Effect of Ti on Evolution of Microstructure and Hardness of Martensitic Fe–C–Mn Steel during Tempering

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The effect of the addition of 0.042 wt.% of titanium on the relation between the evolution of the microstructure and the softening kinetics of quenched martensite in high-purity Fe–C–Mn steel has been studied during tempering at 300 and 550°C. The evolution of the microstructure is characterized by measuring the cementite particle size, the martensite block size, the area fraction of martensite regions which contain a high dislocation density, the macroscopic hardness, the nano-hardness of martensite blocks boundaries, the nano-hardness of the matrix and the TiC-precipitate size during tempering. Nucleation of TiC-precipitates take place during annealing at 550°C and starts earlier in regions close to the block boundaries, after 5–10 minutes, and thereafter in the matrix, after 10–30 minutes, due to the higher dislocation density in the regions close to the block boundaries. The TiC-precipitates slow down the recovery in regions of high dislocation density compared to the alloy without TiC-precipitates. The TiC-precipitates increase the macroscopic hardness of the steel after 30 minutes annealing at 550°C. The growth of TiC-precipitates in martensite is simulated in good agreement with experimental observations by a model that takes into account: 1) capillarity effects, 2) the overlap of the titanium diffusion fields between TiC-precipitates, and 3) the effect of pipe diffusion of titanium atoms via multiple dislocations. The average, experimentally-observed, TiC-precipitate size is 69 ± 48 Ti atoms.

KEY WORDS: martensite; microstructure; recovery; electron backscatter diffraction; nano-hardness; atom probe tomography.

1. Introduction

Tempered martensitic steel of strengths up to 1 200 MPa is the most commonly used material for high-strength fasteners in mass-produced car engines today. The recommended maximum temperature during service is 150°C.15 These are the typical requirements for the service conditions of fasteners for mass-produced passenger cars. However, the current trend of engine down-sizing has resulted in higher mechanical and thermal loading of the engines. There is a need for stronger (and yet tough) steels at higher temperatures for engine fasteners. The design of this steel must fulfill additional requirements. The alloying elements should be abundantly available and should be added in low quantities to assure cost and material formability. Furthermore, heat-treatment must be possible using industrial heat-treatment equipment and tempering temperatures above 425°C according to the ISO898-1 standard.15

Precipitates have for decades been used in steels in order to improve mechanical properties of steel. Good examples are the improved fire-resistance of construction steel,2) the temperature and wear resistance of tool and high-speed steels,3) and the creep-resistance of 9–12 Cr martensitic steels for the power generation industry.4–6) These improvements of properties are based on a fine dispersion of precipitates, which act like pinning points for dislocations and hinder dislocation movement and recovery. Recent research suggests that TiC-precipitates are good candidates for improving the strength of martensite at elevated temperature due to their slow coarsening rate.7) Martensitic steel with medium carbon content and a small addition of Ti (around 0.04 wt%) is therefore an interesting candidate steel for making steels for fasteners that are stronger at higher temperatures. Furthermore are TiC-precipitates known to act as hydrogen traps8–10) and improve the resistance to hydrogen-induced damage, a very desirable feature when creating a high-strength steel for the automotive industry.

In order to optimize the microstructure and properties of the steel we need fundamental understanding of the relation between the evolution of the microstructure and the softening kinetics during tempering of martensite with small additions of titanium. Previous research has shown that the strength of as-quenched and tempered, medium-carbon, martensitic steel strongly depends on the grain boundaries.11–14) The grain boundaries of the martensite blocks bring a so called grain boundary effect to the steel; the boundaries

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are harder than the grain interior and therefore increase the macroscopic strength.

We know that TiC-precipitates nucleate near dislocations and that the nucleation rate is increased by increasing dislocation density. However, the interplay is not clear between the nucleation and early growth of TiC-precipitates and the softening of the martensite due to the redistribution of carbon and titanium atoms into cementite and TiC and the dislocation annihilation during tempering.

The aim of this study is to determine the effect of titanium in solid solution and TiC on the evolution of the microstructure and the softening kinetics of quenched martensite in Fe–C–Mn steel during tempering at 300 and 550 °C. A special focus of our research is to differentiate between the hardness of block boundaries and the matrix, because previous research has shown that the strength of medium-carbon, martensitic steel strongly depends on martensite block boundaries.

2. Method

One Ti-containing and one Ti-free alloy of Fe–C–Mn is investigated. The steel compositions are given in Table 1. Both steels are received with a carbon concentration of 0.11 wt.% and subsequently carburized to a carbon concentration of 0.39 wt.% C. The steel cylinders are cut into 10 mm long specimens for heat-treatment in a Bähr 805 A/D dilatometer (Bär-Thermoanalyse GmbH, Hüllhorst Germany). Both steels are quenched to room temperature from their respective austenization temperatures, using He-gas, at a cooling rate of approx. 175–180 °C/s from the start of quench to the martensite start (Ms) temperature and the softening of the martensite due to the redistribution of TiC-precipitates the oxygen ion count at 16 Da is compared with the natural isotope abundance. For the Ti atoms in the TiC precipitates the oxygen ion count at 16 Da is scaled according to the known nominal concentration of oxygen in the steel and the excess count is attributed to Ti.

The quantitative APT analysis of C atoms is based on isotope distributions of different ions of relevant atom types. Overlaps involving Ti atoms exist at 24 Da (given by Ti2+ or one molecular ion consisting of two 12C) and 16 Da (given by Ti+ or O2). We correct the number of Ti counts at 24 Da with the Ti counts in the surrounding peaks, 23, 23.5, 24.5 and 25 Da. The surrounding peaks have no overlap with other atom types and the Ti count at 24 Da is scaled according to the natural isotope abundance. For the Ti atoms in the TiC precipitates the oxygen ion count at 16 Da is compared with the known nominal concentration of oxygen in the steel and the excess count is attributed to Ti.

