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Characterization of (Ti,Mo,Cr)C nanoprecipitates in an austenitic stainless steel on the atomic scale

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Abstract

Nanometer sized (Ti,Mo,Cr)C (MX-type) precipitates that grew in a 24% cold worked Ti-stabilized austenitic stainless steel (grade DIN 1.4970, member of the 15-15Ti alloys) after heat treatment were fully characterized with transmission electron microscopy (TEM), probe corrected high angle annular dark field scanning transmission electron microscopy (HR-HAADF STEM), and atom probe tomography (APT). The precipitates shared the cube-on-cube orientation with the matrix and were faceted on {111} planes, yielding octahedral and elongated octahedral shapes. The misfit dislocations were believed to have burgers vectors $a/6\langle 112 \rangle$ which was verified by geometrical phase analysis (GPA) strain mapping of a matrix-precipitate interface. The dislocations were spaced five to seven atomic planes apart, on average slightly wider than expected for the lattice parameters of steel and TiC. Quantitative atom probe tomography analysis of the precipitates showed that precipitates were significantly enriched in Mo, Cr and V, and that they were hypostoichiometric with respect to C. These findings were consistent with a reduced lattice parameter. The precipitates were found primarily on Shockley partial dislocations originating from the original perfect dislocation network. These novel findings could contribute to the understanding of how TiC nanoprecipitates interact with point defects and matrix dislocations. This is essential for the application of these Ti-stabilized steels in high temperature environments or nuclear fast reactors.

Keywords: Precipitation; Stainless steel; Interface structure; Transmission electron microscopy; Atom probe tomography

1 Introduction

Austenitic steels containing stabilizing elements such as Ti or Nb find a multitude of applications in high temperature environments such as steam generators and fuel cladding in fast spectrum nuclear fission reactors. At elevated temperatures, the stabilizing elements combine with C to form small NaCl structured MX precipitates ($M = \text{Ti, Nb, V, Mo, Zr, ...}$ and $X = \text{C, N}$) on dislocations and other lattice defects. Originally, the purpose of stabilization in stainless steel was to neutralize carbon that would otherwise bind with Cr and sensitize the steel to intergranular corrosion. Fine control of the ageing heat treatment (HT) can achieve a nano-sized MX precipitate population, which significantly enhances creep properties [1,2]. For applications in high-energy radiation environments such as the cores of fast flux reactors, it is also speculated that (semi-)coherent nano-sized precipitates act as point defect recombination centers. This improves the resistance against degradation of these materials under irradiation by delaying onset of swelling, which makes these materials prime candidates for nuclear fuel cladding in fast spectrum nuclear reactors [3].

Despite extensive investigations dedicated to MX precipitates, many questions remain related to their precipitation mechanism and their role as point defect recombination centers when the material is subject to irradiation. Silcock et al. [4,5] found that NbC nanoprecipitates form on Frank partials of dissociated sessile dislocations in a solution annealed Nb stabilized steel, causing the stacking faults to expand. Kesternich et al. [6,7] studied coarsening kinetics of TiC in an identical steel to the one used in the present paper only with a lower level of cold work. The excessively slow coarsening mechanism led them to devise a precipitation mechanism whereby climbing dislocations sweep up solute elements, causing local supersaturation and subsequent precipitation on perfect dislocations. In a recent paper [8], the present authors found that precipitation and dislocation dissociation appeared to occur simultaneously, which suggests the two effects are related. The type of dissociation or the nature of the stacking fault was, however, not investigated, so Silcock's work could not be corroborated.

There persists some confusion in the community as to the type of interface these precipitates share with the matrix. Latha et al. [9], Rouxel et al. [10] and Liu et al. [11] have all referred to TiC nanoprecipitates being coherent with the matrix. Coherent precipitates trap point defects at their interface, thereby acting as point defect recombination centers [12]. The large misfit between austenite and MX phases (~18-20%) makes it impossible for precipitates to be fully coherent, except for the very smallest ones. Therefore, most precipitates are semi-coherent, with a network of interface dislocations at the phase boundary to accommodate the large misfit. The semi-coherent nature of the precipitates and the presence of interface dislocations was used by Gopalan et al. [13] to study nucleation and growth of MX precipitates by positron annihilation. Knowledge on the interface configuration matters: recent modeling work has shown that the interaction between point defects and semicoherent interfaces is highly dependent on the nature of the interface dislocation network [14–17], and that there is a large potential for designing interfaces with radiation resistance in mind. Choudhury et al. [18] have demonstrated experimentally that the stress fields of interface dislocations on metal/metal-oxide interfaces can cause inhomogeneous segregation of solute elements to the phase boundary under irradiation.

To maximize interfacial area, the goal of materials designers is to make the MX precipitate distribution as fine and numerous as possible. How much of the phase is able to precipitate depends on the composition of the matrix [19], but also the composition of the precipitates. The latter is non-trivial for MX phases, because they can be significantly hypostoichiometric with respect to carbon [20] and incorporate other elements like Cr and Mo on the M sublattice [21].

A more detailed description of the precipitates may shed light on their precipitation mechanisms as well as their role in capturing point defects under irradiation. To this pursuit, in this paper Ti-C precipitates formed by heat treatment in a new heat of nuclear grade 15-15Ti steel were characterized by modern techniques such as 3D atom probe tomography (APT) and probe corrected scanning transmission electron microscopy (STEM). High resolution transmission electron microscopy

(HRTEM) images were analyzed with geometric phase analysis (GPA) [22,23] strain mapping. The aim was to elucidate shape and composition of the precipitates, as well as their relationship to the matrix.

