Tetragonal fcc-Fe induced by κ-carbide precipitates: Atomic scale insights from correlative electron microscopy, atom probe tomography, and density functional theory

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Correlative scanning transmission electron microscopy, atom probe tomography, and density functional theory calculations resolve the correlation between elastic strain fields and local impurity concentrations on the atomic scale. The correlative approach is applied to coherent interfaces in a κ-carbide strengthened low-density steel and establishes a tetragonal distortion of fcc-Fe. An interfacial roughness of ~1 nm and a localized carbon concentration gradient extending over ~2–3 nm is revealed, which originates from the mechano-chemical coupling between local strain and composition.

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I. INTRODUCTION

Designing internal phase boundaries has become a highly successful strategy to develop structural and functional materials with superior mechanical or electronic properties [1,2]. A challenge in designing such materials is that fundamental mechanisms on the coupling of elastic and chemical effects at interfaces remain elusive, even when applying modern characterization techniques. The dispersion of nanometer-scale coherent precipitates in a solid solution, for example, is an effective way to design materials with outstanding mechanical properties even at high temperatures where classical mechanisms, such as solid-solution hardening, fail [3]. Complex internal stress states develop around and in between these nano-precipitates that affect the interaction with dislocations, the elastic self-interaction, and local chemical equilibrium [4–8].

Powerful metrological techniques to resolve atomic scale compositional fluctuations at interfaces in complex materials are high resolution transmission electron microscopy (TEM) and atom probe tomography (APT) [9,10]. Despite the enormous progress made over the past decades in improving their spatial and elemental resolution, both techniques suffer from limitations that restrict their capabilities to resolve structural and compositional features individually. Correlative approaches, that combine experimental techniques with \textit{ab initio} simulations can overcome the limitations of a single technique, but require the development of new strategies to spatially align sample features on a nanometer or even atomistic scale.

Aberration-corrected scanning TEM (STEM) enables one to resolve complex materials with atomic resolution, and, when a convergent beam is scanned over the sample, the image intensity is directly proportional to the mean atomic number [11]. The precision to locate atomic columns in STEM micrographs was shown to be in the picometer range, giving access to atomic column displacements, local crystallography, and composition [9,12–14]. The detection of light elements, such as carbon (C) and oxygen (O), still remains challenging in STEM due to their low interaction with the electron beam. Aberration correction increased the chemical sensitivity of spectroscopic techniques to below 0.1 at. %, but it strongly depends on the sample geometry, and highest sensitivity is only obtainable with a loss in spatial resolution [9]. An ideal technique to correlate with STEM is APT, that not only can detect elements down to hydrogen (H), but also gives access to the three-dimensional (3D) elemental distribution within the specimen. APT provides the highest elemental sensitivity, but the anomalous field evaporation behavior and local magnifications at or near interfaces induce aberrations in the ion trajectories that alter the precision of the 3D reconstruction [15]. The correlation of (S)TEM and APT is a way to overcome the limitations of both techniques and has been established on a variety of material systems [16–20]. Nevertheless, \textit{ab initio} calculations are required to explore the atomistic origins of local chemical equilibrium. Density functional theory (DFT) approaches in combination with thermodynamic concepts have successfully been applied to complex, interface dominated materials to unravel elastic and magnetic effects on phase stability [21,22].

In this work, we show how atomic resolution STEM, APT, and DFT can be correlated and are able to resolve elemental distributions, elastic strain fields, and their relationship on the nanometer scale. The power of the presented threefold correlative approach is demonstrated on interfaces in a nano-precipitation hardened, low-density steel. The tetragonal structural information from STEM is used to calibrate the APT reconstruction (see Fig. 1). The refined compositional information from APT, in particular the concentration of interstitial C atoms, is an essential component for the \textit{ab initio} simulations to fully explore the connection of local lattice distortions on the C solubility. In return, the computations...
was investigated by electron backscatter diffraction (EBSD) at 600 K. Precipitates that are formed during the annealing heat treatment of a steel with a composition of Fe-26.7% Mn-14.0% Al-5.3% C are observed and their orientation is determined using EBSD. After determining deformations, the specimens were welded to electropolished Mo half-grids for final sharpening by focused ion beam (FIB) milling from the bulk. Samples were extracted and were used for further analysis.