The quantitative APT analysis of C atoms is based on ions detected at 6, 6.5, 12 and 13 Da, plus all ions which exceeded the expected Ti level at 24 Da (as two C ions).

The detection and visualization of TiC-precipitates is done via isoconcentration-surfaces enclosing regions which

<table>
<thead>
<tr>
<th>Steel</th>
<th>C (wt%)</th>
<th>Mn (wt%)</th>
<th>Si (wt%)</th>
<th>P (wt%)</th>
<th>S (wt%)</th>
<th>Al (wt%)</th>
<th>Ti (wt%)</th>
<th>Cu (wt%)</th>
<th>Cr (wt%)</th>
<th>O (wt%)</th>
<th>V (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-free</td>
<td>0.39</td>
<td>0.870</td>
<td>0.0035</td>
<td>0.0010</td>
<td>0.0007</td>
<td>0.0050</td>
<td>–</td>
<td>0.0012</td>
<td>0.00018</td>
<td>0.0080</td>
<td>0.0023</td>
</tr>
<tr>
<td>Ti-containing</td>
<td>0.39</td>
<td>0.870</td>
<td>0.0040</td>
<td>0.0011</td>
<td>0.0007</td>
<td>0.0047</td>
<td>0.0420</td>
<td>0.0012</td>
<td>0.0022</td>
<td>0.0046</td>
<td>0.0022</td>
</tr>
</tbody>
</table>

Transmission electron microscopy (TEM) is used to control that no TiC-precipitates are present in the steel after quenching and Atom probe tomography (APT) is used to measure the TiC precipitate size after annealing of the martensite. The TEM specimens are produced with the in-situ lift-out method using a FEI Strata DB235 DualBeam workstation combining a focused ion beam with a scanning electron microscope (FIB-SEM). The TEM specimens are analysed in a FEI Tecnai G2 transmission electron microscope working at 200 kV with a LaB6 filament. APT specimens are produced with an in-situ lift-out method using the FEI Strata 235 DualBeam workstation. The specimen is sharpened by Ga+ sputtering using a pattern shaped as an annulus circle. The voltage used is 30 kV with an initial current of 3 000 pA which is decreased as the specimen becomes sharper. The final sputtering is performed at 10 kV and 300 pA in order to decrease the gallium implementation in the specimen.

The APT specimens are analysed in an Imago LEAP 3000X HR atom probe tomography instrument. The analyses are performed using laser pulsing at 200 kHz and the laser energy of 0.2 nJ. The specimen temperature is 30–50 K and the evaporation rate is 1%. The reconstruction and data evaluation is performed using IVAS 3.6.1 software. The quantitative analysis is based on isotope distributions of different ions of relevant atom types. Overlaps involving Ti atoms exist at 24 Da (given by Ti2+ or one molecular ion consisting of two 12C) and 16 Da (given by Ti+ or O2). We correct the number of Ti counts at 24 Da with the Ti counts in the surrounding peaks, 23, 23.5, 24.5 and 25 Da. The surrounding peaks have no overlap with other atom types and the Ti count at 24 Da is scaled according to the natural isotope abundance. For the Ti atoms in the TiC precipitates the oxygen ion count at 16 Da is compared with the known nominal concentration of oxygen in the steel and the excess count is attributed to Ti.

The quantitative APT analysis of C atoms is based on ions detected at 6, 6.5, 12 and 13 Da, plus all ions which exceeded the expected Ti level at 24 Da (as two C ions).

The detection and visualization of TiC-precipitates is done via isoconcentration-surfaces enclosing regions which
contain a Ti concentration that exceeds the nominal steel concentration by 20 times (high enough to avoid local fluctuations or segregations of Ti atoms and low enough to avoid ruling out very small TiC precipitates). The diameter of the precipitates is determined from the number of Ti atoms measured by APT, together with the lattice parameter of TiC. We count 4 Ti atoms per unit cell of TiC.

Micro-Vickers hardness is measured at 20 locations on polished specimens using a load of 500 g. CSM nano-indentation measurements are performed on electro-polished specimens using an Agilent G200 nano-indentor equipped with a Berkovich-indenter and oscillation amplitude of 2 nm. The tip is calibrated using a reference specimen of fused silica and the hardness values are determined following the method of Oliver and Pharr.\textsuperscript{25} We perform $8 \times 8$ indents to a depth of 70 nm on each sample. The location of each individual indent is derived via the methodology developed by Ohlund \textit{et al.}\textsuperscript{11} The method is based on the fact that the shape of the nano-hardness and the E-module curves, as a function of indent depth, has a steeper increase during the first 20–25 nm for indents located at block boundaries, whereas indents located in the matrix show a gradual increase of the values. The method was validated previously by us determining the location of the indents by EBSD measurements\textsuperscript{13} where 13 indents on block boundaries and 17 indents in the matrix were compared. Block boundaries were defined as boundaries with a misorientation that exceeded 10\textdegree and IPF mapping revealed that the majority of all block boundaries in the investigated specimen had a misorientation in the range of 45–60\textdegree.

