Characterization of NbC and (Nb, Ti)N nanoprecipitates in TRIP assisted multiphase steels

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Abstract

Multiphase steels utilising composite strengthening may be further strengthened via grain refinement or precipitation by the addition of microalloying elements. In this study a Nb microalloyed steel comprising martensite, bainite and retained austenite has been studied. By means of transmission electron microscopy (TEM) we have investigated the size distribution and the structural properties of (Nb, Ti)N and NbC precipitates, their occurrence in the various steel phases, and their relationship with the Fe matrix. (Nb, Ti)N precipitates were found in ferrite, martensite, and bainite, while NbC precipitates were found only in ferrite. All NbC precipitates were found to be small (5–20 nm in size) and to have a face centred cubic (fcc) crystal structure with lattice parameter $a = 4.36 \pm 0.05$ Å. In contrast, the (Nb, Ti)N precipitates were found to have a broader size range (5–150 nm) and to have a fcc crystal structure with lattice parameter $a = 8.09 \pm 0.05$ Å. While the NbC precipitates were found to be randomly oriented, the (Nb, Ti)N precipitates have a well-defined Nishiyama–Wasserman orientation relationship with the ferrite matrix. An analysis of the lattice mismatch suggests that the latter precipitates have a high potential for effective strengthening. Density functional theory calculations were performed for various stoichiometries of NbC\textsubscript{x} and Nb\textsubscript{x}Ti\textsubscript{y}N\textsubscript{z} phases and the comparison with experimental data indicates that both the carbides and nitrides are deficient in C and N content.

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Keywords: Multiphase steel; NbC; (Nb, Ti)N; Precipitation; Transmission electron microscopy

1. Introduction

High strength steels can achieve a good balance of strength and ductility by utilising combinations of grain refinement, precipitation strengthening, and composite strengthening. Modern multiphase (MP) steels rely primarily on grain refinement and composite hardening. However, microalloying additions may provide effective means for further strengthening via enhanced grain refinement and/or precipitation. The role of microalloying additions in multiphase steels requires further clarification. Many investigations have focused on the role of Nb [1–4] in steels. NbC precipitates are formed during the hot rolling process, which reduces the size of the recrystallized grains by pinning the grain boundaries and refines the final microstructure, resulting in an increase in yield strength and tensile strength. These precipitates also form an obstacle to the movement of dislocations [5] and an increase in strength is achieved while maintaining good toughness.

In steels containing both Nb and Ti there was a delay in precipitation of NbC due to the formation of stable...
(Nb, Ti)(C, N) [6]. Wang and Wang [7] observed that a thermo-mechanical heat treatment transformed the (Nb, Ti)(C, N) precipitates from a cubical to a rectangular shape. In other investigations it was found [8,9] that deformation during hot rolling accelerates the precipitation of NbC and (Nb, Ti)(C, N) precipitates. Weiss and Jonas [10] observed that 5% pre-strain increased the rate of precipitation of NbC precipitates by about one order of magnitude. Recently Moon and Lee [9] investigated the effect of stress state (tensile or compressive stress) on the coarsening behaviour of (Nb, Ti)(C, N) particles during a thermo-mechanical treatment. Their results showed that compressive stress was more effective than tensile stress.

The main aim of the current work was to structurally characterize the nanosized precipitates of NbC and (Nb, Ti)N in a multiphase (MP) steel containing fractions of bainite (B), martensite (M), and retained austenite (RA) in a predominantly ferritic matrix. Particular attention has been paid to assessing the precipitation state in the individual phases.

2. Experimental procedure

The chemical composition of the Nb alloyed MP steel used in the present work is listed in Table 1. The material is produced on an industrial hot dip galvanising line using a conventional intercritical annealing cycle, which is standard practice for dual phase (DP) and transformation-induced plasticity (TRIP) steels. The microstructures were studied by optical microscopy (OM) and transmission electron microscopy (TEM). A stepped etching procedure was followed to reveal the optical microstructure [11]. Electron transparent TEM samples were made using standard electropolishing to reveal various phases in the TEM microstructures. The specimens for electropolishing were pre-thinned by grinding along the transverse direction using SiC paper with roughnesses from 350 down to 4000. Electropolishing was carried out in a twin jet polisher using 5% perchloric acid solution at a temperature of −20 °C. TEM analysis was performed using Philips CM30T and FEI Tecnai F20ST/STEM microscopes operating at 300 and 200 keV, respectively, to identify microstructure and precipitates. Selected area diffraction (SAD) was used to distinguish different phases and to characterize the precipitates in this steel and the orientations of the diffraction patterns were defined with respect to the electron beam. The analytical methods of energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) were employed to investigate chemical compositions.

