of this steel with 0.1 wt.% Ti added, the Charpy fracture energy at −79 °C was greater than 360 J (264 ft lb), since the specimen bent without breaking in the Charpy apparatus [26]. Commercial Cu precipitation-hardened steels need to contain Ni to prevent segregation of Cu to grain boundaries and thus prevent hot-shortness, that is, crack formation during hot rolling, and Mn additions to getter sulfur impurities. From a technological point of view steels need to contain Ni to prevent segregation of Cu to grain boundaries and thus prevent hot-shortness, that is, crack formation during hot rolling, and Mn additions to getter sulfur impurities. From a technological point of view Cu alloyed steels containing Ni and Mn are of significant interest. Essentially the steel was developed by eliminating the Mo and Cr from the U.S. Navy’s high-strength low-carbon HSLA 100 steel and optimizing the precipitation-hardening process [25].

The APT analyses presented here reveal a significant interfacial segregation of Ni and Mn at coherent bcc Cu-rich precipitates with an average diameter, \( D \), of 2.5 ± 0.3 nm. The Gibbsian interfacial excesses relative to Fe and Cu, determined by the methodology introduced in Section 2.2, are 1.5 ± 0.4 atoms nm\(^{-2}\) for Ni and 1.0 ± 0.3 atoms nm\(^{-2}\) for Mn.

2. Methods

2.1. Experimental procedures

The steel was fabricated at the Ispat-Inland Inc. Research Center, East Chicago, Indiana. A 45.5 kg (100 lb) laboratory heat was vacuum induction melted, cast into molds, hot rolled to 13 mm thick plates, and air cooled. Subsequent hot rolling to 2.5 mm was followed by a cold rolling step to the final thickness of 1.6 mm. The average composition of this steel, as provided by the Ispat-Inland Inc. Research Center, East Chicago, Indiana. A 45.5 kg (100 lb) laboratory heat was vacuum induction melted, cast into molds, hot rolled to 13 mm thick plates, and air cooled. Subsequent hot rolling to 2.5 mm was followed by a cold rolling step to the final thickness of 1.6 mm. The average composition of this steel, as provided by the Ispat-Inland Inc. Research Center, is given in Table 1. Following an austenitization treatment at 1100 °C for 0.5 h, the specimens were quenched directly from this temperature to different aging temperatures and aged for 100 min [3]. Direct aging was conducted for a fundamental study of the nucleation and growth of precipitates in this steel [3,4].

The hardness was measured as an indicator for strength and to track the course of the precipitation. A Rockwell hardness tester was utilized, applying a 10 kg minor load, 150 kg major load, and a 1.6 mm ball corresponding to the Rockwell G scale. At least five hardness measurements were recorded for each sample tested, with the average being logged as the actual hardness value, and the standard deviation as the uncertainty of that value.

FIM tips were prepared by electropolishing, using initially a solution of 10 vol.% perchloric acid in acetic acid at 20 V dc at room temperature, and then a solution of 2 vol.% perchloric acid in butoxyethanol at 15–12 V dc at room temperature for the final tip preparation.

Conventional APT analyses were performed at a residual pressure of 3 × 10\(^{-8}\) Pa, utilizing a pulse–voltage-to-dc–voltage ratio of 20% at a pulse repetition frequency of 1500 Hz. Visualization and data evaluation of the three-dimensional atom-by-atom datasets were performed with custom software, ADAM 1.5, developed at Northwestern University [29]. Composition profiles with respect to distance from the α-Fe matrix/precipitate heterophase interface were obtained with ADAM 1.5 using the proximity histogram method or proxigram for short [30,31]. A 10 at.% Cu isoconcentration surface served as a reference surface for the proxigram analysis. This concentration threshold provided a reliable and topologically stable representation of the precipitates, that is, the changes of the morphology, size, and number of the precipitates were small when varying the threshold around 10 at.% Cu. Isoconcentration surfaces were generated with ADAM 1.5 employing the adaptive marching cube algorithm. The parameters used to obtain a noise-free isoconcentration surface in ADAM 1.5 were a voxel size of 0.8–1.0 nm and a delocalization distance of 1.0 nm [32]. No additional noise suppression was applied, that is, the confidence sigma parameter of ADAM 1.5 [29–32] was kept at a value of zero.