3. Results

3.1. Cementite Particle Size Evolution

Figure 1 shows SEM images of Ti-free martensite (a-b) and Ti-containing martensite (c-d) in the as-quenched condition and after tempering for 60 minutes at 550\textdegree C. The intermediate tempering times at both 300\textdegree C and 550\textdegree C were also examined by SEM but are not shown here. The SEM images in Figs. 1(a) and 1(c) show that the microstructures of both steels are similar in the as-quenched state. Two types of regions exist: auto-tempered regions which contain small iron-carbides and non-tempered regions which are smooth and carbide-free.\textsuperscript{11} The area fraction of tempered martensite in the as-quenched state is larger in the Ti-containing steel. The SEM images in Figs. 1(b) and 1(d) show that the microstructures of both steels consists of tempered martensite with cementite particles after tempering at 550\textdegree C for 60 minutes.

Figure 2 shows the average cementite particle radius and number density as a function of annealing time during annealing at 300\textdegree C and 550\textdegree C, which are derived from the SEM images. We observe that the average cementite particle size is larger during annealing at 550\textdegree C than during annealing at 300\textdegree C, for each annealing time. Furthermore, we observe that the average cementite particle size is larger in the Ti-containing martensite than in the Ti-free martensite during the first 10 minutes of tempering at 550\textdegree C. Both steels show comparable carbide sizes during tempering at 300\textdegree C. The number density of cementite particles decreases rapidly between 5–10 minutes and is thereafter decreasing at a slower rate.

3.2. Martensite Block Size and Area Fraction of Block Boundaries and Regions of High Dislocation Density

Figure 3 shows the martensite blocks and the boundaries between the martensite blocks, as measured by EBSD, of the Ti-free and the Ti-containing martensite after quenching and after tempering at 550\textdegree C for 60 minutes. The left panels (Figs. 3(a), 3(c), 3(e) and 3(g)) show the band contrast (BC) prior to noise reduction: dark grey regions indicate poor band contrast, light grey regions indicate good band contrast, and white regions indicate such poor band contrast that crystallographic indexing is not possible. Degradation of the band contrast typically arises from surface roughness, grain boundaries, elastic strain, and strain induced by dislocations.\textsuperscript{26} We observe that the BC is degraded close to non-indexed (white) regions. Furthermore we observe that the BC is improved and that the width of the non-indexed regions is reduced during annealing (compare 3a and c with 3e and f, respectively).
The right views (Figs. 3(b), 3(d), 3(f) and 3(h)) show the inverse pole figure (IPF) maps of the same EBSD images as the left view (created after noise reduction) where martensite block boundaries are marked by black lines. The martensite block boundaries are defined as boundaries located between two neighbouring pixels which have a misorientation that exceeds 10° in agreement with Morito et al.\textsuperscript{27,28} We observe that the block boundaries are located in formerly non-indexed regions.

There is no significant difference (95% confidence interval) comparing the block size of Ti-containing and Ti-free martensite, and no block coarsening takes place during 60 minutes of annealing at both tempering temperatures. As no grain coarsening take place during annealing and the surface roughness and elastic strain is comparable for all specimens (specimen preparation was the same), we derive that all improvements of Kikuchi pattern quality during annealing is a result of recovery. We note that non-indexed regions cover both martensite block boundaries and areas adjacent to the block boundaries. Indexing of block boundaries is not affected by annealing. The reduction of non-indexed points is therefore representative for recovery within areas of the martensite block matrix that are directly adjacent to the martensite block boundary. We call these regions boundary regions. The boundary regions are expected to consist of parallel laths separated by lath boundaries, similar to the matrix in the centre of the martensite block.

We observe that no significant improvement of indexing takes place after 10 minutes of annealing. Therefore, we consider the 60 minute level to be representative for the fully recovered state within the boundary regions for the annealing temperature applied. The area fraction of non-indexed points is hereafter used to estimate the area fraction of boundary regions and the evolution of recovery within these regions.

3.3. TiC-precipitate Size

The TEM investigation did not reveal the presence of any TiC-precipitates in the as-quenched state of the Ti-containing steel.

Figure 4 shows the APT measurements of the Ti-containing martensite specimen where (a) displays Ti atoms in solid solution and TiC-precipitates and (b) displays C atoms, after 60 minutes of tempering at 550°C. Figure 4(a) shows that both TiC-precipitates and Ti atoms in solid solution are present in the martensite after 60 minutes of tempering at 550°C. The amount of Ti in solid solution is measured to be 0.015 at% which indicate that approx. 67% of all Ti atoms have precipitated as TiC. The number of Ti atoms in the largest TiC particle is approximately 160 Ti atoms and the smallest particle contains approximately 35 Ti atoms (here the detection efficiency of 37% has been accounted for). The average precipitate size, based on all six precipitates is 69 ± 46 Ti atoms (standard deviation). 69 Ti atoms correspond to a diameter of 1.39 nm.

It shows that there is an increase in the carbon concentration along a planar feature in the examined volume. This planar feature could correspond to a lath boundary in the martensite.\textsuperscript{29} The concentration of carbon atoms in the lath boundary is 0.21 at.% and the concentration of carbon atoms in the matrix outside the lath boundary is 0.012–0.030 at.%. We observe that five out of the six TiC-precipitates in Fig. 4(a) are located on the lath boundary that is visible in Fig. 4(b). The average number of atoms in the five precipitates inside the lath boundary is 76 ± 48 Ti atoms (standard deviation).

The small TiC-precipitates in the APT reconstruction are close to spherical and the larger TiC-precipitates appear to be more ellipsoidal. We expect that some degree of com-
pression in the analysis direction can take place and the true shape of the larger precipitate can therefore be closer to spherical. APT measurements on specimens with shorter annealing time were not performed due to that the expected TiC precipitate sizes in these samples are too small to allow us to accurately differentiate between local fluctuations or possible Ti atom segregation and TiC precipitates.