3. Results and discussion

The microstructure of the steel studied in this work contains multiple phases (ferrite, martensite, retained austenite and bainite). The precipitation behaviour of (Nb, Ti)(C, N) carbonitrides can be expected to be different in the different phases within the steel, primarily because of different solubilities and mobilities of the alloying elements in these phases. Therefore, we first briefly discuss the general microstructure before showing the TEM results on the occurrence and type of precipitates found in the various phases.

3.1. Light microscopic analysis of microstructures

The typical microstructure of the steel is shown in Fig. 1, in which the large brown areas represent ferrite, and the fine dark and grey areas represent bainite. Martensite is generally etched in a straw tint colour and retained austenite is of white colour in the optical micrographs [11]. The fractions of retained austenite, ferrite, martensite and bainite in Fig. 1 were quantified using Image analyser. The retained austenite constitutes 2.88%, while martensite, bainite and ferrite constitute 3.9%, 6.49% and 77.07% of the area fractions, respectively. It can be seen from Fig. 1 that the average ferrite grain size of Nb-containing MP steels is about 5 µm, which is small in comparison with intercritically annealed DP steel [12]. Furthermore, the fractions of bainite and martensite are considerably higher, while the fractions of retained austenite are lower than TRIP-aided DP steel [12].

3.2. TEM analysis of microstructures

In order to investigate precipitation in conjunction with the presence of the various phases grains of each of the phases were inspected for the presence of precipitates using TEM. The analysis was carried out on more than 15 bulk samples that were thinned for electron transparency. In combination, the total volume probed by means of TEM is about 7500 µm³. The results displayed below are typical examples of observations that were found throughout the analyses. Table 2 gives an overview of the occurrence of the precipitates in the steel phases.

Fig. 2 shows a grain of ferrite. The TEM micrograph shows a pole where diffraction bands meet, corresponding to the (1 1 1) orientation of ferrite as identified by electron diffraction (inset in Fig. 2). The ferrite grain is bent because of the thinning required for TEM analysis. The ferrite grain contains precipitates with different size ranges: coarse precipitates in size range 100–150 nm, medium sized precipitates in the size range 50–60 nm and fine precipitates with

<table>
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<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Cr</th>
<th>Nb</th>
<th>V</th>
<th>Ti</th>
<th>Ni</th>
<th>Cu</th>
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<td>0.149</td>
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<td>0.515</td>
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<td>0.004</td>
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<td>0.024</td>
<td>0.017</td>
<td>0.011</td>
<td>0.002</td>
<td>&lt;0.0001</td>
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Table 1
Overall chemical composition (wt.%) of the TRIP-assisted MP steel.
a size of 10–20 nm, as shown in the schematic representation in Fig. 2.

Fig. 1. Optical microstructure of the TRIP-assisted MP steel.

Fig. 2. Ferrite in MP steel with precipitates and dislocations surrounding the precipitates. The features (indicated by arrows) are discussed in the text. The \(\alpha\)-Fe (111) diffraction pattern is also shown.

Considering the austenite phase, two types of grains were found in this steel: block type retained austenite grains, and film type austenite plates. The block type retained austenite grains in Fig. 3 had an angular deviation of 5.3 ± 0.2° between (0 0 1)\(_a\) and \((\frac{1}{2} \frac{1}{2} 1)\)\(c\) planes and was found near the Nishiyama–Wasserman (N–W) relationship commonly seen between the face centred cubic (fcc) \(\gamma\)-Fe and body centred cubic (bcc) \(\alpha\)-Fe phases in metallic materials [13]. The N–W relationship is defined by
\[
(110)\_a \parallel (111)\_\gamma \quad \text{and} \quad [001]_a \parallel [110]_\gamma
\]  

(1)

Fig. 4 shows a film type austenite grain with a neighbouring ferrite grain and Fig. 5a shows a grain of bainite and film austenite surrounded by a ferrite grain. The angular deviation between the neighbouring ferrite grain and film type austenite was 0.5 ± 0.2° between (1 1 1)\(_a\) and (1 1 0)\(_c\), which is close to the Kurdjumov–Sachs (K–S) relationship [13]. The K–S relationship is defined by
\[
(011)\_a \parallel (111)\_\gamma \quad \text{and} \quad [111]_a \parallel [110]_\gamma
\]  

(2)

Alternating regions of ferrite and austenite were seen with a plate thickness of the order of a few hundred nanometers and surrounded by dislocation loops. No precipitates were found in either the block type austenite grains or film type austenite grains. (Nb, Ti)N precipitates were found, though, in the bainitic ferrite plates. These precipitates were faceted in shape and were found inside the bainitic ferrite and in adjacent ferrite grains, as seen in Fig. 5a.

