Reverted austenite in PH 13-8 Mo maraging steels

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1. Introduction

The development and production of martensitic hardenable steels (maraging steels) started in the early 1960s in the USA with steels containing 18\% Ni and 8–9\% Co \cite{1,2}. Due to the sharp drop of the availability and the raising costs of Co, alternatives to cobalt containing maraging steels were in demand. Much effort was laid on developing Co-free maraging steels with appropriate mechanical properties \cite{3}. This resulted in a variety of steels with different precipitating elements, e.g. Al, Ti, Cu and also alloys with lowered Ni content. One example for these developments are the PH 13-8 Mo alloys, which are hardenable steels (maraging steels) that were characterized using transmission electron microscopy (TEM) and atom probe tomography (APT). Two types of austenite, i.e. granular and elongated, are present after aging at 575 °C, whereby the content of the latter increases during aging. The investigations revealed that the austenite phase is enriched in Ni, which prevents the transformation to martensite during cooling. Inside and next to the austenitic areas, Mo and Cr-rich carbides, which form during the aging treatment, were found. Various aging treatments were performed to obtain the activation energy for the formation of reverted austenite. Additionally, the experimental data are compared with thermodynamic and kinetic simulations. Based on these results and the chemical composition changes of the phases, a model for the formation of reverted austenite is presented. It is concluded that precipitation of B2-ordered NiAl and formation of reverted austenite take place simultaneously during aging and that dissolution of precipitates is not essential for the initial formation of reverted austenite.

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austenite, lath-like austenite and recrystallized austenite. Matrix austenite grows from retained austenite or nucleates on prior austenite grain boundaries. Lath-like austenite can develop within the martensite lath or grow along the lath boundaries of martensite. Recrystallized austenite forms at higher aging temperatures or longer aging times, and is characterized by a very low density of defects and dislocations. In high Ni alloyed and Ti-containing maraging steels, which are hardened by Ni3Ti precipitates, the occurrence of Widmanstätten austenite is also mentioned [22,23]. However, it has been shown that the particular type of austenite depends on the applied aging temperature [19]. The orientation relationship between austenite and martensite is generally reported to be of Kurdjumow–Sachs or Nishiyama–Wassermann type [17,24,25].

The formation mechanism of reverted austenite in maraging steels is often related to a diffusion-controlled process. Hereby, it is assumed that the formation of reverted austenite is determined by dissolution of precipitates during aging, which results in a local enrichment of austenite stabilizing elements [23,26–30]. Sinha et al. [17] exclude the mechanism of dissolution of precipitates for the formation of reverted austenite. They suggest that Ni diffuse to dislocations and defects, resulting in microsegregation of austenite stabilizing elements in localized areas. Kim and Wayman [22] suggested that the formation of lath-like austenite in high Ni maraging alloys is shear dominated but assisted by a diffusion-controlled process. However, the author’s best knowledge, there exists no investigation about the formation mechanism of reverted austenite in PH 13-8 Mo alloys. There is a lack of information concerning the morphology, size and chemical composition of reverted austenite in such kind of steels.

The aim of this work is to characterize reverted austenite in a PH 13-8 Mo alloy by the two complementary methods transmission electron microscopy (TEM) and atom probe tomography. Based on experimental results and simulations, the formation mechanism of reverted austenite is discussed.

2. Experimental

The chemical composition of the investigated PH 13-8 Mo maraging steel is given in Table 1. The alloy was commercially produced and provided by the company Bohler Edelstahl GmbH & Co KG as a rolled bar. The material was subjected to solution annealing at 900 °C for 1.5 h and subsequent cooling in air. Aging was performed at 575 °C for various times, up to 1000 h. TEM investigations and APT were conducted on samples, which have been aged for 3 h, 5 h, 10 h and 100 h. The determination of the austenite phase fraction was conducted by X-ray diffraction measurements on a Siemens D500 using CuKα radiation. For evaluation of the diffraction scans, the method of direct comparison of the integrated intensities of the martensite and austenite peaks [31] was applied. The TEM investigations were performed on polished and electrolytically etched samples on a Phillips CM12 microscope, which was operated at 120 kV.