3.4. Hardness Evolution in Matrix and Boundaries

Figure 5 shows the (a) macroscopic hardness and (b-c) the nano-hardness of the boundary regions and the matrix of both steels as a function of annealing time at 300°C and at 550°C. Figure 5(a) shows that the addition of Ti to the steel increases the macroscopic hardness of the steel. Both steels soften rapidly during early stages of annealing, where a higher annealing temperature result in a higher degree of softening. After 10 minutes of annealing the softening decreases or stops. We observe a hardness increase (approx. 18 HV) for the Ti-containing martensite between 30 and 60 minutes of annealing at 550°C.

Figures 5(b)–5(c) shows the nano-hardness of the tempered matrix (both auto-tempered and normal tempered regions), non-tempered matrix and of boundaries, measured at 60 nm depth, as a function of annealing time for (b) the Ti-free martensite and (c) the Ti-containing martensite at 300°C and at 550°C. Only one data point exists for non-tempered matrix, at t = 0 minutes, because these regions disappear within 5 minutes of annealing. We observe that both steels have a higher nano-hardness in the boundaries as compared to the tempered matrix, for each tempering time, at both annealing temperatures.

Figure 5(b) shows that the majority of the nano-hardness reduction in all regions of the Ti-free martensite takes place during the first 5 minutes of annealing. After 5 minutes no significant further softening takes place for both annealing temperatures. Figure 5(c) shows that the nano-hardness reduction of the Ti-containing martensite at 300°C is similar to the nano-hardness reduction of Ti-free martensite, the majority of the hardness reduction takes place during the first 5 minutes of annealing and thereafter no further softening take place. However, at 550°C we observe an increase of the boundary nano-hardness in the Ti-containing martensite between 5 and 10 minutes of annealing followed by a nano-hardness increase of the matrix between 10 and 30 minutes. We furthermore observe that the average nano-hardness of the boundaries remains unchanged between 10 and 30 minutes and that after 30 minutes the nano-hardness of both the boundaries and the tempered matrix increase in parallel.

4. Discussion

4.1. Hardness and Microstructure Evolution

The influence of Ti in solid solution is a macroscopic strengthening effect is approx. 105 MPa which correlate to the equilibrium volume fraction (0.00084) as measured by APT). The volume fraction of TiC is 67% of both the boundaries and the tempered matrix increase in parallel.

Fig. 5. Martensite hardness measured as a function of annealing time at 300°C and 550°C showing (a) the Microvickers hardness (HV0.5) of both steels and (b, c) the nano-hardness measurement the Ti-free martensite and the Ti-containing martensite respectively, where the nano-hardness of boundaries, non-tempered matrix and matrix are separated. The extrapolated line in (a) represents the expected martensite hardness if no TiC nucleation would take place and the black arrow shows the hardness increase due to Ti in solid solution. The error-bars represent a 95% confidence interval.

minutes of annealing at 550°C, see Fig. 5(a). The measured hardness increase of 16 HV shows that the TiC-precipitates we observe by APT have added precipitation strengthening to the steel.

We calculate the precipitate strengthening after 60 minutes of annealing according to: 

\[ \sigma_p = 0.538 G b f^{1/2} \left( \frac{d}{2b} \right) \ln \left( \frac{d}{2b} \right) \]

where \( G \) is the shear modulus (81 600 MPa for iron), \( b \) is the Burgers vector in iron, \( f \) is the volume fraction of TiC and \( d \) is the average precipitate diameter of 1.39 nm (69 Ti atoms acc. to APT). The volume fraction of TiC is 67% of the equilibrium volume fraction (0.00084) as measured by APT and calculated by ThermoCalc, (TCFE6). The strengthening effect is approx. 105 MPa which correlate to approx. 35 HV, according to the conversion \( R_p \text{(in MPa)} = 3.0 \text{ HV} \). This precipitation hardening effect is counteracted by the redistribution of Ti atoms from solid solution to TiC, where 67% of the solid solution strengthening effect will disappear. This correspond to a hardness reduction of approx. 21.4 HV. We furthermore calculate that the smallest precipitate size which gives a strengthening effect to the martensite is approximately 35 Ti atoms.
The net effect of TiC precipitates on the Ti-containing steel can be estimated using two methods. The first method is the linear addition of the hardening mechanisms, which have been suggested for quenched low carbon martensite. The second method is based on separate treatment of dislocations and hard particles and had successfully been applied on high strength low alloy aluminium.

Linear addition results in a net hardness increase of approx. 13.6 HV, which is in good agreement with the measured hardness increase of 16 HV and the approximation in Fig. 5(a) (see the extrapolated line in Fig. 5(a)). For the separate treatment of dislocations and hard particles we need to consider the recovery of the martensite.

Figure 6 shows the effect of Ti in solid solution and as TiC-precipitates on the hardness and microstructure evolution of martensite during annealing at 300°C (left column) and at 550°C (right column). Figures 6(a)–6(b) shows the evolution of dislocation recovery, with respect to the fully annealed state, in boundary regions a) at 300°C and b) at 550°C. The degree of recovery is calculated from the EBSD indexing results. We consider the indexing result measured at 60 minutes to be representative for full recovery (100%) at the respective tempering temperature, and the indexing result in the as-quenched state to be representative for 0% recovery. We observe that the evolution of recovery is similar in both steels during annealing at 300°C. As no TiC-precipitates are present at this tempering temperature, we conclude that Ti atoms in solid solution have no effect on the recovery rate.

Annealing at 550°C results in different recovery evolution in the Ti-free and the Ti-containing steel. The Ti-free steel is similar to the two steels at 300°C; rapid recovery during the first 10 minutes, followed by no recovery during the remainder of the 60 minutes. The lack of recovery after 10 minutes of annealing and the EBSD map (see Fig. 3(e)) suggest that the non-indexed regions, which remain in the Ti-free steel after 10 minutes of annealing, mainly consist of martensite block boundaries.