The fourth phase (besides ferrite, austenite and bainite) is martensite. Fig. 5b shows a martensite grain (\(\alpha'\)) where the lathes are oriented along the \((\frac{3}{2} \frac{3}{2} 1)\) orientation. (Nb, Ti)N precipitates can be observed in these martensite grains and reflections are found in the diffraction pattern, which originate from the precipitates, as shown in Fig. 5c.

3.3. Precipitates containing Nb and Ti

It is known that elements like Nb, V and Ti have a strong affinity for bonding with C and N. Consequently,
Microalloying additions of Nb, Ti, and V to MP steel can lead to precipitation of Nb, Ti, and V carbides and nitrides. TEM inspection of many areas shows that this steel mainly contains (Nb, Ti)N precipitates in the size range 10–150 nm. A dark field recording using the $g = 404$ reflection in the $\frac{1}{2} 111/C_{22} 1$ projection of (Nb, Ti)N is shown in Fig. 6a. Here (Nb, Ti)N precipitates can be observed which are in a (1 1 1) orientation inside the grain of ferrite that is in a (1 1 0) orientation, as is also clear from the corresponding diffraction pattern in Fig. 6b. The precipitates are distributed throughout the material and have a wide size dispersion. Fig. 6c shows a large precipitate inside a ferrite grain. EDX analysis of the precipitate by converging the electron beam on the precipitate shows a higher concentration of Ti in comparison with Nb. Different precipitates were found to have varying Ti/Nb atomic ratios (in the range 2.4–4.5). An average value for the Ti/Nb atomic ratio was determined from seven larger precipitates as $2.83 \pm 0.81$. In the EDX analysis minor contributions from Al, Si, S, Mn, Fe, and Cr also appear in these precipitates, since the EDX signal in TEM comes not only from the precipitate but also from the matrix phase surrounding the precipitate, as a large part of the sample is hit by stray electrons. Electron energy loss spectroscopy (EELS) analysis was also carried out on the same precipitates which showed the presence of N but no evidence of C, as shown in Fig. 7, indicating a Nb$_x$Ti$_{1-y}$N$_z$ type of precipitate. When combining the Ti/Nb ratio obtained by means of EDX with the Ti/N ratio found from EELS the overall composition is approximately Nb$_{0.35}$Ti$_{1.0}$N$_{0.63}$.

In order to determine the unit cell a large (Nb, Ti)N precipitate was chosen, as shown in Fig. 6c, and a diffraction tilt series was performed in two orientations using SAD, as shown in Fig. 8a and b. The unit cell reconstructed from the tilt series is fcc with lattice parameter $a = 8.09 \pm 0.05$ Å. In comparison, pure TiN and pure NbN are rock salt phases (space group $Fm \overline{3} m$) with lattice parameters $a_{\text{TiN}} = 4.27$ Å [14] and $a_{\text{NbN}} = 4.44$ Å [15]. Therefore, the experimentally found lattice parameter 8.09 Å of the composite (Nb, Ti)N phase suggests a doubling of the rock salt unit cell (i.e., a rock salt superstructure with a certain (partial) ordering of the Nb and Ti atoms on the non-carbon sites). However, in that case the rock salt lattice would be substantially compressed by 4–9% with respect to the pure NbN and TiN phases. Therefore, the possibility of a non-rock salt type structure cannot be ruled out. In Section 3.5 below the results of density function theory (DFT) calculations will be presented for qualitative comparison with the experimental data in order to elucidate the crystal structure of the precipitates.

