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Atomistic multiscale simulations on the anisotropic tensile behaviour of copper-alloyed alpha-iron at different states of thermal ageing

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The mechanical behaviour of steels is strongly related to their underlying atomistic structures which evolve during thermal treatment. Cu-alloyed α-Fe undergoes a change in material behaviour during the ageing process, especially at temperatures of above 300°C, where precipitates form on a large time-scale within the α-Fe matrix, yielding first a precipitation strengthening of the material. As the precipitates grow further in time, the material strength decreases again. This complex process is modelled with a multiscale approach, combining Kinetic Monte Carlo (KMC) with Molecular Dynamics (MD) simulations in a sequential way and exploiting the advantages of both methods while simultaneously circumventing their particular disadvantages. The formation of precipitates is modelled on a single-crystal lattice with a diffusion based KMC approach. Transferring selected precipitation states at different ageing times to MD simulations allows the performance of nano tensile tests and the analysis of failure initiation. The anisotropic tensile behaviour is investigated in the [100], [110] and [111] directions, showing monotonically decreasing tensile strengths and deformation strains. Hence precipitation strengthening is mainly due to dislocation–precipitate interactions which are non-existent at small tensile loadings in this scenario. At the point of ductile failure, dislocations are generated at the interfaces between precipitates and the Fe matrix. Straining in the [100] direction, they lie on {110} and {112} glide planes, as expected. With the method presented here, the changes of the anisotropic tensile moduli are related to different states of thermal ageing, i.e., to nucleation, growth and Ostwald ripening of Cu precipitates.

Keywords: multiscale; Kinetic Monte Carlo; Molecular Dynamics; precipitation; ferritic alloy; nano tensile test; sequential coupling

1. Introduction

Due to the large industrial applicability of the resulting steels, precipitation of small Cu clusters in ferritic alloys has been extensively studied within the last decades

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experimentally as well as by various simulation techniques. On the experimental side, cluster formation of Cu atoms has been observed, e.g., by small-angle neutron scattering (SANS) [1] and high-resolution tomography [2,3]. On the modelling side, Kinetic Monte Carlo (KMC) techniques allow one to simulate the process of precipitation via a diffusion based mechanism, i.e., by a series of atomic site exchanges of a vacancy with neighbouring atoms where the probability of a vacancy jump depends on the surrounding atom configuration. By this means, thermal ageing and specific heat treatments can be simulated for long time-scales (years). Expectedly, the formed clusters show radii distributions which are similar to those predicted by the Lifshitz–Slyozov–Wagner (LSW) theory [4]. The mean precipitate radius increases monotonically in time. However, the simulation samples cannot be deformed, a fact that is also referred to as the Rigid Lattice Method (RLM) [5]. Due to the RLM, discrete energy values are sufficient to describe the interactions. Additionally considering only the local environment of the vacancy in each time step, the computation times for cluster formation become feasible.

Molecular Dynamics (MD) simulations reflect the atomic interactions of all simulated atoms yielding atomic trajectories. In the case of metals, EAM (Embedded Atom Method) potentials are typically applied for the description of the interactions as they account for the local electron charge density. MD simulations have been carried out to investigate the material tensile properties of Fe [6]. Nano shear tests with implemented edge dislocations and arranged Cu precipitates show precipitation strengthening on the atomistic level due to dislocation–precipitate interaction [7,8]. The typical length-scales in MD simulations are of the same order as in the aforementioned KMC simulations. Unfortunately, only very short time-scales are accessible with MD simulations as the time steps are in the order of femtoseconds and each atom has to be taken into account in order to compute the following time step. In this paper a novel multiscale approach is presented in which the KMC and MD methods are coupled in a sequential way, overcoming the disadvantages of each method, i.e., the rigid lattice of KMC and the short time-scales of MD. Focusing on dislocation-free starting configurations, the effect of realistic Cu precipitate distributions on the anisotropic tensile behaviour of Cu-alloyed α-Fe at different states of thermal ageing is investigated and the failure mechanism due to the presence of precipitates is analysed.

The modelling schemes of the two isolated simulation procedures (KMC and MD) will be described in detail in Section 2.1 and Section 2.2, respectively. The sequential multiscale coupling approach will be introduced in Section 2.3. In Section 2.4, the starting atomic configuration will be extended in different crystallographic directions conserving the periodicity in all directions and simultaneously maintaining the underlying precipitation statistics. Simulation results of the precipitation process will be presented and discussed in Section 3. The effect on the mechanical properties of the resulting materials will be investigated in Section 4 by performing MD nano tensile tests in the [100], [110] and [111] directions. A detailed analysis of the resulting tensile strength and deformation strain will be given in Section 4.1. The region of deformation initiation will be discussed in Section 4.2. Considering the anisotropic elastic properties in Section 4.3, Young’s modulus will be related to the thermal ageing time and the density of precipitates, both obtained
by KMC simulations. Section 5 closes the paper with concluding remarks on the coupling procedure and the obtained results.