II. EXPERIMENTAL DETAILS

The face-centered cubic (fcc) iron (Fe) matrix, referred to as γ-Fe for the remainder of the paper, in a low-density steel with a composition of Fe-26.7% Mn-14.0% Al-5.3% C (at. %), is strengthened by nanoscale, coherent κ-carbide precipitates that are formed during the annealing heat treatment at 600°C (873 K) [23–26]. The detailed processing procedure is described elsewhere [27]. Samples were extracted by focused ion beam (FIB) milling from the bulk and were welded to electropolished Mo half-grids for final sharpening [19]. Before sample extraction, the crystallographic orientation was determined using electron backscatter diffraction (EBSD) to lift out samples such that (001) corresponds to the length axis of the APT specimens and electron beam direction in the TEM, respectively. The needle-shaped specimens were first characterized in a C$_p$-probed needle probed Titan Themis 60-300 instrument operated at 300 kV acceleration voltage. Electron probe currents of ~75 pA were utilized with a semiconvergence angle of 17 mrad. The inner and outer semicollection angles of the annular detectors were chosen to be 7 to 13 mrad for annular bright field (ABF) and 58 to 285 mrad for high angle annular dark field (HAADF). To reduce the influence of scan distortions and instabilities on the obtained atomic resolution STEM images, a serial acquisition scheme of typically 20 images with pixel dwell times of 5 μs was chosen. Consecutive images are aligned and averaged using the nonrigid registration strategy from [12], but with one novel extension. After determining deformations $\phi_i$ such that the deformed $i$th frame $f_i \circ \phi_i$ resembles the average $f$ via [12], these deformations are reduced by computing a deformation $\psi$ that minimizes $\sum_{i=1}^{n} \int_{\Omega} |\phi_i(\psi(x)) - x|^2 dx$. This way, $\psi$ collects the inverse of the bias, and the bias is removed by replacing $\phi_i$ with $\phi_i \circ \psi$ and $f$ with $f \circ \psi$. After this additional step, the new average is computed as in [12]. After STEM observations, samples were cleaned with 2 kV Ga$^+$ ions to remove any contaminants and oxides before each APT measurement. Knowledge of the specimen’s orientation from preceding STEM analysis was used to exploit the partial crystallographic information retained within the APT data, allowing for precise calibration of the reconstruction.

APT data were acquired on a CAMECA LEAP 3000 XR and LEAP 5000 XS in voltage-pulsing mode at ~70 K with a pulse repetition of 200 kHz, a pulse fraction of 15%, and a target evaporation rate of 5 ions per 1000 pulses, according to the parameters optimized for these samples [27]. The detection efficiency of the former is ~37% and the latter ~80%. The collected APT data were reconstructed and analyzed using the commercial software package IVAS (version 3.6.14). By selecting the orientation of the grain from which the specimens are prepared along the (001), we maximized the chances of detecting atomic planes within the atom probe tomographic reconstruction. A pole was detected in the detector map, as shown in Fig. 2(a), which is the trace of the presence of a set of crystalline planes at the specimen’s surface [28]. This was expected from the atomic arrangement observed from the STEM image (Fig. 1). Within the reconstruction, we made use of the spacing between the imaged planes to calibrate the depth of the reconstruction following the protocol outlined in Ref. [29] and shown in Fig. 2(b), making use of split radial distribution functions known as spatial distribution maps, displayed in Fig. 2(c), to estimate the average spacing between planes [30]. With only a single pole detected, a full calibration of the two main reconstruction parameters could not be performed [31]. The overall depth is calibrated based on the interspacing, and then the image compression factor and field factor were optimized to maximize the flatness of the planes as suggested in the article by Bas et al. [32] on which the current generation of reconstruction algorithms is based. In addition, the distortions linked to errors in the reconstruction parameters on relatively small reconstructed volumes, such as the one shown in Fig. 4, are negligible [29,33]. For instance, for the volume shown in Fig. 4, the image compression factor was 1.53 and the field factor 4.7 for an assumed evaporation field of 33 V nm$^{-1}$. The same approach was used to calibrate the reconstruction shown in Fig. 1.

The theoretical results were obtained using density functional theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP) [34–36]. The electron-ion interaction is described by using projector augmented-wave (PAW) potentials [37,38]. The generalized-gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) [39] was employed. The Methfessel-Paxton method [40] was used for the Fermi surface smearing with a 6 × 6 × 6 Monkhorst-Pack grid [41] in a 2 × 2 × 2 40-atom supercell (SC) for the κ-carbide and 2 × 2 × 2 32-atom supercell for the γ-Fe matrix. The single-electron wave functions were expanded by using plane waves up to an energy cutoff of 500 eV. The energies converged to a precision of better than 1 meV/atom. We chose double-layer antiferromagnetic (AFMD) and paramagnetic (PM) states for the γ matrix, whereas ferromagnetic (FM) ordering was chosen for the κ carbide. The PM energies were...
obtained with the aid of the special quasirandom structure (SQS) scheme [42] for a $2 \times 2 \times 2$ SC of $\gamma$-Fe. Local relaxations were performed until the forces on each atom were below 0.01 eV/Å for all the magnetic states under consideration.