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**Fig. 3.** Block type austenite grain in MP steel which is close to the N–W relationship. (a) Bright field TEM image. The boundary between the grains is indicated by yellow lines. (b) Diffraction pattern of ferrite in the (0 0 1) projection. (c) Diffraction pattern of austenite in the (1 1 0) projection. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4.** Film type austenite grain in MP steel with an orientation relation with the neighbouring ferrite grain that is close to the K–S relationship. (a) Bright field TEM image. (b) Diffraction pattern of ferrite in the (1 1 1) projection. (c) Diffraction pattern of austenite in the (1 1 0) projection.
In Fig. 8b the (Nb, Ti)N precipitate is in a $(\bar{1}12)$ orientation. In the diffraction patterns in Fig. 8a the (Nb, Ti)N precipitate is in the $(111)$ orientation and the ferrite matrix is in the $(011)$ orientation. Thus these (Nb, Ti)N precipitates have a N–W orientation relationship with the ferrite matrix:

\[
(011)\alpha-Fe \parallel (\bar{1}11)(Nb, Ti)N
\]

\[
[100]\alpha-Fe \parallel [111](Nb, Ti)N
\]

Other, smaller (Nb, Ti)N precipitates with very similar chemical compositions were analysed as well and were found to have the same orientation relationship, so that this can be considered a general result for the (Nb, Ti)N/$\alpha$-Fe precipitate–matrix system.

In Table 3 the experimentally determined lattice parameter of (Nb, Ti)N is listed, as well as the lattice mismatch calculated in three perpendicular directions. Here the lattice mismatch is calculated with Fe as a reference, \( \eta = |d_{(NbTi)N} - d_{Fe}|/d_{Fe} \). In one direction, $(100)\alpha-Fe \parallel (110)(Nb-Ti)N$, there is a good fit with a very small lattice mismatch $(0.0 \pm 1.1\%)$. In the other two directions the mismatch is large, $16\%$ and $18\%$. The probability that a certain orientation relationship occurs is determined by the interface energies that are associated with that orientation relationship. The interface energy can be considered to consist of two contributions: short-range contributions which are determined by the local relaxed atomistic configuration at the interfaces, and long-range contributions such as strain in the embedding ferrite matrix caused by mismatch of the unit cells, which is sometimes partly relieved by misfit dislocations. The lattice mismatches listed in Table 3 suggest that there is little strain in one direction and considerable strain in the other two directions, indicating that the orientation relationship is partially based on a semi-coherent interface. Such precipitates are more likely to effectively strengthen steels [16] than precipitates that have fully incoherent interfaces, which is expected for the NbC precipitates discussed below that have a random orientation relationship with the matrix.

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**Fig. 5.** (a) Bainite in MP steel with precipitates and dislocations in the surrounding ferrite grain. The phases within the bainite were identified by means of electron diffraction. (b) Precipitates observed inside a grain of martensite. (c) The inset shows the diffraction pattern of martensite with the precipitates. Green arrows point to medium sized faceted precipitates and red arrows to small sized precipitates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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**Fig. 6.** (a) Dark field image showing (Nb, Ti)N precipitates in ferrite, using the \( g = 404 \) reflection of (Nb, Ti)N. (b) The corresponding diffraction pattern. The white circle indicates the \( g = 404 \) reflection. (c) A large (Nb, Ti)N precipitate inside a grain of ferrite.
3.4. Precipitates containing Nb and C

Very small precipitates (5–20 nm) were also observed in some grains of ferrite, as shown in Fig. 9. The NbC precipitates were very close to each other and the EDX analysis confirmed higher concentrations of Nb and C than the surrounding ferrite matrix. From the literature [17–19] it is known that Nb can form Nb(C, N), Fe2Nb (Laves phase) and Fe3Nb3C (M6C) particles in Nb-containing ferritic stainless steel. SAD was performed on these precipitates and it was found that these precipitates had a lattice parameter which was close to that of NbC (Fig 10). The NbC precipitates were identified as cubic with lattice parameter $a = 4.36 \pm 0.05$ Å. In contrast to the (Nb, Ti)N precipitates, the NbC precipitates were found in random orientations and thus have no preferred orientation relationship with the surrounding ferrite. In the literature [20] it has been reported that the orientation relationship between NbC and ferrite is cube on cube (which would result in a lattice mismatch of 23%, see Table 3), whereas no orientation relation was observed in the present work.