2. Modelling scheme

2.1. Cu precipitation – Kinetic Monte Carlo simulations

The process of Cu precipitation in $\alpha$-iron is simulated by the application of a Kinetic Monte Carlo (KMC) method which is based on a vacancy diffusion mechanism on a rigid bcc crystal lattice, also referred to as the Rigid Lattice Method (RLM) [5]. Although in nature Cu has the fcc structure, it is well known that Cu clusters with sizes smaller than 2 nm are coherently embedded on $\alpha$-iron lattice sites [9,10], justifying the RLM. The KMC simulation used in this study was first described by Soisson et al. [5] and further extended for up to four metallic elements by Binkele et al. [11] where a detailed description of the KMC algorithm presented here can be found. A size of $L=64$ lattice constants as starting configuration yields $N=2L^3=524,288$ lattice sites and a cubic box with an edge length of 18.3 nm. The box surfaces have normals in $(100)$ directions, respectively. Periodic boundary conditions are set in all directions to approximate single crystalline bulk behaviour. Specific amounts of iron atoms are replaced randomly by copper atoms to obtain iron–copper solid solutions with 1 at.% Cu and 10 at.% Cu, respectively. The chemical binding between atoms is described by first- and second-nearest neighbour pair interactions $\epsilon_{Fe-Fe}^{(i)}$, $\epsilon_{Cu-Cu}^{(i)}$ and $\epsilon_{Fe-Cu}^{(i)}$ with $i \in \{1, 2\}$ where $i$ denotes the $i$th nearest neighbour (see Figure 1). The energies $\epsilon_{Fe-Fe}^{(1)}$ and $\epsilon_{Cu-Cu}^{(1)}$, $i \in \{1, 2\}$, were

![Figure 1. One possible lattice configuration. The jump probability depends on the local environment of the vacancy (white sphere) due to the varying arrangements of Cu (grey) and Fe atoms (black).](image-url)
estimated from the cohesive energies of the pure metals assuming $\epsilon_{Fe-Fe}^{(2)} = \epsilon_{Fe-Fe}^{(1)}/2$ and $\epsilon_{Cu-Cu}^{(2)} = \epsilon_{Cu-Cu}^{(1)}/2$ (see [15]). The binding between atoms and vacancy is described by first-nearest neighbour interactions $\epsilon_{Fe-V}$ and $\epsilon_{Cu-V}$. A vacancy within the simulation box allows the movement of an atom by site exchange between the vacancy (V) and a neighbouring atom (Fe, Cu). This thermally activated change is given by the transition rates

$$
\Gamma_{Fe,V} = \nu_{Fe} \exp\left(-\frac{\Delta E_{Fe,V}}{k_B T}\right),
$$

$$
\Gamma_{Cu,V} = \nu_{Cu} \exp\left(-\frac{\Delta E_{Cu,V}}{k_B T}\right),
$$

where $\nu_{Fe}$ and $\nu_{Cu}$ denote attempt frequencies and $\Delta E_{Fe,V}$ and $\Delta E_{Cu,V}$ the activation energies which depend on the local atom configuration with the corresponding chemical binding interactions (see Figure 1). The attempt frequencies are estimated using the diffusion constants of the pure metals. The annealing temperature is set to 500°C in order to ensure supersaturated solutions as well as relatively fast Cu-cluster formation. For each neighbour of the vacancy V, the jump frequencies $\Gamma_1, \ldots, \Gamma_8$ are calculated. By applying a rejection-free residence time algorithm [12], one of these eight possible jumps is selected. The weighted random jumps are repeated over $10^{11}$ times during the simulation of precipitation. The time-scale is adjusted according to the number of Monte Carlo steps and the vacancy concentration, i.e.,

$$
t_{\text{real}} = \left(\frac{c_{V,\text{sim}}}{c_{V,\text{real}}}\right) t_{MC},
$$

where $c_{V,\text{sim}}$ and $c_{V,\text{real}}$ denote the vacancy concentrations in the simulation and in reality. $t_{MC}$ is given by the averaged residence time

$$
t_{MC} = \left(\sum_{j=1}^{8} \Gamma_j\right)^{-1}.
$$

As reported in [12], the calculated time-scale depends sensitively on the energies employed, which are listed among further material data in Table 1. Ab initio (AI) calculations by Vincent et al. [14] find the cohesive energy of pure bcc Cu to be $E_{\text{coh,Cu}}^{AI} = 3.49$ eV. Setting $E_{\text{coh,Cu}} = E_{\text{coh,Cu}}^{AI}$ yields a strong vacancy trapping which has been intensively studied by Soisson et al. [16]. Once a few precipitates have formed, the vacancy stays mainly on precipitate–matrix interface sites and hardly diffuses into the Fe matrix. Thus, computation times as well as annealing times become very long. A way to overcome the latter limitation is to consider only vacancy jumps which are performed within the iron matrix as suggested in [16]. In this way, vacancy jumps at the precipitate–matrix interface do not account for the calculation of $t_{MC}$ and the annealing times move to more realistic time-scales. However, the computation time to obtain larger precipitates then becomes unfeasible. In the present study, the cohesive energy of copper is supposed to lie between the cohesive energy for pure bcc copper and the cohesive energy of pure
α-iron, i.e., between 3.49 eV and 4.28 eV. This assumption takes into account that the interaction range of the atoms is longer than the second-nearest neighbour distance which is assumed in this KMC model. A simple approach is given by

$$E_{\text{coh,Cu}} = E_{\text{coh,Cu}}^{\text{Al}} + \xi \left( E_{\text{coh,Fe}}^{\text{Al}} - E_{\text{coh,Cu}}^{\text{Al}} \right), \quad (5)$$

where $0 \leq \xi \leq 1$. Choosing $\xi = 3/4$ yields $E_{\text{coh,Cu}} = 4.08$ eV. This efficiently reduces the vacancy trapping effect and consequently moves the annealing times and additionally the computing times for sufficiently large precipitates to realistic time-scales. Although the simulation time periods obtained in this way have to be considered with some care, the calculated times are directly proportional to real time which gives a justification of the assumption presented here. Table 2 summarizes the parameters used for the KMC simulations.