For APT, small rods were cut from the bulk material and then etched to sharp needles by a standard two-step electro polishing technique [32]. The second polishing step was conducted in a 25% perchloric acid in 2-butoxyethanol. APT was performed on a LEAP™ 3000X HR atom probe in laser mode at a base temperature of 20 K. The laser energy was adjusted to 0.2 nJ and the repetition rate was set to 200 kHz. Data reconstruction was conducted using the software package IVAS™.

Thermodynamic and kinetic simulations were performed with the software package MatCalc 5.30 [33–35] and the corresponding thermodynamic and diffusion databases ‘mc_steel’ [36] and ‘mc_sampledata’ [37], respectively. The calculations were performed taking into account the phases FCC, A1 (austenite), BCC_A2 (ferrite) and BCC_B2 (ordered bcc NiAl) and based on the entire time-temperature history of the experiment. For the NiAl precipitates, homogeneous bulk nucleation was assumed, while, for the reverted austenite, only the grain boundaries and subgrain boundaries were considered. A measured prior austenite grain diameter of 25 µm and a subgrain diameter of 1 µm were utilized. Furthermore, a shape factor of H/D = 0.2 (see ref. [38]) was used for the reverted austenite to take into account the elongated shape. For the precipitation simulation, the interfacial energy of the precipitate phases was calculated using the generalized nearest-neighbor broken-bond approach [39], and taking into account size effects for the critical nucleus [40]. Entropic contributions to the interfacial energy stemming from finite interface thickness and mixing across the interface are taken into account by a constant factor of 0.8 for the NiAl phase. No corrections were made for the FCC precipitates at grain boundaries and subgrain boundaries.

3. Results

Aged samples and a solution-annealed sample as reference material were characterized in order to reveal the phase fraction and morphology of austenite, the presence of carbides and the chemical composition of austenite and precipitates.

3.1. Phase fraction of austenite

To determine the amount of reverted austenite present after the applied aging treatments, X-ray diffraction experiments were conducted. Fig. 1 shows the phase fraction of austenite versus aging time for an aging temperature of 575 °C. After solution annealing, the material contains no retained austenite or the amount is below the detection limit of X-ray diffraction of about 3 vol.%. Aging up to 100 h leads to a nearly linear increase of the austenite phase fraction. This is due to the reverse transformation of martensite into austenite during isothermal aging at 575 °C. After 100 h of aging, the austenite phase fraction reaches a plateau at 29 vol.%. No further increase of the austenite phase fraction is observed, even after 1000 h of aging.

3.2. TEM investigations

TEM investigations have been conducted on samples in the as-quenched state as well as after aging at 575 °C for 3 h, 5 h, 10 h and 100 h. The sizes of reverted austenite resulting from evaluation of numerous TEM images are summarized in Table 2. The evaluation of the reverted austenite size was performed separately for granular and elongated shapes. The solution-annealed state did not show any retained austenite and is therefore not depicted here. Furthermore, no carbides were found in the solution-annealed state. Fig. 2 illustrates a bright-field TEM image of a sample aged at 575 °C for 3 h. Small austenite grains with an elliptic shape are present on prior austenite grain boundaries or triple points. The dominant

![Fig. 1. Phase fraction of austenite as function of aging time. The aging temperature was kept constant at 575 °C.](image-url)
Table 2
Average values of the size dimensions of reverted austenite after different aging times (aging temperature = 575 °C). The 100 h aged sample exhibit lath-like austenite which can have a length dimension of more than 2000 nm.