The fact that a minority (less than 10%) of the ferrite grains contained these NbC precipitates points to an inhomogeneous distribution of the alloying elements over the material, which leads to heterogeneous precipitation of these precipitates within a single phase. The heat treatment cycle might also play a role in the precipitation behaviour. There are two types of ferrite formed during the heat treatment process; intercritical ferrite, which is formed at intercritical annealing temperatures, and bainitic ferrite, which is formed at bainitic temperatures. The precipitation in these two types of ferrite can be different. The observations that NbC precipitates are found only in ferrite grains, as in Table 2, is in agreement with the observations by Pereloma et al. [2]. These NbC precipitates could have been formed in austenite [20] but were not observed in austenite grains at room temperature, suggesting that the ferrite grains might have nucleated at the carbon-depleted NbC precipitate sites in austenite. These smaller precipitates, which are uniformly distributed in the ferrite matrix with short interprecipitate distances, are known to cause dislocation pinning, leading to a substantial improvement in the strength of this steel [5].

3.5. Density functional theory calculations

From the experiments the lattice parameters and the space group of the (Nb, Ti)N phase were determined,
however, without a full determination of the crystal structure, as the atomic positions were not resolved. Here we perform DFT calculations in order to obtain a greater insight into the energetically most favourable stoichiometry and in order to investigate whether the composite phase yields a smaller lattice parameter. Our experimental results on the (Nb, Ti)N precipitates show that the space group is $Fm\overline{3}m$, with a lattice parameter of 8.09 Å. This suggests a rock salt superstructure with a lattice parameter that is approximately twice the lattice parameter of TiN, but smaller. The calculations were conducted employing the VASP code [21–23] within the projector-augmented wave (PAW) approach [24,25] employing the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) potentials [26]. The cut-off energy of the wave functions was 500 eV, while the cut-off energy of the augmentation functions was 645 eV. The electronic wave functions were sampled on a $12\times12\times12$ grid in the irreducible Brillouin zone of the $2a_0\times2a_0\times2a_0$ supercells ($a_0$ is the lattice parameter of a convention cell of NaCl type structure), using the Monkhorst and Pack method [27]. The calculations were performed for a temperature of 0 K and for zero pressure. For the calculation of formation enthalpies the solutes of Nb, Ti, N and C in bcc (ferrite) Fe were used as a reference. The enthalpies of the solutes were calculated using 54 atom bcc Fe supercells (dimensions $3a_\text{Fe} \times 3a_\text{Fe} \times a_\text{Fe}$), in which Nb, Ti solutes are positioned at substitutional sites (Fe$_{53}$Nb, Fe$_{53}$Ti) while solutes of N and C are positioned at interstitial sites (Fe$_{54}$N, Fe$_{54}$C). The enthalpies of the solutes are then determined as $H^\text{sol}(M) = H(\text{Fe}_{53}M) - 53H(\text{Fe})$ for $M = \text{Nb}$ or Ti and $H^\text{sol}(X) = H(\text{Fe}_{54}X) - 54H(\text{Fe})$ for $X = \text{C}$ or N. It was verified that the cut-off energies and the density of the $k$ meshes were sufficiently high for good energy convergence ($<1$ meV per atom). Although solution energies are not directly used in the current calculations, the enthalpy values of $H^\text{sol}(A)$ enable calculation of the corresponding solution energies for these elements in bcc Fe by subtracting the energy of the pure elements (bcc Nb, hcp Ti, the N$_2$ molecule, and graphite) as $\Delta E^\text{sol}(A) = H^\text{sol}(A) - H(A)$, where $A = \text{Nb, Ti, N or C}$. Solution energies for Nb, Ti, N and C in ferrite are then obtained as $-0.135$, $-0.799$, $-0.006$, and $0.582$ eV, respectively. Here the reference energies $H(A)$ of graphite and N$_2$ were calculated as explained by Fang and co-workers [28–30].

For the precipitate phases calculations were performed for different chemical compositions using different unit cells. For NbC$_{\alpha}$ a conventional rock salt (NaCl type) cell was used with $0 < x < 1$, and for Nb$_x$Ti$_y$N$_z$ a supercell was used ($2a_0 \times 2a_0 \times 2a_0$) in which the Nb/Ti ratio was varied. The nitrogen content was also varied within the composition Nb$_{0.25}$Ti$_{0.75}$N$_z$ ($0 < z < 1$), as this composition...
is closest to the experimentally found Nb/Ti ratio. Structural optimisations were performed for both the lattice parameters and the relative atomic coordinates.