The diameter, \( D \), of a precipitate containing \( n \) atoms in the reconstruction was equated to the diameter of the volume equivalent sphere:

$$ D = \left( \frac{6 n \Omega}{\pi f} \right)^{1/3}, \quad (1) $$

where the atomic volume, \( \Omega \), is equal to 1.178 × 10\(^{-2}\) nm\(^3\) for bcc Fe, and the overall detection and reconstruction efficiency, \( f \), is estimated to be 0.6. The number of atoms, \( n \), belonging to a precipitate was determined employing the envelope method [33], based on clusters with more than 20 Cu atoms separated not farther than a maximum separation distance of 0.5 nm and employing an envelope grid spacing of 0.15 nm.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Nb</th>
<th>Mn</th>
<th>Cu</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>0.59</td>
<td>0.49</td>
<td>0.079</td>
<td>0.49</td>
<td>1.37</td>
<td>0.82</td>
<td>0.034</td>
<td></td>
</tr>
<tr>
<td>Balance</td>
<td>0.27</td>
<td>0.97</td>
<td>0.047</td>
<td>0.50</td>
<td>1.20</td>
<td>0.78</td>
<td>0.07</td>
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</table>
2.2. Determination of the relative Gibbsian excess of solute at an interface

At constant temperature and pressure, the Gibbs adsorption isotherm for a planar heterophase interface in a system with two phases, \( \alpha \) and \( \beta \), and \( n \geq 3 \) components is \([34]\)

\[
\frac{d\sigma}{d\mu_i} = -\sum_{i=3}^{n} \Gamma_{i}^{(\text{relative})} d\mu_i, \tag{2}
\]

where \( \sigma \) is the interfacial free energy, \( \mu_i \) the chemical potential of component \( i \), and the relative Gibbsian interfacial excess of component \( i \) is given by

\[
\Gamma_i^{(\text{relative})} = \Gamma_i - \Gamma_1 \left( \frac{c_1^\alpha c_1^\beta - c_1^\beta c_1^\alpha}{c_1^\alpha c_1^\beta - c_1^\beta c_1^\alpha} \right) - \Gamma_2 \left( \frac{c_2^\alpha c_2^\beta - c_2^\beta c_2^\alpha}{c_2^\alpha c_2^\beta - c_2^\beta c_2^\alpha} \right), \tag{3}
\]

where \( c_i^k \) is the concentration of component \( i \) in phase \( k = \alpha, \beta \). The quantity \( \Gamma_i^{(\text{relative})} \) is independent of the position of the dividing interface \([35]\) and can be calculated employing Eq. (3) from the measured Gibbsian excesses, \( \Gamma_i \), obtained for a specific choice of the position of an interface. The values \( \Gamma_i \) are determined utilizing proxigram concentration profiles for a specific interface \([30,31]\) from

\[
\Gamma_i = \rho \Delta x \sum_{m=1}^{n} (c_m^i - c_k^i), \tag{4}
\]

where \( \rho \) is the known atomic density, \( \Delta x \) is the distance between the \( p \) concentration data points in the proxigram, and \( k = \alpha \) on the matrix side and \( k = \beta \) on the precipitate side of the heterophase interface. The determination of interfacial excesses \( \Gamma_i \) for one-dimensional concentration profiles across grain boundaries in a two-component system by a similar method has been discussed elsewhere \([36,37]\).

One advantage of writing the Gibbs adsorption theorem in the form of Eq. (2) is that the \( (n-3) \) values of \( d\mu_i \) \((i = 3, \ldots, n)\) can be varied independently, and therefore a coefficient for the reduction of the interfacial free energy at a respective chemical potential, \( \mu_i \), is given by

\[
\frac{\partial \sigma}{\partial \mu_i} \bigg|_{T,p,\rho_1,\ldots,\rho_{n-1},\rho_n} = -\Gamma_i^{(\text{relative})}. \tag{5}
\]

This coefficient can be obtained directly from the interfacial excesses, \( \Gamma_i^{(\text{relative})} \), determined from Eq. (3). Using Henry’s law for dilute solutions, Eq. (5) can be rewritten in the form

\[
\frac{\partial \sigma}{\partial c_i} \bigg|_{T,p,\rho_1,\ldots,\rho_{n-1},\rho_n} = -kT \frac{\Gamma_i^{(\text{relative})}}{c_i}, \tag{6}
\]

which is used to determine the coefficient of interfacial energy reduction at a concentration \( c_i \) due to segregation of component \( i \) at the heterophase interface, with a Gibbsian interfacial excess \( \Gamma_i^{(\text{relative})} \).