<table>
<thead>
<tr>
<th>Aging time</th>
<th>Austenite morphology</th>
<th>Length [nm]</th>
<th>Width [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 h</td>
<td>Granular</td>
<td>342</td>
<td>133</td>
</tr>
<tr>
<td></td>
<td>Elongated</td>
<td>469</td>
<td>115</td>
</tr>
<tr>
<td>5 h</td>
<td>Granular</td>
<td>340</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>Elongated</td>
<td>542</td>
<td>143</td>
</tr>
<tr>
<td>10 h</td>
<td>Granular</td>
<td>263</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>Elongated</td>
<td>798</td>
<td>140</td>
</tr>
<tr>
<td>100 h</td>
<td>Granular</td>
<td>412</td>
<td>183</td>
</tr>
<tr>
<td></td>
<td>Elongated</td>
<td>≈2000</td>
<td>227</td>
</tr>
</tbody>
</table>

Fig. 2. Bright-field TEM image of a sample aged at 575 °C for 3 h. Matrix austenite (marked with arrows) on prior austenite grain boundaries can be seen.

Austenite morphology after 3 h of aging is a granular one with a length of approximately 340 nm and a width of 130 nm. EDS analyses of the austenite grains revealed that the austenite is enriched in Ni, showing a content of approximately 13 at.% Ni compared to 4 at.% Ni in the martensitic matrix. In Fig. 3 TEM images of a sample aged at 575 °C for 5 h are displayed. Clear evidence of different types of austenite was available from the TEM micrographs. The austenite visible in Fig. 3a shows a granular morphology and it has formed within a martensite lath. However, it is noticeable that these austenite regions sometimes contain precipitates (marked with an arrow in Fig. 3a). The TEM image in Fig. 3b shows another type of austenite. It is located along martensite lath boundaries and exhibits an elongated shape. This austenite type grew to an average length of 540 nm and an average width of 140 nm, corresponding to an aspect ratio of 0.25. Fig. 4 provides bright-field TEM images of a sample, which has been aged for 10 h. It can be seen that the fraction of both the elongated austenite (Fig. 4a) as well as the granular (Fig. 4b) has increased. However, in this condition the content of the elongated austenite exceeds the content of the granular one. Mainly the length of the elongated austenite has increased to almost 800 nm resulting in a lowered aspect ratio of 0.18. Fig. 5a and b are illustrations of the microstructure after 100 h of aging, which was observed by TEM investigations. Several austenite laths can be seen inside one martensite lath. Thus, aging at 575 °C for 100 h led to a lamellar structure of alternating austenite and martensite laths. The austenite laths have grown to a length of more than 2000 nm, whereas the increase of the width is small. This results in an aspect ratio of almost 0.10. However, in this condition, almost no granular austenite can be found inside the martensite laths (see Fig. 5b). Fig. 5c also reveals that fine precipitates are present in the austenite. EDS analyses indicate an enrichment of Mo.

However, there is no indication for NiAl precipitates inside the austenite phase. EDS analyses of the austenite grains on the different aged samples have shown that the content of the alloying elements remain constant during aging.

3.3. Atom probe investigations

The chemical composition changes between matrix, precipitates and reverted austenite are in the nm-scale and were therefore analyzed by APT. In Fig. 6, the three-dimensional reconstruction of the atomic positions of a sample aged at 575 °C for 100 h is illustrated. The left image shows the measured volume and the rectangle on the right provides a detail of this volume with the atom positions of Ni, Al and Cr. It can be seen that the analyzed volume consists of different enriched areas, which correspond to different phases. The Ni-enriched area on the top of the analyzed volume is followed by a region with a lower Ni content. In this region small spherical enrichments of Ni and Al are present. These areas correspond to the bcc-B2-ordered NiAl precipitates in the martensitic matrix. On the lower side of the tip, again, a Ni-enriched area can be observed. According to EDS analyses in TEM, it is con-
Fig. 4. TEM images of a sample aged at 575 °C for 10 h. (a) Elongated austenite along and inside the martensite lath can be seen. (b) Bright-field TEM image of an area with granular austenite.