Two different definitions of formation energy were used to consider the relative stability of Nb$_x$Ti$_y$X$_z$ ($X$ can be either N or C). The formation energy $\Delta H_{\text{form}}^1$ is defined with respect to the solutes of Nb, Ti, C and N in bcc Fe

$$\Delta H_{\text{form}}^1 = H(\text{Nb}_x\text{Ti}_yX_z) - [xH^{\text{sol}}(\text{Nb}) + yH^{\text{sol}}(\text{Ti}) + zH^{\text{sol}}(X)]$$

while the formation enthalpy $\Delta H_{\text{form}}^2$ is defined with respect to the pure compounds Ti$X$ and Nb$X$ ($X = \text{C or N}$) as

$$\Delta H_{\text{form}}^2 = H(\text{Nb}_x\text{Ti}_yX_z) - \{z/(x+y)\}[xH(\text{Nb}) + yH(\text{Ti})] + \{1 - z/(x+y)\}[xH^{\text{sol}}(\text{Nb}) + yH^{\text{sol}}(\text{Ti})]$$

in which the last term in Eq. (6) corrects for N or C deficiency (in the case $z < x + y$).

Table 4 summarises the calculated lattice parameters and formation enthalpies of NbC, NbN, TiN and (Nb, Ti)N type phases. The formation enthalpies are defined in Eqs. (5) and (6) above. Three groups of NbC and (Nb, Ti)N precipitates are considered in which either the C content, the N content or the Nb/Ti ratio is varied. d-NaCl indicates a defective NaCl type structure; enthalpies are in electron volts per formula unit (fu). It is known that the transition monocarbides MC (M = Ti, Nb, V, etc.) can exhibit carbon deficiency, and that their lattice parameters vary with the carbon concentration [31]. As summarized by Nagakura and Oketani [32], the lattice parameter of NbC$_{x}$ is about 4.433 Å for $x = 0.82$, and 4.470 Å for $x \approx 1.0$. Our calculated lattice parameter for NbC is slightly larger (less than 1%) than the experimental value. This is not unusual for the DFT–GGA approximation, which gives high accuracy formation energies but tends to overestimate the lattice parameters.

Considering the formation energies of the NbC$_{x}$ phases (group A) listed in Table 4, it is clear that carbon deficiency is energetically favourable for the composition range between NbC$_{0.50}$ and NbC$_{0.75}$. Here the formation enthalpy of NbC$_{0.50}$ is considerably lower ($\Delta H_{\text{form}}^2 = 0.46$ eV fu$^{-1}$) than that of NbC$_{0.75}$ ($\Delta H_{\text{form}}^2 = 0.02$ eV fu$^{-1}$), however, the structure of NbC$_{0.50}$ is perfectly ordered (implying zero configurational entropy), while the structure of NbC$_{0.75}$ does result in configurational entropy. Therefore, at elevated temperatures where entropy plays a role both compositions are expected to be energetically favourable with respect to pure NbC (which also has zero configurational entropy) and C in solution. Considering the lattice parameters, it is difficult to directly compare the experimental and calculated values (a

| $a$-Fe & (Nb, Ti)N & NbC & NbC$_{0.50}$ | NbC$_{0.75}$ |
|---|---|---|---|---|
| Lattice parameter (Å) & $a = 8.09 \pm 0.05$ & $a = 4.36 \pm 0.05$ & $a = 4.86$ |
| Lattice mismatch (%) & $\eta = 0.0$ & $\eta = 15.5$ & $\eta = 18.4$ |
| $[1 0 0]$ $a$-Fe || [1 1 0] (Nb, Ti)N | $\gamma = 23.8$ | $\gamma = 7.8$ |

Table 3

<table>
<thead>
<tr>
<th>Experimentally obtained lattice parameters and calculated lattice mismatch in three directions for $a$-Fe, (Nb, Ti)N, and NbC.</th>
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<tr>
<td>$ \begin{array}{c} \text{Lattice parameter (Å)} \ \text{(Nb, Ti)N} \ \text{NbC} \ \text{$a$-Fe} \end{array} $ &amp; $ \begin{array}{c} a = 8.09 \pm 0.05 \ a = 4.36 \pm 0.05 \ a = 4.86 \end{array} $ &amp; $ \begin{array}{c} \eta = 0.0 \ \eta = 15.5 \ \eta = 18.4 \end{array} $ &amp; $ \begin{array}{c} \gamma = 23.8 \ \gamma = 7.8 \end{array} $</td>
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Fig. 9. Several NbC precipitates inside a grain of ferrite.