### 2.2. Nano tensile tests – Molecular Dynamics

Molecular Dynamics (MD) nano tensile tests are carried out using the IMD (ITAP Molecular Dynamics) code [19] which provides relaxation simulations as well as

| Table 1. Material data for Fe and Cu applied during the Kinetic Monte Carlo simulations. |
|---------------------------------|---------------------------------|
| Cohesive energy Fe             | $E_{\text{coh,Fe}} = 4.28$ eV  |
| Cohesive energy Cu (Al)        | $E_{\text{coh,Cu}}^{\text{Al}} = 3.49$ eV |
| Cohesive energy Cu             | $E_{\text{coh,Cu}}^{\text{Cu}} = 4.08$ eV |
| Vacancy formation Fe           | $E_{\text{V,Fe}} = 1.95$ eV  |
| Vacancy formation Cu           | $E_{\text{V,Cu}}^{\text{Cu}} = 0.88$ eV |
| Vacancy migration Fe           | $E_{\text{M,Fe}} = 0.68$ eV  |
| Vacancy migration Cu           | $E_{\text{M,Cu}}^{\text{Cu}} = 0.57$ eV |
| Lattice constant               | $a = 0.287$ nm                |
| Mixing energy                  | $\omega = -0.545$ eV          |
| Diffusion constant Fe          | $D_{\text{Fe}} = 2.01 \cdot 10^{-4}$ m² s⁻¹ |
| Diffusion constant Cu          | $D_{\text{Cu}} = 2.16 \cdot 10^{-4}$ m² s⁻¹ |
| Attempt frequency Fe           | $v_{\text{Fe}} = 2.44 \cdot 10^{15}$ s⁻¹ ($D_{\text{Fe}}^{1/2}$) |
| Attempt frequency Cu           | $v_{\text{Cu}} = 2.62 \cdot 10^{15}$ s⁻¹ ($D_{\text{Cu}}^{1/2}$) |

| Table 2. General conditions of the Kinetic Monte Carlo (KMC) simulations. |
|-------------------------------|---------------------------------|
| Lattice constants             | 64                              |
| Box edge length               | 18.3 nm                         |
| Number of atoms               | 524 287                         |
| Number of vacancies           | 1                               |
| Cu concentrations             | 1 at.% , 10 at.%                |
| Annealing temperature         | 500°C                           |
| Boundary conditions           | Periodic in x, y, z              |
| Number of KMC steps           | 101·10⁹                         |
calculations in different ensembles and allows for massively parallel computations. Furthermore, elastic constants can be calculated directly from relaxed configurations. Stress tensors and pressure tensors can be derived for relaxed structures as well as for homogeneously deformed structures. For metals, the interactions between atoms are typically described by EAM (Embedded Atom Method) potentials as they include, besides pair interactions of the atoms, an additional embedding term accounting for the local electron charge density in the lattice. They are of the form

$$V = \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij}) + \sum_i U_i(n_i),$$  \hspace{1cm} (6)

$$n_i = \sum_{i \neq j} \rho_j(r_{ij}),$$  \hspace{1cm} (7)

where $U_i$ describes the energy of embedding atom $i$ in a density $n_i$, which is the sum of contributions $\rho_j$ from neighbours $j$ at distances $r_{ij}$.

To describe the Fe–Cu system, the recently published EAM (Embedded Atom Method) potential by Bonny et al. [20] is applied which includes the interactions between Fe, Cu and additionally Ni, although Ni is not the subject of this study. The potential of the ternary system is based on potentials of the pure species, namely on the Fe potential by Mendelev et al. [21], the Cu potential by Mishin et al. [22], the Ni potential developed by Voter and Chen [23] and the corresponding binary metal potentials [24,25]. For Fe and Cu a list of properties can be found in Table 3 and further details in [20,21,22]. For the performance of nano tensile tests, a given structure is first relaxed to $T = 0$ K (10,000 MD steps). Then, employing pressure as well as temperature control (NpT ensemble), the structure is heated up to room temperature (300 K, 25,000 MD steps). The diagonal elements of the pressure tensor are relaxed to zero by volume rescaling along the coordinate axes. Thereafter, tensile loading is applied (100,000 MD steps) by homogeneously and uniaxially straining the sample at a constant strain rate of $10^{-6}$ in each MD step ($5 \times 10^8$ s$^{-1}$) while, as in the case of the KMC simulations, periodic boundary conditions are applied in all directions to approximate bulk behaviour as well as to avoid surface effects. Perpendicular to the loading direction, the pressure is kept equal to zero (NpT ensemble). In contrast, there is no pressure relaxation in the loading direction. The MD simulation parameters are summarized in Table 4.
2.3. Multi-time-scale approach

The Kinetic Monte Carlo (KMC) method and the Molecular Dynamics (MD) simulations which are described in the previous sections are based on different physical modelling approaches. With the probability-driven KMC method, the ageing process of Cu-alloyed C11-iron can be simulated for very long time-scales yielding cluster formation from a starting solid solution configuration. The velocity of this algorithm is due to the fact that calculations in a KMC time step focus on the local environment of the vacancy instead of taking all atoms of the simulated sample into account. On one hand, the applied rigid lattice reduces the necessity of inputting energy values to a minimum. On the other hand, it does not allow any deformation of the lattice and thus the investigation of, e.g., the tensile behaviour of the thermally aged material. In turn, this is possible with MD simulations which yield trajectories of each atom of the simulation sample by integrating the equations of motion. The drawback of this method is the limitation of simulating only short times, which lie in the order of nanoseconds. The simulation of a vacancy jump with MD would require long computation times and the further simulation of precipitation becomes almost impossible. One aim of this study is to introduce a novel multiscale method. By transferring different precipitation states from KMC to MD, tensile tests can be performed at different states of thermal ageing. Due to the sequential coupling (one method after the other), the advantages of both methods can be exploited. Simultaneously, the particular disadvantages of each method are cancelled out. As both methods are applied on similar length-scales, the combination of KMC and MD can be understood as a sequential multi-time-scale approach.