Fig. 5. Bright-field TEM images of a sample aged at 575 °C for 100 h. (a) Lath-like austenite can be seen. (b) NiAl precipitates are only visible in the martensite laths. The austenitic phase is free of this precipitates. (c) Mo-enriched particles inside or next to austenite are shown.

cluded that this Ni-enriched area corresponds to the austenite phase. The measurement shows that this analyzed volume is free of NiAl precipitates. A one-dimensional concentration profile (Fig. 7) along the analysis direction was obtained by positioning a box of 5 nm × 5 nm × 250 nm through the different regions as shown in the left image in Fig. 6. It can be seen that the Ni content in the austenite is increased to about 14 at.% and the aluminium content remains almost the same as in the martensitic matrix. In contrast, both the Ni and Al content are increased in the precipitate. The Ni content in the core of the precipitates reaches the stoichiometric 50 at.%, whereas the Al content is much lower due to a high amount of Fe incorporated in the precipitates.

In Fig. 8, a three-dimensional reconstruction of the atom positions of a sample aged for 10 h is illustrated. The atom positions reveal four different regions by visual inspection. The lower half of the analyzed volume consists of a region where spherical Ni-

Fig. 6. Three-dimensional reconstruction of a sample aged at 575 °C for 100 h. In the left image the different phases are marked. The large rectangle shows a detail of the measured volume and the distribution of the Ni, Al and Cr atoms. The box in the left image corresponds to a volume, which was analyzed separately to gain details of the chemical variations.
Fig. 7. One-dimensional concentration profile of Ni and Al along the analysis axis of the marked volume from Fig. 6. The areas with Ni increased only represent the reverted austenite.

Table 3
Results of the NiAl precipitates obtained by atom probe data analysis with isosurfaces.

<table>
<thead>
<tr>
<th>Radius [nm]</th>
<th>Number density [m⁻³]</th>
<th>vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 h⁺</td>
<td>3.4 ± 1.1</td>
<td>1.98E+23</td>
</tr>
<tr>
<td>5 h⁺</td>
<td>4.0 ± 1.6</td>
<td>1.16E+23</td>
</tr>
<tr>
<td>10 h</td>
<td>5.2 ± 2.1</td>
<td>6.2E+22</td>
</tr>
<tr>
<td>100 h**</td>
<td>9.4</td>
<td>1.1E+22</td>
</tr>
</tbody>
</table>

* Not depicted here.
** Values with higher uncertainty because of poor statistics.

and Al-enriched volumes are present. This area corresponds to the martensitic matrix with NiAl precipitates. On the upper half of the analyzed volume, a Ni-enriched region, supposed to be reverted austenite, can be recognized. Attached to this region, a Mo- and C-enriched area can be observed. Fig. 9 provides a one-dimensional concentration profile along the analysis axis of a box of 5 nm × 5 nm × 150 nm as shown in Fig. 8a. In the area where austenite is present, a higher Ni content of approximately 15 at.% is observed and the region enriched in Mo shows also a slightly higher C content. The increased Ni and Al content in the precipitates are also visible. A Ni content of about 50 at.% and an Al content of about 30 at.% are reached in the core of the precipitates.

The evaluated radius, number density and volume fraction of the NiAl precipitates after different aging conditions are summarized in Table 3. An increase of the radius, a decrease of the number density and an approximately constant volume fraction of the precipitates with prolonged aging time are observed.

4. Discussion

4.1. Microstructure evolution during aging

Reverted austenite was characterized by transmission electron microscopy on samples, which had been aged for various times. By using TEM, on the one hand, it is possible to gain information about the shape, distribution and size of reverted austenite, on the other hand it is difficult to obtain chemical information in the sub-nm range. By applying atom probe tomography, compositional changes with near atomic resolution can be measured.