Fig. 10. Electron diffraction pattern of NbC precipitates, some of which are in a near (1 0 0) projection.
small deviation in the Nb/Ti ratio can have a relatively large effect on the lattice parameter deviation). However, the DFT calculations show qualitatively that carbon deficiency leads to a considerable decrease in the lattice parameter. The experimentally determined lattice parameter for NbC_x in this work (a = 4.36 ± 0.05 Å, Table 3) is significantly smaller than the experimental lattice parameter of stoichiometric NbC_1.0 [3 3 2], and therefore the precipitates studied in the current work are most likely deficient in carbon content.

In group B in Table 4 the Nb/Ti ratio within the composition Nb_{0.75}Ti_{0.75}N_x is varied. When considering the formation enthalpy ΔH^f_{form} (defined with respect to pure NbN, TiN) all values are positive, thus NbN and TiN have a negative entropy of mixing and the partial sum of the two components is always energetically more favourable than the compound. On the other hand, when taking the solutes in bcc Fe as the reference ΔH^f_{form} it is clear that the formation of mixed Nb, Ti compositions is always associated with an energy gain. Therefore, the mixed compositions are favourable with respect to the solute elements in fcc Fe, but are metastable with respect to phase separation into NbN and TiN. The composition (Nb_{0.75}Ti_{0.75})N_x is closest to the experimentally observed Ti/Nb ratio of 2.83 ± 0.81. In group C in Table 4 the N content was varied for the composition Nb_{0.25}Ti_{0.75}N_x with 0 < x < 1. From the values of ΔH^f_{form} in Table 4 it is clear that N deficiency is never favourable. The calculations show qualitatively that the lattice parameter of the compound Nb_{0.25}Ti_{0.75}N_{0.25} phase (8.35 Å) is smaller than twice the lattice parameter of NbN and TiN (4.26 and 4.45 Å, respectively, group B in Table 4), and that the lattice parameter decreases with decreasing N content. In combination with the literature values for the lattice parameters of NbN, TiN, this indicates that the experimentally observed precipitates are likely deficient in N content.

The question now arises why the calculations predict that Nb/Ti mixing is not favourable, while it is observed experimentally, and, second, why N deficiency is predicted to be unfavourable while it is observed experimentally. Here the most important difference between the experiment and the calculations is that the calculations are performed for a temperature of 0 K and zero pressure, while the precipitates are formed at high temperatures of 1500–1700 K in steel [9,33]. At these high temperatures the entropy S contributes very significantly to the free energy as F = H – TS. Both Ti/Nb mixing and N deficiency would contribute to configurational entropy at elevated temperatures. In addition, at these high temperatures the steel is no longer ferritic, but austenitic, so that the reference point for the formation enthalpies (now calculated with respect to the solute elements Nb, Ti, N, C in bcc Fe) is also not valid at these temperatures. Finally, the calculations are valid for bulk phases, while for precipitates interface energies and strain fields between the precipitate and the matrix are also of importance. The main conclusion that can be drawn from the calculations on the formation enthalpies is that the carbon-deficient NbC_x precipitate phases (with 0.50 < x < 0.75) are stable at low temperatures (0 K to room tempera-