3. Results

Fig. 1 displays an isochronal hardness curve for 100 min of direct aging at each different temperature. The maximum value for the hardness is 85.2 \( \pm \) 0.1 Rockwell G, which is obtained at an aging temperature of 500 \( ^\circ \)C. Each hardness value is the average of five independent measurements, and the error is the standard deviation of the five values. A near-peak hardness condition with a high number-density of nanometer-sized precipitates was studied by conventional APT. The Cu-rich precipitates formed during aging at 490 \( ^\circ \)C for 100 min are distinctively visible in a three-dimensional atom-by-atom reconstruction, Fig. 2, displaying the positions of individual Cu atoms in the analysis volume.

The spatial distributions of the solute components Cu, Ni, Si, Al, and Mn are shown in the three-dimensional reconstructions in Fig. 3, representing a subset of the data of Fig. 2, containing three Cu precipitates. It is seen qualitatively that Ni, Al, and Mn are enriched at the locations of the Cu-rich precipitates. When interpreting Fig. 3, however, account must be taken of the fact that the reconstruction represents atomic density rather than concentration. In fact, during field evaporation, the precipitates develop a surface slightly recessed with respect to the average curvature of a tip’s surface, that is, a surface with a larger radius of curvature, since Cu has a lower vaporization field (30 V nm\(^{-1}\)) than does Fe (36 V nm\(^{-1}\)) \([38]\). Consequently, atoms field-evaporating from the Cu-rich precipitates are projected toward the detector at a lower magnification than atoms field-evaporated from the \( \alpha \)-Fe matrix. This causes an apparent higher atomic density for the precipitates than the matrix in the three-dimensional reconstruction, since the parameters used for the reconstruction are calibrated with respect to the \( \alpha \)-Fe matrix. Fortunately, this effect affects only the two lateral dimensions of the reconstruction. The third dimension, the depth, vertical in Fig. 2, is not affected and the precipitates therefore appear slightly elongated along this direction. This distortion of a reconstructed Cu
precipitate in an $\alpha$-Fe matrix, resulting from this local magnification effect, has been investigated in greater detail employing computer simulation [39].

To determine the average precipitate diameter, $\langle D \rangle$, independently of the distortions due to the local magnification effect, the diameter of a volume equivalent undistorted sphere is calculated from the number of atoms in each precipitate employing Eq. (1). Only precipitates fully contained in the reconstruction volume, that is, which are not cut by the surface of the reconstructed volume, are taken into consideration. The average diameter is $\langle D \rangle = 2.5 \pm 0.3$ nm. At this diameter, the precipitates are expected to have a metastable bcc structure and to be fully coherent with the $\alpha$-Fe matrix.

The reconstructed volume displayed in Fig. 2 contains 30 Cu-rich precipitates, of which 15 are cut by the surfaces of the reconstruction volume. Counting the cut precipitates as one-half, a number density, $N_v$, of $(1.1 \pm 0.3) \times 10^{24}$ m$^{-3}$ is obtained.