The investigations showed that, in the as-quenched state, this alloy contains no retained austenite. Thus, it is assumed that the entire austenite, which is present in the aged conditions, can be related to reverted austenite. This is in disagreement to the results reported by Mittra et al. [8], who have found retained austenite in the as-quenched state. The reason for that might be the higher solution annealing temperature and the fast quenching rate applied in the study by Mittra et al. [8]. TEM investigations revealed two morphologies of reverted austenite in the investigated steel, namely granular and elongated austenite. Following the classification of Shiang and Wayman [16],
the observed austenite belongs to matrix austenite and lath-like austenite. However, there was no evidence of recrystallized austenite or Widmanstätten austenite, as had been observed in high Ni containing maraging alloys [23]. Non-recrystallized austenite is difficult to distinguish from recrystallized austenite as it is only possible via the dislocation density. The investigations did not reveal austenitic areas showing significant differences in dislocation density. This could be due to the applied aging temperature of 575 °C, which might be too low for recrystallization of austenite. The fractions of the two observed types of austenite change with prolonged aging. After 3 h of aging, only matrix austenite is present. Aging for 10 h leads to additional formation of lath-like austenite, being the dominant morphology after 100 h of aging. The preferred formation of matrix austenite at short aging times might be caused by the low nucleation energy at the prior austenite grain boundaries. Nucleation within the martensite laths might be caused by the high dislocation density, providing numerous low-energy sites for nucleation. The size of the granular austenite during aging is almost constant. In contrast, the elongated austenite increases in size. The growth rate parallel to the lath boundaries is much faster. This indicates that matrix austenite is formed at the beginning of aging and the increase of the phase fraction of austenite during aging can be attributed to the formation and grow of lath-like austenite. A similar behaviour was reported by Shiang and Wayman [16]. These authors assumed that the restricted growth perpendicular to the length axis is due to the inhibition of adjacent austenite laths. However, probably, this is also the reason for the preferred growth direction of reverted austenite in this study. An influence of carbides that hinder the growth of austenite can be excluded because of their minor content present in this alloy.

In addition to TEM investigations, APT measurements were performed to gain information on the processes occurring during reverted austenite formation. The measured chemical compositions of reverted austenite for the 10 h and 100 h aged states are listed in Table 4. The Ni content of reverted austenite varies on different sites between 11 and 16 at.%, which might be an effect of locally different nucleation and growth conditions. The content of other alloying elements in the austenite remains almost constant during aging, which suggests that no redistribution of alloying elements between martensite and austenite takes place. In this study, also, Mo- and Cr-rich carbides located on lath boundaries between austenite and martensite as well as within the austenite were found. This nucleation inside or next to the austenite is due to the higher solubility of C in austenite compared to martensite. In contrast to Mittra et al. [8], who reported the presence of primary carbides in this type of steel, it is assumed that these carbides precipitate during aging, since no carbides were observed in the as-quenched state.

### 4.2. Formation of reverted austenite

In order to understand the formation mechanism of reverted austenite, it is essential to consider the distribution of alloying elements during aging. Table 5 shows the chemical composition of the present phases, which have been obtained by separation during atom probe data evaluation. The NiAl precipitates were defined by isosurfaces, austenite and martensite were exported to separate volumes. For the 3 h and 5 h aged samples, only the chemical composition of the martensitic matrix and the precipitates are listed, because no reverted austenite has been detected in atom probe in a random run mode. The values for the 100 h aged sample are connected with high uncertainty, due to the limited number of large precipitates measured by APT. The NiAl precipitates contain a significant amount of Fe in all aging conditions. However, the amount of Al increases at the expense of Fe with prolonged aging. According to our calculations, the diffusion of Al atoms is approximately 10 times faster compared to the diffusion of Ni atoms in a PH 13-8 Mo alloy. The amount of Ni in the martensitic matrix decreases slightly during aging, whereas the Fe content increases. The amount of all other alloying elements remains almost constant in the martensitic matrix during aging.

To aid interpretation of the experimental data and to gain information on the initial states of austenite formation, thermodynamic and kinetic calculations were performed. The experimental results, i.e. phase fraction of NiAl precipitates and reverted austenite are compared to values obtained by simulations, using the software package MatCalc 5.30 (rel. 1.075) [33–35]. For the simulations, both, the BCC_B2 phase (ordered bcc-B2 NiAl) as well as the FCC_A1 (austenite) are defined as precipitate phases, which can form in the ferritic matrix (BCC_A2). The comparison of the computed results and the experimental measurements (taken from Fig. 1 and Table 3) are presented in Fig. 10. It can be seen that the simulation describes the obtained experimental data quite well. In accordance with the experimental results, the phase fraction of austenite (Fig. 10) increases after 3 h of aging and reaches a constant value after approximately 100 h. It seems that the amount of 30 vol.% is the equilibrium phase fraction of austenite at 575 °C, as this amount remains constant even after 1000 h of aging. The formation of NiAl precipitates and reverted austenite is predicted to start from the

### Table 4
Chemical composition of reverted austenite obtained by TEM and APT of samples aged at 575 °C for 10 h and 100 h (APT data taken from Table 5, all values in at.%).