2.4. Periodic crystal extension

The aim is to investigate the effect of realistic precipitate distributions on the anisotropic tensile behaviour of the thermally aged alloy. As described in Section 2.1, the surfaces of the simulation sample are oriented with normals in (100) directions. A typical procedure to obtain samples with surfaces with other normal vectors for crystalline structures is to cut a smaller sample out of the existing one. However, this is only possible for highly periodic structures and is neither applicable for the solid solutions nor for the thermally aged samples as the Cu atoms as well as the Cu precipitates are not symmetrically distributed. Therefore, we developed a method which extends the crystal to obtain surfaces with the desired normal vectors in [110]
and [111] directions, respectively. Simultaneously, periodicity in all directions as well as particle statistics within the sample remain conserved. According to Figure 2, the starting configuration is extended in the \( xy \)-plane (1). Rotating it afterwards around the \( z \)-axis (2) provides the starting configuration for the second extension (4), followed by a rotation (arctan(\( \sqrt{2} \))) around the x-axis which results in the final structure with surface normals in [111]-, [110]- and [112]-directions, respectively.

Table 5. Properties of the MD simulation samples. During the periodic extension process sample sizes increase. Only the crystal directions in the positive coordinate axes \((x, y, z)\) directions are indicated.

<table>
<thead>
<tr>
<th>Volume</th>
<th>Surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting sample</td>
<td>( V_0 )</td>
</tr>
<tr>
<td>Extension I</td>
<td>2 ( V_0 )</td>
</tr>
<tr>
<td>Extension II</td>
<td>6 ( V_0 )</td>
</tr>
</tbody>
</table>
the z-axis (2) results in a structure twice as big as the starting one, with normals in [110], [110] and [001] directions, respectively. Extending this new sample (3) in the yz-plane (4) and rotating it around the x-axis ([110] direction) (5) results in the final structure with normals along [111], [110] and [112], respectively. Due to the second extension, the size of the sample increases another three times. Although the bigger sample sizes go with longer computation times, the underlying particle statistics as well as the periodicity in all directions are conserved, making the MD simulation results comparable. Further details of the simulation samples are summarized in Table 5.

Simulation results of the KMC–MD multi-time-scale approach for anisotropic tensile tests of thermally aged Fe–Cu alloys will be presented in the following section.

3. Simulation of precipitation – Kinetic Monte Carlo

The Kinetic Monte Carlo (KMC) simulations are performed as described in Section 2.1. Two starting configurations, with 1 at.\% Cu and 10 at.\% Cu, respectively, are thermally aged at 500°C. In total, over 10^{11} KMC steps are performed during the simulation yielding the formation of small Cu clusters. During the simulation, the Cu concentration within the solid solution (matrix m) is calculated and the result is compared to the concentration at equilibrium which is given by

\[ c_m(t \to \infty) \approx \exp\left(\frac{\Delta S_{\text{nc}}}{k_B}\right) \cdot \exp\left(\frac{\omega_{\text{Fe-Cu}}}{k_B T}\right), \]

where the non-configurational entropy \( \Delta S_{\text{nc}} \) is set to 1 \( k_B \) according to \([16]\). The ratio

\[ \xi(t) = \frac{c_m(t = 0) - c_m(t)}{c_m(t = 0) - c_m(t \to \infty)} \]

Figure 3. (A) Degree of advancement: Higher copper concentrations yield a faster precipitation process. The annealing temperature of 500°C is kept fixed throughout the thermal treatment in α-Fe. (B) Atomic configurations at the beginning of the simulation (lower row) and after 10^{11} KMC steps (upper row).
can be interpreted as the degree of advancement (Figure 3), $c_m(t=0)$ being the starting Cu concentration and $c_m(t)$ the remaining Cu concentration in the matrix at time $t$. At the beginning of the simulation, i.e., for a solid solution, $\xi(t=0)$ equals zero. During simulation, the amount of Cu within the Fe matrix decreases due to precipitation. As a consequence, $\xi(t)$ increases, saturating at a value of one where all remaining matrix Cu atoms are perfectly solved. It is well known [5] that $\xi(t)$ approximately follows the equation

$$\xi(t) \approx 1 - \exp\left(-\left[\frac{t}{\tau}\right]^n\right), \quad (10)$$

which is derived from the theory Johnson–Mehl–Avrami–Kolmogorov (JMAK) [28–30]. In addition to the degree of advancement of this process, the density of precipitates as well as their mean radius is calculated (Figure 4). At a certain time, the density of precipitates reaches a maximum value. From this point on, some precipitates dissolve again while other precipitates grow further in time yielding an overall monotonically increasing mean radius of precipitates (Figure 3B). This is also referred to as Ostwald ripening. Comparison of Figure 3A with Figure 4A shows that this process starts long before $\xi(t)$ reaches a value of one, i.e., when the solid solution in the matrix is still supersaturated. After the KMC simulation, the atom configurations at several time steps are transferred to MD simulations specifying the coordinate position and element type of each atom. The respective result from nine ageing periods between the beginning (solid solution) and the end of the KMC simulation (10^9 MC steps) are selected to perform the nano tensile tests.