The Ti-containing steel shows a delay in the recovery process between 5 and 10 minutes (at 55% of the fully recovered level), followed by slow recovery from 10 to 60 minutes. At 60 minutes the Ti-containing steel reaches a similar recovery level as the Ti-free steel. The complete recovery stop between 5–10 minutes indicates that the dislocations present at 5 minutes are pinned and cannot annihilate. The pinning of the dislocations is believed to be caused by the presence of TiC precipitates. We calculate the hardness contribution to the steels, due to dislocation strengthening, at different annealing times according to the expression derived by Bailey and Hirsch:

\[ \sigma = M \alpha G b \rho^{1/2} \]  

Where \( \alpha \) is the dislocation hardening factor, \( M \) is the Taylor factor (\( M \alpha = 0.34 \) for pure iron), \( \rho \) is the dislocation density and \( G, b \) have the meaning of Eq. (1). The dislocation density in the as-quenched state is set to the average value of 14.2 \( \times 10^{14} \) m\(^{-2}\) and the dislocation density after full recovery at 550°C is set to 0.025 \( \times \rho_{\text{asQ}} \). The dislocation density after 5 minutes of annealing at 550°C correlate to 55% of the fully recovered state (see Fig. 6(b)).

The hardness contribution to the steel due to dislocation strengthening in the fully recovered state is expected to be
homogeneous in the material (no boundary regions remain) and is calculated to 15 HV for both steels.

The hardness contribution due to dislocation strengthening after 10 minutes of annealing is different in the Ti-free and the Ti-containing steel. The Ti-free steel will have a hardness contribution that reflects a fully recovered structure (15.0 HV), whereas the hardness of the Ti-containing steel is affected by the boundary regions where recovery only has reached 55% of the fully recovered level. The boundary regions in the Ti-containing steel (excluding the block boundaries) account for 9% of the material and have a higher hardness due to the higher dislocation density. The average hardness contribution due to dislocation strengthening of the Ti-containing steel, taking the boundary regions into account, is thereby calculated to be 19.0 HV. This higher degree of dislocation induced hardness is however counteracted by the hardness loss caused by redistribution of titanium and carbon atoms from solid solution to TiC via nucleation of TiC-carbides in the boundary regions. These newly nucleated TiC precipitates are most likely smaller than 35 atoms, and will not add any precipitate strengthening. Linear addition of the hardening mechanisms is therefore possible. We estimate that the hardness loss due to reduction of Ti atoms in solid solution caused by the nucleation of TiC-precipitates in the time interval between 5 and 10 minutes, is approx. 3.9 HV. We here assume that the critical TiC nucleus size is 14 Ti atoms (one unit cell of TiC), which is approx. 18% of the average TiC-precipitate size we measure in the laths after 60 minutes of annealing by APT. We furthermore assume that no further nucleation of new precipitates take place after 10 minutes as the TiC nucleation rate is reported to be high.\(^{21}\) The hardness decrease due to depletion of Ti atoms in solid solution during nucleation is therefore expected to be approx. 18% of the total hardness reduction due to depletion of Ti atoms from solid solution as measured after 60 minutes of annealing at 550°C (21.4 HV acc. to earlier paragraph). The hardness change of the Ti-containing steel at 10 minutes of annealing due to dislocation density and redistribution of Ti atoms is therefore close to 0 HV (not taking the depletion of carbon atoms into account). We now compare the methods of linear addition\(^{21}\) and separate treatment of dislocations and hard particles\(^{22}\) to estimate the net hardness increase of the Ti-containing steel after 60 minutes of annealing at 550°C, including precipitation strengthening of TiC, Ti atoms in solid solution and dislocation strengthening. Linear addition predict a net hardness increase (comparing the state after 10 minutes of annealing and the state after 60 minutes of annealing) of 5.7 HV and the separate treatment of dislocations and hard particles predict a hardness reduction of 6.2 HV. We conclude that linear addition is suitable for martensitic steel containing TiC precipitates.

Figures 6(c)–6(d) shows the ratio of the boundary-to-matrix nano-hardness, as a function of annealing time, calculated from the nano-hardness measurements 6(c) at 300°C and 6(d) at 550°C. The evolution of the ratio of boundary to matrix nano-hardness shows if the nano-hardness evolution is different in these two regions during annealing. Figure 6(c) shows that the evolution of the nano-hardness ratio is similar for the Ti-free and the Ti-containing martensite during annealing at 300°C. Therefore, we conclude that Ti atoms in solid solution have little effect on the nano-hardness evolution of martensite.

Figure 6(d) shows that the nano-hardness ratios of the two steels are similar during the first 5 minutes of annealing at 550°C. This indicates that nucleation of TiC precipitates has not yet taken place. However, between 5 and 10 minutes of annealing at 550°C the nano-hardness ratio is increased in the Ti-containing martensite followed by a decrease between 10 and 30 minutes of annealing at 550°C. The ratio increase is believed to be the result of the nucleation of TiC-precipitates in the boundary regions close to the block boundaries. The higher dislocation density of boundary regions promotes faster TiC nucleation due to a higher number of possible nucleation sites (the nucleation of TiC-precipitates is reported to take place on/near dislocations\(^{16,18,19}\)) and the possibility of rapid pipe diffusion for solute Ti atoms.