<table>
<thead>
<tr>
<th></th>
<th>10 h</th>
<th>100 h</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>APT</td>
<td>TEM</td>
</tr>
<tr>
<td>Al</td>
<td>0.8</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>14.1</td>
<td>15.0 ± 1.0</td>
</tr>
<tr>
<td>Ni</td>
<td>16.0</td>
<td>13.7 ± 2.3</td>
</tr>
<tr>
<td>Mo</td>
<td>0.9</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>68.2</td>
<td>68.9 ± 2.4</td>
</tr>
</tbody>
</table>

### Table 5
Chemical composition of the phases detected by atom probe tomography (all values in at.%).

<table>
<thead>
<tr>
<th>at.%</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Al</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3h</td>
<td>Matrix</td>
<td>79.65 ± 0.03</td>
<td>12.99 ± 0.01</td>
<td>5.02 ± 0.01</td>
<td>1.06 ± 0.003</td>
<td>0.77 ± 0.002</td>
<td>0.06 ± 0.001</td>
<td>0.04 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Precipitates</td>
<td>28.39 ± 0.09</td>
<td>3.32 ± 0.03</td>
<td>41.46 ± 0.11</td>
<td>0.29 ± 0.001</td>
<td>25.93 ± 0.08</td>
<td>0.53 ± 0.001</td>
<td>0.06 ± 0.003</td>
</tr>
<tr>
<td>5h</td>
<td>Matrix</td>
<td>80.16 ± 0.04</td>
<td>13.21 ± 0.01</td>
<td>4.78 ± 0.01</td>
<td>1.05 ± 0.004</td>
<td>0.70 ± 0.003</td>
<td>0.06 ± 0.0009</td>
<td>0.04 ± 0.0007</td>
</tr>
<tr>
<td></td>
<td>Precipitates</td>
<td>24.67 ± 0.10</td>
<td>2.62 ± 0.03</td>
<td>43.84 ± 0.15</td>
<td>0.31 ± 0.001</td>
<td>27.77 ± 0.11</td>
<td>0.50 ± 0.001</td>
<td>0.05 ± 0.004</td>
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<tr>
<td>10h</td>
<td>Matrix</td>
<td>81.75 ± 0.04</td>
<td>12.51 ± 0.01</td>
<td>3.98 ± 0.01</td>
<td>0.92 ± 0.003</td>
<td>0.72 ± 0.003</td>
<td>0.07 ± 0.001</td>
<td>0.04 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Precipitates</td>
<td>23.67 ± 0.08</td>
<td>2.29 ± 0.02</td>
<td>43.21 ± 0.12</td>
<td>0.28 ± 0.001</td>
<td>29.91 ± 0.10</td>
<td>0.50 ± 0.001</td>
<td>0.10 ± 0.001</td>
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<td></td>
<td>Austenite</td>
<td>68.05 ± 0.13</td>
<td>14.03 ± 0.05</td>
<td>16.01 ± 0.05</td>
<td>0.90 ± 0.001</td>
<td>0.84 ± 0.001</td>
<td>0.13 ± 0.004</td>
<td>0.05 ± 0.003</td>
</tr>
<tr>
<td>100h</td>
<td>Matrix</td>
<td>82.40 ± 0.09</td>
<td>12.26 ± 0.03</td>
<td>3.43 ± 0.01</td>
<td>0.79 ± 0.001</td>
<td>1.01 ± 0.001</td>
<td>0.05 ± 0.002</td>
<td>0.04 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>Precipitates</td>
<td>19.15 ± 0.10</td>
<td>1.00 ± 0.02</td>
<td>45.23 ± 0.16</td>
<td>0.15 ± 0.001</td>
<td>33.88 ± 0.13</td>
<td>0.47 ± 0.001</td>
<td>0.09 ± 0.001</td>
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<tr>
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<td>Austenite</td>
<td>71.21 ± 0.18</td>
<td>13.59 ± 0.06</td>
<td>13.33 ± 0.06</td>
<td>0.86 ± 0.002</td>
<td>0.72 ± 0.001</td>
<td>0.15 ± 0.001</td>
<td>0.06 ± 0.004</td>
</tr>
</tbody>
</table>