The proxigram method [30,31] is used to determine both matrix and precipitate composition and interfacial segregation. Since the proxigram measures compositions with respect to distance from an isoconcentration surface, with no restrictions on the morphology of a precipitate, the elongated shape of the precipitates due to the local magnification effect does not affect their measured composition. Likewise, for the proxigram, it does not matter if a precipitate is cut by the surface(s) of the reconstructed volume. Isoconcentration surfaces drawn at the 10 at.% Cu level are used to delineate the Cu-rich precipitates and to define the origin of the proxigram, serving as a fiducial mark for measuring distances into a precipitate (positive values) and $\alpha$-Fe matrix (negative values). Fig. 4 displays the proxigram concentration profiles for an individual precipitate. The center region of this precipitate is represented by the last data point on the right-hand side of the diagram (positive distances) and is enriched in Cu to 69 ± 4 at.%, Fig. 4(b), and contains 29 ± 4 at.-% Fe, Fig. 4(a). Nickel and Mn are enriched in the interfacial region near the origin of the diagram, Fig. 4(c) and (d), with peak concentrations of 2.8 ± 0.4 at.-% Ni and 2.6 ± 0.4 at.-% Mn, respectively, which is a significant enrichment by a factor of 3 and 5, respectively, with respect to the $\alpha$-Fe matrix concentrations of 0.95 and 0.55 at.%. The precipitate contains 0.5 ± 0.2 at.-% Al, averaged from the last two data points in Fig. 4(e), which is an enrichment by a factor of 10 with respect to the $\alpha$-Fe matrix concentration of only 0.05 at.-% Al.

To improve the statistics and to extract quantitative average values for concentrations and interfacial excesses, a proxigram of all precipitates in the reconstructed volume, Fig. 2, was calculated and is displayed in Fig. 5. Since all precipitates are enveloped by a 10 at.% Cu isoconcentration surface, the proxigram corresponds to a weighted superposition of concentration profiles across the interfaces of all precipitates, with all profiles aligned with the 10 at.% Cu level at the origin of the integral proxigram. A complete set of phase concentrations for all elements for Cu-rich precipitates and the ferritic $\alpha$-Fe matrix derived from Fig. 5 is provided in Table 2. The center region of the precipitates,
that is, the plateau region consisting of the last two data points at the right-hand side of Fig. 5, has an average Cu concentration of 64.0 ± 1.0 at.% and an average Fe concentration of 33 ± 0.9 at.%%. These concentrations are very close to the ones given above for a single precipitate. An Fe concentration this high in precipitates with \( \langle D \rangle = 2.5 \pm 0.3 \text{ nm} \) or less is consistent with previous atom-probe studies [6,7] of Cu-rich precipitates of similar size in thermally aged alloys. SANS experiments, however, indicate that precipitates with \( \langle D \rangle \) larger than 1 nm are essentially devoid of any Fe [13,24], even though some Fe (\(~10\text{ at.}%\)) can obviously not be accounted for by the SANS technique, as discussed in [24]. The Ni and Mn
concentrations in the centers of the precipitates, 1.2 ± 0.2 at.% Ni and 0.76 ± 0.16 at.% Mn, are not strongly enhanced with respect to the α-Fe matrix concentrations of 0.95 ± 0.01 at.% Ni and 0.55 ± 0.01 at.% Mn, respectively. Aluminum, however, is, as noted above for a single precipitate, strongly enriched, by a factor of 10, in the interior of the precipitates with 0.50 ± 0.10 at.% Al in the precipitate center versus 0.047 ± 0.003 at.% Al in the α-Fe matrix. The core of the Cu-rich precipitates is depleted in Si, with a core concentration of 0.60 ± 0.14 at.% Si versus a matrix concentration of 0.99 ± 0.01 at.%.

An α-Fe matrix/precipitate interface location is indicated in Fig. 5 by the vertical line. The interface position is arbitrarily chosen at the location with the mean value of matrix and precipitate Cu concentration, and thus it is not identical with the origin of the proxigram. As discussed previously, relative interfacial excesses, Γ\text{relative}^i, are independent of the specific position of the dividing interface. Also, because of the possibility of an ion trajectory overlap effect, due to the reduced local magnification, the interface may appear broader in the proxigram concentration profile than in reality. Any artificial intermixing across the heterophase interface that results in a linear superposition of matrix and precipitate atoms does not, however, affect the individual interfacial excesses, Γ\text{i}, since the matrix and precipitate concentrations are used as reference concentrations, which are subtracted in Eq. (4). Nickel and Mn show significant segregation peaks at the interface with concentrations of up to 2.5 at.% Ni and 1.8 at.% Mn, respectively, Fig. 5(c) and (d), corresponding to enhancement factors of 2.6 for Ni and 3.3 for Mn.