Figure 5(c) clearly shows a small increase in nano-hardness of the martensite block boundary regions and a parallel decrease in the nano-hardness in the matrix during annealing from 5–10 at 550°C. The former can be the result of the small hardness increase caused by a lower degree of recovery due to TiC nucleation in boundary regions and the latter indicates that nucleation of TiC-precipitates has not started yet in the matrix.

The reduction in the nano-hardness ratio between 10 and 30 minutes annealing at 550°C for the Ti-containing steel is the result of the onset of TiC nucleation in the matrix (see the hardness increase of the matrix in Fig. 6(c) during annealing between 10–30 minutes at 550°C). After 30 minutes of tempering the ratio remains unchanged as the nano-hardness of the boundaries and the matrix increase in parallel (see Fig. 5(c)).

Figures 6(e)–6(f) shows the macroscopic softening rate during annealing, as a function of annealing time 6(e) at 300°C and 6(f) at 550°C, calculated from the macroscopic hardness measurements. We observe that the softening rate is slightly higher in the Ti-containing steel than in the Ti-free steel during the first 5 minutes of annealing and thereafter (5 to 10 minutes) the macroscopic softening rate is lower in the Ti-containing steel, at both annealing temperatures. This higher initial (0–5 minutes) softening kinetics of the Ti-containing martensite is the result of the faster cementite formation in the Ti-containing martensite, as shown in Fig. 2, which is in agreement with the fact that titanium is a cementite stabilizer.\(^{17}\)

We furthermore observe that after 30 minutes of annealing at 550°C the Ti-containing steel shows a negative softening rate due to the hardness increase measured at 60 minutes (see Fig. 5(a)). The hardness increase is a direct result of precipitation hardening from the TiC-precipitates we observe by APT (in the size of approximately 70 Ti-atoms), see Fig. 4.

4.2. Diffusional TiC-precipitate Growth

The high dislocation density of martensite is expected to influence the growth rate of TiC in martensite, as compared to nucleation and growth of TiC in ferrite or austenite. Our results indicate that the nucleation of TiC-precipitates starts earlier in boundary regions (which have a higher dislocation density), than in the matrix of martensite.
We model the growth of spherical TiC precipitates in martensite according to three different models, in order to investigate the influence of the dislocations on the growth of TiC. In all three models we assume that the nucleation of TiC starts in the regions close to martensite block boundaries after 5 minutes of annealing, based on the measured recovery results (Fig. 6(b)).

Furthermore, we model the start of nucleation of TiC-precipitates in the matrix regions between 10–30 minutes of annealing, based on the increase of the nano-hardness measured for the same time interval (see Fig. 5(c), matrix, 550°C, Ti-containing steel). We assume that all TiC-precipitates nucleate at the same time in each region since the nucleation rate of TiC-precipitates in ferrite is reported to be high.\(^{21}\)

The influence of cementite on the growth of TiC-precipitates is considered to be negligible in the calculations, because the majority of the volume fraction of cementite has formed before 5 minutes of annealing (prior to nucleation of TiC in both regions).

In the first model, the growth is modelled to be controlled by volume diffusion only. In the second and the third model, the growth rate is assumed to be controlled by a combination of volume diffusion and diffusion along dislocations. We use the tracer diffusivity of \(^{44}\)Ti, as measured in large single Fe crystals,\(^ {38}\) as the lattice diffusivity of Ti in martensite, \(D_{f/m}\) for all three models. The diffusivity data of Ti in \(\alpha\)-iron, as measured by Moll and Ogilvie\(^ {39}\) is not used for the calculations as this data is derived from polycrystalline materials, which is believed to overestimate the lattice diffusivity. We furthermore assume that the concentration of carbon (interstitial element) of the martensite does not influence the diffusivity of Ti (substitution element).\(^ {30}\) ThermoCalc simulations (TCFE6) show that the atomic fraction of Mn in the TiC phase is in the range of 0.2 at\% and we therefore do not expect Mn to have a significant influence on the nucleation and growth of TiC due to partitioning.

### 4.2.1. Volume-diffusion Growth

The growth of TiC-precipitates is modelled according to classical diffusion-controlled growth theory. The early stages of precipitate growth, when the diffusion fields of neighbouring TiC grains do not overlap, is described by the Zener model where the radius of a precipitate, \(R_n\), as a function of time, is given by\(^ {41}\)

\[
R_n(t) = 2.102 \left( \frac{c_{eq}^m - c_{eq}^m}{c_{eq}^m - c_{eq}^{TiC}} \right)^{0.5871} \sqrt{D_{eq}}(t-t_0) \quad \text{...(3)}
\]

Where \(t_0\) is the moment of nucleation and \(t\) is the annealing time. \(c_{eq}^m\) and \(c_{eq}^{TiC}\) are the equilibrium concentrations of Ti in the matrix and in the TiC-precipitate, respectively, and \(c_{eq}^{Ti}\) is the concentration of Ti atoms in the parent phase far away from the precipitate. \((D_{eq})\) is the average diffusion coefficient of Ti in martensite.

For the later stages of TiC-precipitate growth, when the diffusion fields have started to overlap, we describe the growth by a model involving the transition from non-overlapping to overlapping diffusion fields developed by Offerman et al.,\(^ {42}\) see Fig. 7. The model still uses Zener-type concentration profiles to calculate the velocity of the interfaces but uses linear concentration profiles to estimate the concentration of Ti-atoms at the position where the diffusion fields overlap.