* Not depicted here.
very beginning of aging. Thus, the simulations indicate that the formation of precipitates and reverted austenite occurs widely independent of each other. The formation of both, austenite and NiAl nuclei, is thermodynamically possible in the virgin martensitic matrix. Thus, dissolution of precipitates is not necessarily the initial driving factor for the formation of reverted austenite.

If the formation of reverted austenite is diffusion controlled, its activation energy can be determined based on an equation of Arrhenius type:

$$\ln(t) = \frac{Q}{RT} + \text{constant}$$

In Eq. (1), $t$ is the time to attain a fixed amount of reverted austenite at a specific temperature $T$, $R$ is the universal gas constant and $Q$ is the activation energy.

As the equilibrium phase fraction of reverted austenite strongly depends on the applied aging temperature, which can be seen in Fig. 11 showing the results from thermodynamic simulations, aging experiments had to be conducted. In this study, the time necessary to achieve 20% of the equilibrium amount of austenite at each temperature was determined. The results are presented in Fig. 12 and it can be seen that the data fit well to a straight line. Based on this analysis, an activation energy of $234 \pm 20 \text{ kJ mol}^{-1}$ was obtained. Slightly different values for the activation energy for the formation of reverted austenite were reported by Nakagawa et al. [41] and Sinha et al. [17]. They found an activation energy of about $250 \text{ kJ mol}^{-1}$, which is in the range of the activation energy for diffusion of Ni in pure iron [42]. Calculation of the activation energy for the diffusion of Ni atoms in a PH13-8 Mo steel based on the mobility database ‘mc_sample_fe’ yielded $213 \text{ kJ mol}^{-1}$, which is in the range of the measured one. The calculated activation energy for diffusion of Al atoms in a PH 13-8 Mo steel is $218 \text{ kJ mol}^{-1}$, which is nearly the same as for the diffusion of Ni atoms. Therefore, it is concluded that diffusion of both elements is decisive for the growth of reverted austenite.

Based on the experimental results and the simulations, the following sequence of mechanisms is proposed for the formation of reverted austenite. Fig. 13 shows a schematic drawing of the proposed mechanism, describing the four different stages of the model as follows:

(I) The initial microstructure, i.e. after quenching from the solution-annealed state, consists of lath martensite with high dislocation density.

(II) From the very beginning of aging, NiAl precipitates nucleate homogeneously in the martensitic matrix. Austenite forms preferentially on prior austenite grain boundaries or on martensite lath boundaries. However, in this stage, the formation of precipitates and reverted austenite occur independent
of each other. The formation of both austenite and NiAl nuclei is thermodynamically possible. 
(III) Growth of reverted austenite on prolonged aging leads to dissolution of adjacent NiAl precipitates. Ni stemming from the dissolved precipitates diffuses to reverted austenite and promotes its further growth. In contrast, Al, which has a higher diffusion coefficient than Ni, is assumed to diffuse to precipitates inside the martensitic matrix, as the Al content in the precipitates increases during aging. The Al content in the austenite is approximately the same as in the matrix. Therefore, Al, which has a higher diffusion coefficient in Fe than Ni, is assumed to diffuse to precipitates inside the martensitic matrix, as the Al content in the precipitates increases during aging.

References

[31] Mobility Database ‘mc_sample_fe’, version 1.03, Institute of Materials Science and Technology, Vienna University of Technology.