4. Simulation of nano tensile tests – Molecular Dynamics

Nano tensile tests are performed as described in Section 2.2. The nine simulation samples from KMC are extended in order to obtain differently oriented surfaces
according to Section 2.4. In addition to the Fe–Cu samples, pure α-Fe samples are provided in the same orientations. All in all, 30 samples are strained uniaxially in the [001], [110] and [111] direction, respectively. After the first relaxation, the elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ of pure α-Fe, of the starting solid solutions and of the final aged states are calculated (Table 6) in order to compare them to each other as well as to the potential data for α-Fe provided by Mendelev et al. [21] (see Table 3). The obtained values for pure α-Fe are in very good agreement with the values given by Mendelev et al. [21]. A comparison with the pure Cu potential data from Mishin et al. [22] is not possible due to the bcc structure of Cu in this scenario. By adding Cu to the α-Fe matrix, $C_{11}$ changes significantly whereas $C_{12}$ and $C_{44}$ changes only slightly (Table 6). At the latest precipitation state, all elastic constants have decreased relative to the solid solution values at the beginning of thermal ageing (Table 6). This behaviour is confirmed as well by the nano tensile tests (Figure 5). The samples are

![Stress-strain curves](image)

Figure 5. Stress–strain curves for different crystallographic orientations [black: pure α-Fe, blue to orange: increasing precipitation times, i.e., 0, 10⁴, ..., 11 KMC steps, also indicated by the green arrows]. Adding Cu to the α-Fe matrix yields a decrease in tensile strength as well as in deformation strain. Comparing the different orientations, deformation starts first when straining in the [100] direction.
strained by a factor of $10^{-6}$ in each time step until defects start to initiate within the sample yielding stress relaxation. In the following, several aspects of the results are discussed in detail.

4.1. Yield stress and deformation strain

The highest stress of each stress–strain curve $\sigma_{\text{max}}$ and the corresponding strain $\varepsilon_{\text{max}} = \varepsilon(\sigma_{\text{max}})$ will be referred to as the tensile strength and deformation strain, respectively. The pure $\alpha$-Fe samples (black solid lines in Figure 5) are stiffer than the binary Fe–Cu samples and have higher tensile strengths. Comparing the different orientations, the [111] straining direction shows the highest yield stress and deformation strain, followed by the [110] and [100] straining directions. Each of the Fe–Cu stress–strain curves corresponds to a precipitation state, i.e., to an amount of vacancy jumps which can be mapped onto real time as shown in Section 2.1. Thus, Figure 6 shows the time-dependent behaviour of the yield stress and the deformation strain. For comparability, the values for each orientation and Cu concentration, respectively, are normalized to the corresponding solid solution stress–strain curves ($\sigma_{\text{max, } 0}$ and $\varepsilon_{\text{max, } 0}$). This gives an impression of how $\sigma_{\text{max}}$ and $\varepsilon_{\text{max}}$ change in time compared to the beginning of the thermal ageing process. All curves remain constant for some time before starting to decrease. The values of samples with 10 at.% Cu start to decrease earlier due to the earlier start of

<table>
<thead>
<tr>
<th>Elastic constants [GPa]</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{44}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure $\alpha$-Fe</td>
<td>243.4</td>
<td>145.0</td>
<td>116.0</td>
</tr>
<tr>
<td>1 at.% Cu (solid solution)</td>
<td>243.1</td>
<td>145.2</td>
<td>116.1</td>
</tr>
<tr>
<td>1 at.% Cu ($10^{11}$ KMC steps)</td>
<td>242.4</td>
<td>145.0</td>
<td>115.8</td>
</tr>
<tr>
<td>10 at.% Cu (solid solution)</td>
<td>239.4</td>
<td>146.2</td>
<td>115.8</td>
</tr>
<tr>
<td>10 at.% Cu ($10^{11}$ KMC steps)</td>
<td>233.3</td>
<td>144.3</td>
<td>113.7</td>
</tr>
</tbody>
</table>

Figure 6. Relative yield stress (A) and relative deformation strain (B) as a function of thermal ageing time. The largest relative change is found for straining the sample in the [111] direction, followed by the [110] and [100] straining directions.
precipitation (see Figure 4A). The relation between yield stress $\sigma_{\text{max}}$ and deformation strain $\epsilon_{\text{max}}$ is depicted in Figure 7A showing linear correlations for the three directions with some concentration dependence in the [100] and [110] straining cases. The largest decrease of yield stress and deformation strain is found for the [111] straining direction, followed by the [110] and the [100] direction. Relating the mean radius of precipitates, a value obtained by KMC simulations, to the yield stress as shown in Figure 7B, emphasizes the dependence of the tensile properties on the sizes of the precipitates. While the precipitates grow, the tensile strength decreases. For larger precipitate sizes, the [110] direction has the highest tensile strength followed by the [111] and [100] straining cases. The fact that yield stress as well as deformation strain decrease for all investigated directions and concentrations gives rise to the conclusion that the sole presence of precipitates yields a weakening of the material. Hence, precipitation strengthening, which is predicted by theory and has also been observed experimentally and by computer simulations (see [31] and the references therein for metals and alloys and [7,32,33] for the special case of $\alpha$-Fe), has to be a consequence of dislocation–precipitate interactions. In the next section it will be shown that the generation of dislocations is facilitated at precipitate–matrix interfaces yielding an earlier initiation of plastic deformation.