Interfacial excesses, Γ\text{i}, are determined from the area under the concentration curves as plotted in Fig. 5, employing Eq. (4), the precipitate and matrix concentration values given in Table 2, and the atomic density of Fe (85 nm\textsuperscript{-2}). Significant positive relative Gibbssian interfacial excesses with respect to Fe and Cu, Γ\text{relative}^i, exist for Ni (1.5 ± 0.4 atoms nm\textsuperscript{-2}) and Mn (1.0 ± 0.3 atoms nm\textsuperscript{-2}). When normalized by the atomic density of a (110) lattice plane of the ferritic α-Fe matrix, 17 atoms nm\textsuperscript{-2}, these values correspond to cumulative projected excesses of 0.09 ± 0.02 monolayers (ML) for Ni and 0.06 ± 0.02 ML for Mn. The normalization of the Gibbssian excess to units of ML, however, does not imply that the solute atoms are actually located in one atomic layer. Aluminum has only a slight tendency to segregate at the interface, with an excess of 0.24 ± 0.23 atoms nm\textsuperscript{-2} (0.01 ± 0.01 ML), and Si, if there is an interaction with the interface at all, has a slight tendency toward depletion at the interface with a negative excess of 0.10 ± 0.11 atoms nm\textsuperscript{-2} (0.006 ± 0.006 ML). Segregation and depletion at an interface are thermodynamically both possible, according to the Gibbs adsorption isotherm.

4. Discussion

While Al segregates only weakly at the α-Fe matrix/precipitate heterophase interface, if at all, it is strongly enriched in the inner portions of the precipitates, 0.5 ± 0.1 at.% Al, compared with a value of only 0.047 ± 0.003 at.% Al in the α-Fe matrix. These values of matrix and precipitate concentrations, \(c_m\) and \(c_p\), result in a partitioning ratio, \(K = c_p/c_m\), of \(K = 10 ± 2\). A value of \(K\) this large indicates a strong attractive interaction for Al atoms in bcc Cu. The binary Al-Cu system possesses a stable bcc Cu(Al) solid solution phase in the concentration range 18–29.4 at.% Al [40] with a lattice parameter of 0.29564 nm [41]. This indicates that Al additions stabilize thermodynamically the bcc Cu phase, even though fcc Cu can dissolve up to 19.7 at.% Al [40]. Knowledge of this stabilizing effect of Al on bcc Cu precipitates may be of technological importance for optimizing the beneficial effects of bcc Cu precipitates in steels.

Niobium and C are not present in the entire three-dimensional reconstruction displayed in Fig. 2. This is consistent with the formation of large niobium carbide precipitates, at a number density below 10\textsuperscript{22} m\textsuperscript{-3}, which is too small a value to be detected by the random-area analysis technique employed by conventional APT. Niobium carbide precipitates are detectable using a selected area analysis approach [42] and by LEAP\textsuperscript{TM} tomography.

Next, we discuss the consequences of limited solid-state diffusion for the kinetics of precipitation and interfacial segregation. The three-dimensional root-mean-squared (RMS) diffusion distance is \(\langle x^2_D \rangle = 6 D_X t\), where \(D_X\) is the impurity diffusivity of the solute species at 490°C and \(t\) is time; for impurity diffusion of atomic species \(X\) in ferromagnetic α-Fe the values are listed in Table 3 [43–48]. The three-dimensional RMS diffusion distance calculated for Cu, 6.2 nm, is almost identical to half the average surface-to-surface inter-precipitate spacing

\[ \langle S \rangle = \left( \frac{3}{4\pi N} \right)^{-1/3} \left( \frac{1}{2} \langle D \rangle \right) \]
of 6.1 nm. This implies that the diffusion zones of neighboring precipitates overlap and the formation of C-rich precipitates has proceeded past the growth stage. Hence, the decomposition reaction is most likely in the growth and coarsening regime. The three-dimensional RMS diffusion distance for Ni, 8.6 nm, is slightly larger, and the ones for Al (39 nm), Mn (23 nm), and Si (35 nm) are much larger than the diffusion distance of Cu, implying that Ni, Al, Mn, and Si can redistribute on a length scale that is larger than that for Cu.