### III. RESULTS AND DISCUSSION

The simultaneously acquired STEM overview images of a representative needle-shaped specimen taken under ABF and HAADF imaging conditions along with the APT reconstruction are shown in Fig. 1. Contributions resulting from diffraction contrast are most pronounced in the ABF image of Fig. 1(a), indicating the localization of strain fields at the matrix-precipitate interfaces. In the HAADF signal of Fig. 1(b) these effects are largely suppressed and the signal mainly represents differences in local composition and thickness. The corresponding reconstructed APT volume is oriented in such a way that the shape of the $\kappa$-carbide particles, as defined by the isoconcentration surface for a C concentration of $\geq 9$ at. %, is corresponding to the observed precipitate structure in the STEM images. The features stemming from strain contrast and the location of $\gamma/\kappa$ interfaces agree extremely well when comparing Fig. 1(a) with 1(c). The APT reconstruction now gives access to the 3D shape and distribution of the $\kappa$-carbide precipitates, and it can be seen that two types of precipitates, with cuboidal and plate shaped geometry, respectively, are present. The atomic structure of a 3 nm narrow matrix channel separated by two adjacent $\kappa$ phases is illustrated in Fig. 3. The HAADF-STEM image of Fig. 3(a) clearly confirms the perfect coherency of adjacent $\kappa$-carbide precipitates separated by a narrow $\gamma$-Fe channel. The color-coded image, based on the nearest-neighbor intensity difference of atomic column peak intensities [Fig. 3(a)], not only highlights the different degree of chemical ordering of both phases but also emphasizes a slight interface roughness of $\sim 1$ nm [43].
The local, in-plane strain state across the narrow matrix channel of Fig. 3 a extracted from the atomic column positions is illustrated in Figs. 3(c)–3(e). The atomic column peak positions are refined by fitting them with two-dimensional nonlinear Gaussian functions. A reference region of $2 \times 2 \text{nm}^2$ was selected in the left $\kappa$-carbide phase, that adopts a cubic lattice, to specify a reference lattice as indicated in Fig. 3(a). This reference lattice was then extrapolated to the whole image and the difference between the actual peak positions obtains the displacement field and hence the strain [44]. As expected from this procedure, the normal and shear strain contributions in both $\kappa$ carbides are $0 \pm 1.5\%$. Interestingly, the strain component perpendicular to the interfaces $\varepsilon_{xx}$ [Fig. 3(c)] decreases to $-5\%$ compressive strain in the narrow $\gamma$-Fe matrix channel. The ratios of the mean, constraint lattice parameters extracted from both adjacent precipitate phases and the matrix phase respectively are $a_{\gamma,xx}/a_{\kappa,xx} = 1.00$ ($a_{\kappa,xx} = 0.379 \text{ nm}$, $a_{\gamma,xx} = 0.362 \text{ nm}$), $a_{\gamma,yy}/a_{\kappa,yy} = 0.95$ ($a_{\kappa,yy} = 0.379 \text{ nm}$, $a_{\gamma,yy} = 0.362 \text{ nm}$), clearly confirming a tetragonal distortion of the narrow $\gamma$-Fe channel. The lattice parameter in the plane of the interface $(a_{\gamma})$ expands by $2.6\%$ to retain coherency with adjacent precipitates, while the perpendicular lattice $(a_{\gamma})$ is compressed by $2.2\%$ with respect to the cubic lattice of a broad matrix channel $[\gamma_1$ in Fig. 4(a)] with $a_{\gamma,xx} = 0.370 \text{ nm}$, $a_{\gamma,yy} = 0.369 \text{ nm}$.