4.2. Deformation initiation and statistical glide plane detection

Comparing the stress relaxation behaviour of all simulated samples (Figure 5) shows that several stress–strain curves in Figure 5E and 5F decrease to zero. The corresponding samples represent early states of thermal ageing and are strained in the [111] direction. The drop down to zero indicates material failure due to crack initiation. This is not the case for later thermal ageing times, i.e., for precipitation states where plastic deformation starts after reaching the deformation strain. Figure 8 shows slices cut out of two strained (in the [111] direction) samples at the end of the MD nano tensile tests. These samples mark the beginning (A) and the end (B) of thermal ageing (simulated with KMC). The crack is clearly visible in Figure 8A and
lies in the \(\{21\bar{1}\}\) slip plane. In order to analyse the dislocations which are generated within the samples, we have developed a statistical glide plane detection procedure. To our knowledge, this is the first time that a statistical analysis, considering angles between specific atoms that are not on perfect crystal lattice sites, is applied in order to determine dominant glide planes. The analysis procedure is described hereafter. First, a common neighbour analysis is performed which is provided by the IMD software. Further calculations are performed with Matlab\textsuperscript{TM}. Within a cut-off radius, the number of atoms is counted at each atomic position. The cut-off radius is set between the second- and the third-nearest neighbour, i.e., \(r_c = 0.34602\) nm. In the case of bcc metals, 14 atoms within \(r_c\) should be counted, i.e., eight first- and six second-nearest neighbours. Deviating numbers indicate defects within the solid. In Figure 9A, which corresponds to a strained, thermally aged sample where

![Figure 8](image1.png)

Figure 8. Slices of two [111] samples (see Figure 5E) where (A) corresponds to the last MD time step of the solid solution (blue line) and (B) to the last MD time step of the thermally aged sample (last orange line). In the case of the solid solution the drop of stress to zero indicates crack initiation which is indeed found (A). In the thermally aged sample, dislocations initiate much earlier and relax the sample, yielding plastic deformation [grey atoms = Fe atoms with 14 neighbours].

![Figure 9](image2.png)

Figure 9. Analysis of Fe defects \((n \neq 14)\). The angles between atom pairs with interatomic distances of \(r_c \leq d \leq R_c = 10 \cdot r_c\) are calculated. The frequency of occurring angle pairs indicates dominant dislocation line directions.
dislocations have already nucleated, a common neighbour analysis yields a visualization of defects. The colouring is performed according to Table 7. Dislocations as well as the precipitates are easily visible as green lines and red spherical particles, respectively. In this dislocation analysis we will focus on the iron atoms with $n = 14$ neighbours within $r_c$. For each pair of these atoms whose distance $d$ between each other is $r_c \leq d \leq R_c = 10 \cdot r_c$ (grey atoms in Figure 9B), the angles $\phi$ and $\theta$ are calculated (Figure 9C), determining the direction of the two atoms to each other. As $r_c \leq d$, single defects hardly contribute. Fe atoms belonging to a dislocation will contribute with angle pairs with a dominant direction which is the direction of the dislocation line. All in all, a huge number of $(\theta, \phi)$-pairs is obtained which

Table 7. Atom colouring with respect to the number of atoms within a specified cut-off radius $r_c$. In bcc crystals, $n = 14$ neighbours have to be found. Deviations ($n \neq 14$) indicate defects within the single crystal. An additional identification of atoms with $n = 12$ neighbours is due to the fact that the corresponding fcc structure would have 12 neighbours within $r_c$.

<table>
<thead>
<tr>
<th>Atom type</th>
<th>Number of neighbours</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$n = 14$</td>
<td>Transparent</td>
</tr>
<tr>
<td>Fe</td>
<td>$n &lt; 14$ &amp; $n \neq 12$</td>
<td>Green</td>
</tr>
<tr>
<td>Fe</td>
<td>$n &gt; 14$</td>
<td>Blue</td>
</tr>
<tr>
<td>Fe</td>
<td>$n = 12$</td>
<td>Light blue</td>
</tr>
<tr>
<td>Cu</td>
<td>$n = 14$</td>
<td>Red</td>
</tr>
<tr>
<td>Cu</td>
<td>$n &lt; 14$ &amp; $n \neq 12$</td>
<td>Orange</td>
</tr>
<tr>
<td>Cu</td>
<td>$n &gt; 14$</td>
<td>Purple</td>
</tr>
<tr>
<td>Cu</td>
<td>$n = 12$</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