For the growth of TiC-precipitates during overlapping diffusion fields, the Zener model is still used, but the concentration \(c_{eq}^m\) in Eq. (3), is replaced by \(c_{eq}^{\alpha}\), which is the concentration of Ti at the position where the linear diffusion profiles intersect:

\[
c_{eq}^{\alpha} = c_{eq}^m - (c_{eq}^m - c_{eq}^{TiC}) \frac{2R + 2L - d}{2L} \quad \text{...(4)}
\]

\((d)\) is the average distance between the neighbouring precipitates and the length \(L\) of the linear concentration profile is given by\(^ {42}\)

\[
L = \left( \frac{1}{3} \left( 44 + 54B + 6\sqrt{54 + 132B + 81B^2} \right)^{1/3} - \frac{2}{3} \left( 44 + 54B + 6\sqrt{54 + 132B + 81B^2} \right)^{1/3} \right) R_n
\]

\( \text{........................................ (5)} \)

where

\[
B = \frac{c_{eq}^m - c_{eq}^{TiC}}{c_{eq}^{\alpha} - c_{eq}^m} \quad \text{........................................ (6)}
\]

The Gibbs-Thomson effect is accounted for by expressing the Ti concentration at the interface of the growing precipitate according to\(^ {43}\)

\[
c_{eq,i}^{\alpha} = c_{eq}^{\alpha} \exp \left( \frac{2\sigma_{eq}^{TiC}}{c_{eq}^{\alpha} R(t) kT} \right) \quad \text{............... (7)}
\]

\(^1\)Correction of typing error in the original publication, from \(\frac{3}{4}\) to \(\frac{4}{3}\).
Where $\sigma$ is the surface tension (approx. 0.3 J/m$^2$).\textsuperscript{21,44,45}

The numerical calculation of the TiC-precipitate radius is done according to:

$$R_n = R_{n-1} + \left(\frac{dR}{dt}\right)_{t=n\Delta t} \cdot \Delta t,$$ \hspace{1cm} (8)

where $R_{n-1}$ is the radius in the previous time step $t_{n-1}$ and $\Delta t = (t_n - t_{n-1})$. The equilibrium concentration of titanium in the matrix and in TiC at 550°C, $C_{eq}^{\text{Ti}}$ and $C_{eq}^{\text{TiC}}$, are calculated using ThermoCalc. $C_{eq}^\text{Ti}$ ($t = 0$) is calculated from the initial steel composition, after removing the equilibrium volume fraction of cementite at 550°C (as calculated by ThermoCalc). $\langle D_n \rangle$ is set to be the lattice diffusion coefficient of Ti in martensite, $D_{L}^{\text{Ti/M}}$.

4.2.2. Dislocation-Assisted Growth

We model dislocation assisted growth according to two mechanisms. The first mechanism is developed by Wang and Shifter\textsuperscript{46} This model describes how the growth rate of a precipitate is affected by the diffusion of solute atoms along a single dislocation attached to the precipitate, and was successfully applied to the growth of precipitates in a well annealed binary alloy of Al–Li. The second mechanism describes dislocation assisted growth of a precipitate by the diffusion of solute atoms along multiple dislocations that are in close proximity to the precipitate. The effective diffusivity of the solute atoms is described as a net diffusivity of solute atoms through the lattice and along dislocations.

4.2.2.1. Single Dislocation Model

The single-dislocation-assisted growth of spherical precipitates is given by:\textsuperscript{46}

$$\left| \frac{dR}{dt}\right|_{\text{total}} = \left| \frac{dR}{dt}\right|_{\text{lattice}} + \left| \frac{dR}{dt}\right|_{\text{pipe}},$$ \hspace{1cm} (9)

where $\left| \frac{dR}{dt}\right|_{\text{lattice}}$ is expressed via Eqs. (3)-(8). The growth rate of the TiC-precipitate due to diffusion is expressed as:

$$\left| \frac{dR}{dt}\right|_{\text{pipe}} = \frac{C_{eq}^{\text{Ti}} - C_{eq}^{\text{TiC}}}{\pi R^2} \sqrt{D_{L}^{\text{Ti/M}} D_{p}^{\text{Ti}} \int f(t') \cdot \Delta t}$$ \hspace{1cm} (10)

$D_{L}^{\text{Ti/M}}$ is the pipe diffusivity of Ti in martensite, $r_0$ is radius of the cylindrical dislocation pipe, $t' = D_{L}^{\text{Ti/M}}/r_0^2$ and $f(t')$ is the integral:

$$f(t') = \int_0^{t'} \frac{\exp(-t'x^2)}{x} \left[ J_0^2(x) + J_1^2(x) \right] dx,$$ \hspace{1cm} (11)

where $J_0(x)$ and $Y_0(x)$ are the zeroth order Bessel functions of the first and second kind respectively. For $r_0$ we use the burgers vector in $\alpha$-iron.

4.2.2.2. Multiple Dislocations Model

The multiple dislocation assisted growth of TiC-precipitates is expressed according to Eqs. (3)-(8), where $\langle D_n \rangle$ in Eq. (1) is replaced by an expression of the effective diffusivity according to:\textsuperscript{47}

$$\frac{\langle D_{Ti,M} \rangle}{D_{L}^{\text{Ti/M}}} = 1 + g \frac{D_{p}^{\text{Ti}}}{D_{L}^{\text{Ti/M}}},$$ \hspace{1cm} (12)

where $g$ is the cross sectional area of dislocation pipe per unit area of matrix. We express the ratio of pipe diffusivity to lattice diffusivity, $\frac{D_{p}^{\text{Ti}}}{D_{L}^{\text{Ti/M}}}$ for Ti diffusion in martensite via the ratio of pipe diffusivity to lattice diffusivity of iron in iron and a scale factor according to the ratio of diffusivities for Ti and Fe in iron ($\frac{D_{p}^{\text{Ti/Fe}}}{D_{L}^{\text{Fe/Ti}}}$).

$$\frac{D_{p}^{\text{Ti/Fe}}}{D_{L}^{\text{Fe/Ti}}} = \frac{D_{p}^{\text{Ti}}/D_{L}^{\text{Ti}}} {D_{p}^{\text{Fe}}/D_{L}^{\text{Fe}}} \times \frac{D_{L}^{\text{Fe/Ti}}}{D_{L}^{\text{Fe/Ti}}}.$$ \hspace{1cm} (13)

The scale factor, $\frac{D_{p}^{\text{Ti/Fe}}}{D_{L}^{\text{Fe/Ti}}}$ accounts for the different atom radius of Ti and Fe, which is believed to affect pipe diffusion of Ti in iron, according to the same proportion as lattice diffusion of Ti in iron is affected.