For a discussion of a possible kinetically induced, diffusion-limited interfacial segregation due to solute pile-up in front of the moving matrix/precipitate interface, we use the one-dimensional RMS diffusion distance, \( \sqrt{D X t} \text{,} \) which provides a conservative estimate for a comparison with the extent of the interfacial segregation zone measured in the proxigram concentration profile because the atoms are diffusing in three dimensions, since the proxigram folds the three-dimensional precipitate geometry into a one-dimensional profile [30]. The one-dimensional RMS diffusion distances of the solute elements (see Table 3) is 3.6 nm for Cu, 5.0 nm for Ni, 22 nm for Al, 13 nm for Mn, and 20 nm for Si. All these diffusion distances are significantly larger than the spatial extent of the zone of interfacial segregation of 1–2 nm, and, consequently, solute diffusion in the matrix is sufficient to establish at the least local metastable equilibrium, and thus the solute enrichment at the precipitate interfaces is not dominated by a diffusion-limited pile-up effect in front of the moving interface of a growing precipitate. A thermodynamic driving force must therefore exist for the observed interfacial segregation.

For a discussion of a potential elastic interaction between solute atoms and the \( \alpha \)-Fe matrix/precipitate interface, we first estimate the linear lattice parameter misfit, \( \varepsilon \), between the \( \alpha \)-Fe matrix and the bcc Cu-rich precipitates. The lattice parameter for bcc \( \alpha \)-Fe at room temperature is \( a_0 = 0.28665 \text{ nm} \) [49], and, with the thermal expansion data given by [50], \( a_0 = 0.28598 \text{ nm} \) at 0 K and \( a_0 = 0.28953 \text{ nm} \) at 490 °C. For bcc Cu or Cu-rich bcc Cu–Fe solid solutions there is, however, to our knowledge no directly experimentally measured lattice parameter available. Lattice parameter measurements of mechanically alloyed Cu–Fe alloys [51] suggest a positive deviation from Vegard’s rule, with a similar atomic volume for both fcc and bcc solid solutions. The lattice parameter values given in [51] result in a lattice parameter mismatch of 0.6% between bcc \( \alpha \)-Fe and bcc Cu–33 at.% Fe. A lattice parameter \( a_0 \) equal to 0.2884 nm has recently been calculated for bcc Cu–33 at.% Fe using cluster-expansion generalization-gradient approximation density-functional theory calculations [52], resulting in \( \varepsilon = 0.85\% \), at 0 K. An earlier molecular dynamics simulation [53], employing empirical potentials, calculated a value of \( a_0 \) equal to 0.29607 nm for pure bcc Cu at 0 K, equivalent to the comparatively large value of \( \varepsilon = 3.2\% \). Better potentials, however, result in smaller values, \( a_0 = 0.2885 \text{ nm} \) or \( a_0 = 0.2880 \text{ nm} \), corresponding to \( \varepsilon = 0.9 \) or 0.7% [53–55], respectively, at 0 K. Assuming that the thermal expansion coefficient of bcc Cu, which is not known, is not very different from bcc \( \alpha \)-Fe, then \( \varepsilon \) is less than about 1% at all temperatures considered. Values of \( \varepsilon \) smaller than 1% are also in agreement with estimates of the bcc Cu lattice parameter from fcc Cu (\( a_0 = 0.36146 \) at room temperature) by simple geometric considerations: Firstly, \( \varepsilon = 0.3\% \) results by equating the atomic volumes of bcc and fcc Cu. Secondly, \( \varepsilon = -0.1\% \) results by calculating the next-neighbor distance and taking into account, following Goldschmidt [56], a 3% contraction for a reduction of the number of next-neighbor atoms from 12 to 8. Thus, since the linear lattice parameter mismatch, \( \varepsilon \), between bcc \( \alpha \)-Fe and bcc Cu–33 at.% Fe is about 1% or less and the linear mismatch of Ni or Mn solute atoms in \( \alpha \)-Fe is only 1.52 or 1.60%, respectively [57], elastic interactions cannot account for the interfacial segregation, as discussed in Ref. [58], and very likely electronic (chemical) effects come into play [61].