Figure 10. (A) Unit vector $\vec{v}$ on a specific slip plane with normal vector $\vec{n}$. By rotating the vector such that $\vec{n} \cdot \vec{v} = 0$, $(\theta, \phi)$-pairs are obtained. For the twelve $\{110\}$ slip planes this yields pattern (B). In case of the $[110]$ slip system, $\phi$ stays constant while $\theta$ takes arbitrary values between zero and $360^\circ$ (or $0 \leq \theta \leq 180^\circ$ and $\phi \in \{45^\circ, -135^\circ\}$ like in (B)).
contains the information of dominant directions of dislocation lines. In bcc metals there are specific planes where glide can occur. These are the {110}, the {112} and the {123} glide planes with 12, 12 and 24 slip systems, respectively [34]. For each slip plane a set of unit vectors, each being perpendicular to the normal vector of the slip plane, can be defined and described by \((\theta, \phi)\)-pairs (Figure 10). If the normal vector of the slip plane has no \(z\)-component, e.g., [110], \(\theta\) can take arbitrary values while \(\phi\) stays constant (Figure 10B). For all other slip systems, \(\theta\) and \(\phi\) are not independent, i.e., \(\phi = \phi(\theta)\). In Figure 10B, a sinusoidally shaped pattern is obtained when visualizing \(\phi(\theta)\) for the {110} slip systems with 2D histograms [35]. Analysing now
the [100] sample with 1 at.% Cu at the latest thermal ageing state (see Figure 5A, orange solid line with lowest $\epsilon_{\text{max}}$) at three different strains near $\epsilon_{\text{max}} = 6.55\%$, i.e., at 6.56%, 6.72% and 7.52%, respectively (column A in Figure 11), the statistical glide plane detection yields the ($\theta$, $\phi$)-patterns of column B in Figure 11. Column A in Figure 11 confirms our assumption that, while straining, defects nucleate at precipitate–matrix interfaces. This effect cannot be observed in solid solution samples, where defects initiate more or less homogeneously distributed within the matrix or, in the case of the [111] straining direction, even brittle fracture occurs (see Figure 8A). Comparing the statistical glide plane detection patterns of column B in Figure 11 with the patterns of the {110} and the {112} slip systems (columns C and D, respectively), yields almost perfect agreement. Of course, not every slip system is activated. But the activated ones clearly lie on the expected glide planes. Note that within the patterns certain points, i.e., angles (dark points), become more and more dominant during the development of dislocations. These angles represent intersection lines of two or more slip systems, i.e., directions that allow for dislocation climb and cross-slip. Thus, dislocations are generated preferably in directions where they have the highest freedom of movement.

After having analysed the deformation initiation part, the focus of the next section will be on the tensile behaviour at the beginning of the nano tensile tests.

4.3. Material stiffness – Young’s modulus

By taking the slope of each stress–strain curve in Figure 5, the corresponding tensile modulus $E$, also referred to as Young’s modulus, is deduced. $E$ can be related to the thermal ageing time similarly as it has been done in the case of the tensile strength and the deformation strain (Figure 6). For the pure $\alpha$-Fe samples there is obviously no time dependence of $E$ as the atomic configuration does not change. As the overall tensile behaviour of the samples is anisotropic, so is Young’s modulus. In the case of pure $\alpha$-Fe this means $E_{100} = 141.5$ GPa, $E_{110} = 197.4$ GPa and $E_{111} = 231.6$ GPa. The tendency is that $E_{100} < E_{110} < E_{111}$ as well as the absolute values are in good agreement with the anisotropic tensile moduli determined elsewhere [36]. However, some discrepancy can be found when $E$ is calculated from the elastic constants in Table 6 using the formula

$$\frac{1}{E_{hkl}} = S_{11} - 2(S_{11} - S_{12}) - S_{44}[(\alpha^2 \beta^2 + \alpha^2 \gamma^2 + \beta^2 \gamma^2)]^{1/2},$$

(11)

according to [34], where $\alpha = \cos([hk\ell],[001])$, $\beta = \cos([hk\ell],[010])$ and $\gamma = \cos([hk\ell],[100])$. The compliances can be calculated via

$$S_{11} = \frac{C_{11} + C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})},$$

(12)

$$S_{12} = \frac{C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})},$$

(13)
Equation (11) yields $E_{100} = 135.1 \text{ GPa}$, $E_{110} = 223.5 \text{ GPa}$ and $E_{111} = 285.8 \text{ GPa}$, showing the same tendencies but deviating absolute values. It is reported, e.g., in [37], that the elastic constants in $\alpha$-Fe are significantly temperature-dependent. However, in this study the elastic constants are calculated from a relaxed structure at $T=0 \text{ K}$. For this reason, the discrepancy can be mainly attributed to the existence of thermal energy during the nano tensile tests.

Considering the 1 at.% Cu and the 10 at.% Cu samples, the time-dependent behaviour of the anisotropic tensile moduli is depicted in Figure 12. The different orientations and concentrations yield different starting values of $E$ which lie very close to the pure $\alpha$-Fe values in the case of 1 at.% Cu copper. For this small amount of $\text{Cu}$, $S_{44} = \frac{1}{C_{44}}$. (14)
of copper, the stiffness stays almost constant for all selected time steps, i.e., throughout thermal ageing: only a slight decrease of $E$ is observable. For 10 at.% Cu, the decrease of the tensile moduli is much more significant and does not start instantaneously. Relating the tensile moduli to the density of precipitates, i.e., the particle density (Figure 13), helps to interpret the time-dependent behaviour. At the beginning of the thermal ageing process very small precipitates nucleate from a solid solution (A) which hardly result in a decrease of $E$. As the nuclei grow, they accumulate Cu atoms from the remaining solid solution yielding a decrease of $E$ (B). During growth, the volume of precipitates as well as their interfaces with the surrounding matrix increase. After having reached a maximum value in particle density, Ostwald ripening becomes the dominant process (C). During the coarsening of particles, the mean radius further increases while the volume of the precipitates remains almost constant and the interface between precipitates and matrix decreases, again yielding a decrease of $E$.