The effective pipe radius of a dislocation is set equal to the burgers vector in $\alpha$-iron, $b$, and we express the cross sectional area of dislocation per unit area of martensite in Eq. (12) as:

$$g = \rho \pi b^2$$ \hspace{1cm} (14)

where $\rho$ is the density of the dislocation. We extend Eq. (12) to include the recovery during isothermal annealing by expressing $g$ as a function of time:

$$g(t) = g_{\text{eq}} \pi b^2 - F(t) \left[ \rho_{\text{eq}} \pi b^2 - \rho \pi b^2 \right].$$ \hspace{1cm} (15)

where $\rho_{\text{eq}}$ is the dislocation density in the as-quenched state, $\rho$ is the dislocation density after recovery and $F(t)$ is a function that describes the evolution of the recovery process. We use the same dislocation densities as in section 4.1. $F(t)$ is modelled to follow the evolution of dislocation recovery as measured by EBSD (Fig. 6(b)).

The ratio $\frac{D_{p}^{\text{Fe/Ti}}}{D_{L}^{\text{Fe/Ti}}} = 57.100$ at 550°C\textsuperscript{48} and $\frac{D_{p}^{\text{Ti/Fe}}}{D_{L}^{\text{Fe/Ti}}}$ is calculated to be 0.30 at 550°C.\textsuperscript{49}

4.3. Comparison of TiC Growth Models

Table 2 shows the calculated average precipitate sizes after 60 minutes of annealing at 550°C in boundary and matrix regions for all three models and the APT measurements. We assume that the precipitates measured in the lath boundary are representative for boundary regions due to the high dislocation density of martensite laths. The volume diffusion model predicts too small precipitate sizes, and we therefore conclude that pipe diffusion strongly contributes to the growth of TiC in martensite.

Table 2 furthermore shows that the single dislocation model overestimates the precipitate size. The reason for the overestimated precipitate size by the single-dislocation model is that the size of the TiC-precipitates within this research is so small that pipe diffusion becomes dominant in the model (small values for the radii results in high values of the diffusion model).

<table>
<thead>
<tr>
<th>Number of measurements (APT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
</tr>
</tbody>
</table>

### Table 2. Precipitate size (number of Ti atoms).

<table>
<thead>
<tr>
<th>Volume diffusion</th>
<th>Diffusion along single dislocation</th>
<th>Diffusion along multiple dislocations</th>
<th>Measured by APT (Standard deviation)</th>
<th>Number of measurements (APT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary</td>
<td>21</td>
<td>252</td>
<td>91</td>
<td>76 ± 48</td>
</tr>
<tr>
<td>Matrix</td>
<td>17–20</td>
<td>168–236</td>
<td>68–85</td>
<td>35</td>
</tr>
</tbody>
</table>
of the term \( \frac{r_i}{R_0} \) in Eq. (10)). The single dislocation model does not take into account the reduction in the dislocation density due to recovery. Moreover, as Wang and Shiflett\(^{6}\) point out, the model does not take into account the competition for Ti atoms between neighbouring TiC precipitates along the same dislocation line, which would slow down precipitate growth.

The multiple dislocation-assisted growth model predicts TiC-precipitate sizes which are in agreement with the APT measurement. The model takes into account the recovery, which means that the model takes into account a reduction in the overall diffusivity of Ti-atoms due to the reduction in dislocation density.

5. Conclusions

Two martensitic steels with and without the addition of 0.042 wt.% of Ti are compared at annealing temperatures of 300°C and 550°C. The macroscopic hardness in both steels and at both temperatures reduces quickly during the first 5 minutes of tempering, due to the redistribution of interstitially dissolved carbon into cementite and due to rapid recovery. The macroscopic hardness remains more or less the same during continued annealing, except for the Ti-containing steel that is tempered at 550°C. This is related to the formation of TiC-precipitates at 550°C. Nucleation of TiC-precipitates starts first in the regions close to the martensite block boundaries (between 5–10 minutes) and thereafter in the block matrix (between 10–30 minutes) during annealing at 550°C, due to the higher dislocation density in the regions close to the block boundaries. The formation of TiC-precipitates has the following effects on the evolution of the microstructure and the hardness:

1) TiC-precipitates slow down the recovery in the regions close to the martensite block boundaries compared to the alloy without TiC-precipitates.

2) The TiC-precipitates increase the macroscopic hardness of the steel after 30 minutes annealing at 550°C.

The growth of TiC-precipitates in martensite is simulated with three models: 1) a model taking into account capillarity effects and the overlap of the titanium diffusion fields, 2) a model that takes into account the above effects plus the effect of the diffusion of titanium atoms along a single dislocation attached to the precipitate, and 3) a model that takes into account the effects of the first model and the effect of pipe diffusion of titanium atoms via multiple dislocations. The third model predicts a TiC-precipitate size that corresponds the closest to the experimentally observed TiC-precipitate sizes.

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REFERENCES