These results were obtained in a region very close to the apex of the needle-shaped specimen, that is difficult to conserve in APT measurements. In a slightly thicker specimen region, both structural and compositional information were obtained from STEM imaging and subsequent correlative APT measurements, illustrated in Fig. 4. The superposition of the HAADF-STEM image agrees well with the corresponding APT reconstruction, as seen in Fig. 4(a). Here, a thin slice of the APT reconstruction is oriented in such a way as to correspond to the viewing direction of [001] in the STEM experiments. Since in this case the APT data are plotted from an inclined perspective, an additional movie revealing the 3D topology of this region is given in the Supplemental Material [45]. The compositional gradients across the interface of a narrow matrix channel extend over $-3-3 \text{ nm}$ with a decrease in C concentration from $12 \text{ at.}\%$ in $\kappa$ to $5 \text{ at.}\%$ in $\gamma$, illustrated in Fig. 4(b). The complex strain state that evolves in the transition region of broad ($\gamma_1$) and narrow ($\gamma_2$) matrix channels indicates that local lattice distortions, as seen in Figs. 4(c)–4(e), play an important role in understanding solute distribution.

DFT calculations, in combination with thermodynamic concepts, are employed to explore the impact of tetragonal lattice distortions of $\gamma$-Fe on C solubility. A detailed description of the basic methodology is given in Ref. [22]. The tetragonal strain is defined in agreement with experiments as $\varepsilon = ((a_{\gamma} - a_{\kappa})/a_{\kappa})$, with $a_{\kappa}$ as the lattice parameter of $\gamma$ perpendicular to the $\gamma/k$ interface and $a_{\kappa}$ in plane with the $\gamma/k$ interface. For both AFMD and PM calculations the C solution enthalpy is observed to increase with a decrease in imposed tetragonal strain, as illustrated in Fig. 5(a).

This trend suggests that the experimentally obtained tetragonal strain of $-5\%$ in the narrow matrix channels leads to an increase in C solubility with respect to the broad channels ($\varepsilon = 0\%$). The comparison of AFMD and PM was chosen because the magnetic low-temperature state of $\gamma$-Fe is AFMD, while the tetragonal distortion of the cubic lattice [vertical arrow in Fig. 5(a)] [46,47]. The PM case gives a more realistic representation of the magnetic state at the annealing temperature of 873 K. Furthermore, the results show that this qualitative trend is independent of the magnetic potential that is determined by the chemical equilibrium between $\gamma$ and $\kappa$. Thus, the partitioning of C atoms between hydrostatically strained $\kappa$ carbide and biaxially strained $\gamma$ is determined by an energy minimization scheme where chemical and elastic energies of both phases are considered along with
and a similar behavior is expected for C partitioning between \( \kappa \) and \( \gamma \) for PM \( \gamma \)-Fe. The impact on the C concentration for hydrostatically strained \( \gamma \) is highlighted by plus and cross symbols at 298 and 873 K for two choices of volume fraction of \( \kappa \) and \( \gamma \), respectively, in Fig. 5(b). For both temperatures, a decrease in C concentration of \( \sim 2 \) at. % at 298 K and \( \sim 3 \) at. % at 873 K can be confirmed, verifying that tetragonally strained \( \gamma \) can dissolve larger amounts of C. These compositional differences are not detected by APT, which is a state-of-the-art technique to resolve nanometer-scale compositional gradients of light elements in a heavy matrix. However, deviations in the field evaporation behavior of the different phases lead to ion trajectory aberrations, which are known to compromise the accuracy of atom probe reconstructions [27,28].

IV. CONCLUSIONS

In conclusion, by interlinking quantitative atomic resolution STEM, APT, and DFT, the connection of complex elastic strain fields at interfaces with local impurity concentrations is established with highest lateral resolution and chemical sensitivity. The structural information from STEM provides insights into the complex strain state across coherent \( \gamma / \kappa \) interfaces, and a tetragonal distortion of nanometer-sized \( \gamma \)-Fe channels is found. APT determines the concentration of C in \( \gamma \)-Fe around the precipitates to \( \sim 5 \) at. %, but compositional differences in the broad and narrow channels are not detectable. The experimentally informed DFT calculations, however, establish that an increasing tetragonal strain leads to an increase in C concentration. This could also explain the experimentally observed broad C concentration gradient across the interface, since the first atomic layers of \( \gamma \) in proximity to the interfaces are under highest strain, that partly relaxes when moving away from the interface.

The computed increase in C concentration in the narrow, tetragonal channels indicates a supersaturation of \( \gamma \)-Fe with C by a factor of 2 or more, in comparison to values obtained from equilibrium phase diagrams. Hence, it is expected that these channels contribute to strengthening by impeding dislocation mobility and affect phase stability by an increase in C diffusivity.

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