In total, the different states of precipitation occurring during the thermal ageing process, i.e., nucleation, growth and Ostwald ripening, can be related very well to the time-dependent change in $E$. Throughout the thermal ageing of the sample, the mean radius $R_{\text{mean}}$ of precipitates monotonically increases (see Figure 4B). As a consequence, the tensile modulus $E$ monotonically decreases in the investigated crystallographic directions $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$.

5. Concluding remarks

In this study we have introduced a sequential multi-time-scale coupling procedure by successfully connecting two simulation methods (KMC and MD, which are based on different physical descriptions) in order to investigate the anisotropic tensile behaviour of Cu-alloyed $\alpha$-Fe at different states of thermal ageing. Concluding remarks on the methodological approach as well as on the physical results will be given in the following.

5.1. The sequential multi-time-scale approach

The Kinetic Monte Carlo (KMC) method with its discrete jump probabilities of a single vacancy within the solid yields statistics of realistic Cu cluster distributions

<table>
<thead>
<tr>
<th></th>
<th>KMC</th>
<th>MD</th>
</tr>
</thead>
<tbody>
<tr>
<td>+/−</td>
<td>simulation of cluster formation possible</td>
<td>trajectories of all atoms are obtained</td>
</tr>
<tr>
<td>+</td>
<td>long time-scales are accessible</td>
<td>deformation of the sample is possible</td>
</tr>
<tr>
<td>−</td>
<td>rigid lattice $\rightarrow$ no deformation possible</td>
<td>only short time-scales are accessible (ns)</td>
</tr>
<tr>
<td>+/−</td>
<td></td>
<td>cluster formation cannot be simulated</td>
</tr>
</tbody>
</table>
after a sufficiently large number of vacancy jumps. The Molecular Dynamics (MD) simulations allow the performance of nano tensile tests at selected states of precipitation by transferring the atomic configuration from KMC to MD. By combining the two methods sequentially, their advantages can be exploited, simultaneously overcoming their particular disadvantages (Table 8). The physical quantities obtained by KMC such as the mean particle radius $R_{\text{mean}}$, the number density of particles or the precipitation time $t$ (see Section 3) can be related to quantities obtained by MD simulations, e.g., tensile strength, deformation strain or Young’s modulus by analysing the MD stress–strain curves (see Section 4).

The coupling of the two methods is limited by a few aspects which we want to note here. Due to the rigid lattice only elements can be considered whose lattice mismatch is not significant. This is the case for $\alpha$-Fe and the coherently embedded Cu. However, growing Cu precipitates undergo a structural bcc $\rightarrow$ 9R $\rightarrow$ 3R $\rightarrow$ fcc phase transition [9,10]. This transition cannot be modelled with the currently available KMC code due to the rigid bcc lattice. This limits the KMC simulations to the formation of small precipitates ($\text{radius} < 2 \text{ nm}$) as the effect of higher eigenstrains on the interaction energies would have to be taken into account additionally. Nevertheless, in the scenario presented here, the Cu precipitates can be assumed to be embedded coherently in the $\alpha$-Fe matrix.

5.2. The anisotropic tensile behaviour of Cu-alloyed $\alpha$-Fe

In order to analyse the tensile behaviour of the thermally aged simulation samples, we have developed a method to extend an existing single crystal with surfaces in $\langle 100 \rangle$ directions to single crystals with surfaces in two other crystallographic directions ($\langle 110 \rangle$ and $\langle 111 \rangle$) without losing periodicity in all directions and conserving the underlying particle statistics (see Section 2.4). The stress–strain curves at different states of thermal ageing, obtained by the MD simulations in Section 4, show a remarkable tensile behaviour. Tensile strength, deformation strain as well as the Young’s modulus decrease during thermal ageing showing a clear dependence on the mean precipitate radius $R_{\text{mean}}$. The decrease of the tensile strength is in contradiction to the predictions of precipitation strengthening. However, in this scenario, single crystals are considered which have very high tensile strengths ($>100 \text{ GPa}$) and deformation strains ($\approx 6–22\%$). The presence of Cu precipitates yields a weakening of the material. This leads to the conclusion that precipitation strengthening is mainly due to dislocation–precipitation interactions.

After analysing the region of deformation initiation in detail by applying a newly developed statistical glide plane detection (see Section 4.2), the following conclusions can be drawn: Straining the sample axially results in defects that initiate at precipitate–matrix interfaces. The generated dislocations lie on the expected glide planes ($\{110\}$, $\{112\}$ glide planes when straining along $\langle 100 \rangle$). Furthermore, dislocations are generated preferably in directions where they simultaneously lie on two or more slip systems enhancing their freedom of movement, e.g., in the course of dislocation climb or cross-slip. At early states of thermal ageing, brittle failure was observed when straining in the $\langle 111 \rangle$ direction (see Figure 8A). With ongoing precipitation, precipitates enable the creation of dislocations at their surfaces before
brittle failure can occur. This behaviour can be interpreted as a brittle-to-ductile transition due to the formation of precipitates.

The deformation mechanisms will be further analysed in our future work in order to predict the glide planes which will be activated preferentially depending on the straining direction.

In this study we have revealed the time-dependent effect of realistic Cu precipitate distributions on the anisotropic tensile behaviour of the Fe–Cu system by sequentially coupling a Kinetic Monte Carlo method with Molecular Dynamics simulations. A further development of this method, e.g., the introduction of preexisting dislocations or grains, can generate valuable information on the mechanical properties of materials by considering their underlying atomistic structure.

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