Eq. (6) is used for calculating a coefficient of the reduction in interfacial free energy

\[
\frac{\partial^2 \sigma}{\partial C_i \partial C_j} \big|_{T,P,\phi_1,\ldots,\mu_{i-1},\mu_i,\ldots,\mu_n}
\]

at a solute concentration \( c_i \) of component \( i \), due to the Gibbsian interfacial excess of this solute component. The value for Ni is \(-1579 \text{ mJ m}^{-2} \text{ (at.fr.)}^{-1} \) and for Mn it is \(-1620 \text{ mJ m}^{-2} \text{ (at.fr.)}^{-1} \). These values are more than one order of magnitude larger than the value of \(-114 \text{ mJ m}^{-2} \text{ (at.fr.)}^{-1} \) reported for the segregation of Si at grain boundaries at 550 °C in an Fe–3 at.% Si alloy investigated by one-dimensional atom-probe microscopy [36], but more than one order of magnitude smaller than the value of \(-100,000 \text{ mJ m}^{-2} \text{ (at.fr.)}^{-1} \) obtained for segregation of Sb to grain boundaries in Fe–0.03 at.% Sb at 350–450 °C by Auger spectroscopy [59] and \(-119,000 \text{ mJ m}^{-2} \text{ (at.fr.)}^{-1} \) measured for the segregation of P to the grain boundaries of an Fe–0.034 at.% P alloy employing a technique based on equilibrating the contractile forces of thin foils [60].

Approximating the unknown dependence of the interfacial free energy on solute segregation by a linear relationship,
a value of the total reduction of the interfacial free energy due to the given interfacial excesses is estimated by multiplying the coefficient of reduction by the solute concentration. With the values given, the interfacial energy of the \( \alpha \)-Fe matrix/precipitate heterophase interface is reduced by 16 mJ m\(^{-2}\) due to Ni segregation, and by 11 mJ m\(^{-2}\) due to the segregation of Mn. The sum of these values (27 mJ m\(^{-2}\)) represents 10% of the interfacial energy of 270 mJ m\(^{-2}\) of bcc Cu precipitates in a binary Fe–1.38 at.% Cu alloy determined from precipitation kinetics [13]. These values for the reduction of interfacial free energy are comparable with the 10 mJ m\(^{-2}\) reduction measured by APT for Mg segregation at coherent interfaces of \( \text{Al}_3\text{Sc} \) precipitates in an \( \text{Al–}2.2 \text{Mg–}0.12 \text{Sc} \) at.% alloy [61].

5. Summary and conclusions

1. APT was utilized to characterize nanometer-sized Cu-rich precipitates with a metastable bcc structure that formed in the ferritic \( \alpha \)-Fe matrix of a recently developed precipitation-hardened high-strength low-carbon steel.
2. After direct isothermal aging at 490 °C for 100 min to a near-peak hardness condition of 84 Rockwell G, the precipitates have an average diameter of 2.5 ± 0.3 nm at a number density of (1.1 ± 0.3) \times 10^{24} \text{m}^{-3}.
3. The core regions of the Cu-rich precipitates contain 64 ± 1 at.% Cu and 33 ± 1 at.% Fe. Al is enriched in the precipitates to 0.5 ± 0.1 at.%, which implies a partitioning ratio of 10 ± 2 with respect to the 0.047 ± 0.003 at.% Al in the \( \alpha \)-Fe matrix. Nickel and Mn do not partition significantly; and the precipitates are depleted in Si.
4. Nickel and Mn are segregated at the \( \alpha \)-Fe matrix/precipitate heterophase interface with Gibbsian interfacial excesses relative to Fe and Cu of 1.5 ± 0.4 nm\(^{-2}\) and 1.0 ± 0.3 nm\(^{-2}\), respectively. Aluminum has only a slight tendency toward segregation, and Si is depleted at this heterophase interface.
5. A coefficient of reduction of interfacial energy is calculated directly from the relative interfacial excesses. The coefficients are −1579 mJ m\(^{-2}\) (at.fr.\(^{-1}\)) for Ni and −1620 mJ m\(^{-2}\) (at.fr.\(^{-1}\)) for Mn. Total reductions of the interfacial free energy of 16 mJ m\(^{-2}\) for Ni and 11 mJ m\(^{-2}\) for Mn are estimated. The sum of these energies is 27 mJ m\(^{-2}\), which amounts to 10% of the interfacial energy of 270 mJ m\(^{-2}\) [13].

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