### Table 4

Calculated lattice parameters and formation enthalpies of the NbC, NbN, TiN, and (Nb, Ti)N type phases.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Lattice parameter (Å)</th>
<th>ΔH^f_{form} (eV fu^{-1})</th>
<th>ΔH^f_{form} (eV fu^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) NbC_x</td>
<td>NaCl</td>
<td>a = 4.506</td>
<td>-1.489</td>
<td>0.000</td>
</tr>
<tr>
<td>NbC_{0.75}</td>
<td>d-NaCl</td>
<td>a = 4.470</td>
<td>-1.028</td>
<td>-0.021</td>
</tr>
<tr>
<td>NbC_{0.50}</td>
<td>d-NaCl</td>
<td>a = 4.417</td>
<td>-1.187</td>
<td>-0.456</td>
</tr>
<tr>
<td>NbC_{0.25}</td>
<td>d-NaCl</td>
<td>a = 4.354</td>
<td>-0.053</td>
<td>+0.247</td>
</tr>
<tr>
<td>NbC_{0.00}</td>
<td>fcc Nb</td>
<td>a = 4.232</td>
<td>+0.451</td>
<td>+0.451</td>
</tr>
<tr>
<td>(B) (Nb_{0.5}Ti_{0.5})N_x</td>
<td>NaCl</td>
<td>a = 4.256</td>
<td>-10.248</td>
<td>0.0</td>
</tr>
<tr>
<td>(Nb_{0.75}Ti_{0.25})N_x</td>
<td>d-NaCl</td>
<td>a = 4.309</td>
<td>-9.256</td>
<td>+0.041</td>
</tr>
<tr>
<td>(Nb_{0.75}Ti_{0.75})N_x</td>
<td>d-NaCl</td>
<td>a = 4.363</td>
<td>-8.280</td>
<td>+0.066</td>
</tr>
<tr>
<td>(Nb_{0.75}Ti_{1.0})N_x</td>
<td>d-NaCl</td>
<td>a = 4.404</td>
<td>-7.297</td>
<td>+0.099</td>
</tr>
<tr>
<td>(Nb_{0.75}Ti_{1.25})N_x</td>
<td>NaCl</td>
<td>a = 4.453</td>
<td>-6.644</td>
<td>0.0</td>
</tr>
<tr>
<td>(C) (Nb_{1.0}Ti_{1.0})N_x</td>
<td>d-NaCl</td>
<td>a = 8.236</td>
<td>+5.681</td>
<td>+5.681</td>
</tr>
<tr>
<td>(Nb_{1.0}Ti_{0.8})N_x</td>
<td>d-NaCl</td>
<td>a = 8.301</td>
<td>+1.870</td>
<td>+4.432</td>
</tr>
<tr>
<td>(Nb_{1.0}Ti_{0.6})N_x</td>
<td>d-NaCl</td>
<td>a = 8.350</td>
<td>-2.053</td>
<td>+3.071</td>
</tr>
<tr>
<td>(Nb_{1.0}Ti_{0.4})N_x</td>
<td>d-NaCl</td>
<td>a = 8.413</td>
<td>-5.073</td>
<td>+2.613</td>
</tr>
<tr>
<td>(Nb_{1.0}Ti_{0.2})N_x</td>
<td>d-NaCl</td>
<td>a = 8.472</td>
<td>-8.268</td>
<td>+1.944</td>
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<tr>
<td>(Nb_{0.75}Ti_{1.0})N_x</td>
<td>d-NaCl</td>
<td>a = 8.452</td>
<td>-11.406</td>
<td>+1.404</td>
</tr>
<tr>
<td>(Nb_{0.75}Ti_{0.75})N_x</td>
<td>d-NaCl</td>
<td>a = 8.497</td>
<td>-13.522</td>
<td>+1.890</td>
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<tr>
<td>(Nb_{0.75}Ti_{0.5})N_x</td>
<td>d-NaCl</td>
<td>a = 8.619</td>
<td>-16.173</td>
<td>+0.810</td>
</tr>
<tr>
<td>(Nb_{0.75}Ti_{0.25})N_x</td>
<td>d-NaCl</td>
<td>a = 8.617</td>
<td>-18.512</td>
<td>+0.082</td>
</tr>
</tbody>
</table>

The formation enthalpies ΔH^f_{form} are defined in Eqs. (5) and (6) of the main text. Three groups of precipitate phases are considered, whereby either the C or N content or the Nb/Ti ratio is varied. d-NaCl indicates a defective NaCl type structure; energies are in electron volts per formula unit (fu). The phases with compositions close to the experimentally found compositions are indicated with an asterisk (*). 

a Half the value of a supercell with lattice parameter 2a.
ture), while the Nb, Ti, N phases are metastable at low temperatures, both with respect to phase separation into TiN and NbN and with respect to N deficiency.

4. Conclusions

In this work we have investigated the microstructures and precipitates in a microalloyed MP steel containing ferrite, bainite, martensite and retained austenite. Precipitates were observed in the ferrite, martensite and bainite phases, but not in the austenite phase. Two kinds of precipitates were found in this steel, (Nb, Ti)N and NbC. (Nb, Ti)N precipitates of different sizes were found, ranging from 10 to 150 nm, with the larger precipitates having a Ti/Nb ratio of approximately 2.83 ± 0.81 and being faceted in shape. Smaller NbC precipitates were found in the size range 5–20 nm. The (Nb, Ti)N precipitates have a well-defined N–W orientation relationship with the ferrite matrix, while the NbC precipitates are in random orientations. Both NbC and (Nb, Ti)N carbide precipitates are expected to strengthen these steels. Comparison of the calculated lattice parameters and experimental lattice parameters indicates that both precipitates are deficient in carbon and nitrogen contents.

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References