2 Materials and methods

The material used in this study was nuclear grade Titanium stabilized austenitic stainless steel with nuclear fuel cladding as intended application. The material was in the form of thin walled tubes with outer diameter 6.55 mm and wall thickness 450 μm . The overall composition as given by the manufacturer is given in Table 1. The material was subjected to a solution heat treatment between 1100-1140 $^{\circ}\text{C}$ for 4 minutes before being cold-drawn to 24% cross sectional area reduction, which is further referred to as as-manufactured material.

Table 1 Chemical composition and measurement uncertainties of DIN 1.4970 cladding tubes as given by the manufacturer. Concentrations were measured by XRF unless otherwise indicated in brackets.

Element	C (HFIR ¹)	Cr	Ni	Mn	Mo	Ti	Si	B (ICP-MS ²)	P
wt. %	0.10 ± 0.01	15.08 ± 0.08	15.04 ± 0.15	1.83 ± 0.03	1.21 ± 0.01	0.49 ± 0.02	0.56 ± 0.06	0.0028 ± 0.0005	0.013 ± 0.001
Element	N (EXTR ³)	S (HFIR)	V	Ta	Cu	Co	Ca (OESG ⁴)	Fe	
wt. %	0.011 ± 0.001	<0.001	0.034 ± 0.005	<0.005	0.026 ± 0.001	0.020 ± 0.002	<0.001	Bal.	
¹ HFIR: combustion technique, see ASTM E1019 [24], ² ICP-MS: inductively coupled plasma mass spectrometry, ³ EXTR: combustion technique, see ASTM E1019 [24], ⁴ OESG: optical emission spectrometer, see ASTM E1086 [25]									

Heat treatments were conducted in air in a Nabertherm furnace between 600 and 800 $^{\circ}\text{C}$ for durations between 10 minutes to 3000 hours. Temperature was monitored by a calibrated thermocouple. Full details on all the conducted heat treatments can be found in an earlier publication [8].

Thin foil specimens for transmission electron microscopy (TEM) observation were made by punching 3 mm diameter discs that were ground to a thickness of 100-200 μm (final grit size: 2000) that were

subsequently jet electropolished in a Struers Tenupol 3 using a 5 vol% of stock perchloric acid in methanol electrolyte (cooled between -30 and -20 °C) at 25-30 V resulting in a current of 0.2-0.25 A.

For conventional TEM and high resolution TEM (HRTEM) observations, a JEOL 3010 and a JEOL 3000F operating at 300 kV were used. A double corrected FEI Titan operating at 400 kV was used for performing high angle annular dark field scanning transmission electron microscopy (HAADF STEM).

Atom probe tomography (APT) specimens were prepared on a CAMECA Microtip® Si needle coupon in a FEI Quanta focused ion beam (FIB). Only the as-received material and material heat treated for 2 h at 800 °C were investigated by APT.

APT measurements were made using an IMAGO LEAP 4000 HR operating in laser mode at 200 Hz and at a sample temperature around 50 K. Reconstruction and analysis were carried out using the IVAS 3.8.0 and 3Depict 0.0.20 [26] software packages.

3 Results

3.1 Precipitate orientation relationship and facets

The first column of Figure 1 shows representative HRTEM images of the precipitates found in material treated for 66 h at 800 °C. The precipitates in Figure 1 (a) and (b) were viewed along the [011] zone, while the precipitate in Figure 1 (c) was imaged along the [001] zones. The second column shows the corresponding Fast Fourier Transform (FFT) patterns of the images in the first column, with the relevant reflections marked. The third column shows inverse FFT images (IFFT) after masking everything in the FFT except the frequencies corresponding to the Ti-C lattice. The fourth column shows the GPA mean dilatation strain map using the matrix reflections as the reference.

The orientation relationship between the Ti-C nanoprecipitates and the matrix is the cube-on-cube orientation relationship: $(100)_{\gamma} || (100)_{Ti-C}$, $[010]_{\gamma} || [010]_{Ti-C}$. This is demonstrated by the FFTs in both zones, which show that the Ti-C reflections are oriented in the same way as those of the

austenite. Also, the Moiré patterns in the HRTEM images of Figure 1 (b) and (c) confirm this orientation relationship.

From the IFFT images, the bounding planes were estimated and shape of the particles were derived. Along the [011] zone axis (ZA) (Figure 1 (a) and (b)), the projections of the Ti-C precipitates look like parallelograms or hexagons, with apparent {111} and {100} bounding planes. Along the [001] ZA (Figure 1 (c)), the projection of the Ti-C particles looked like squares and rectangles bound by {110} planes.

Apparent bounding planes are not necessarily crystal planes but could also be bounding edges projected on the image plane. Edges result where bounding planes at an angle to the ZA direction intersect. Having only {110} bounding planes in the $\langle 100 \rangle$ zones is not consistent with only {111} and {100} bounding planes in the $\langle 110 \rangle$ zones. If {110} planes were actual bounding planes they should also be visible in some of particles imaged in the $\langle 110 \rangle$ orientation. However, this was never the case, which means that the apparent {110} bounding planes seen along the $\langle 100 \rangle$ ZA are projected edges. These can result from two intersecting {111} bounding planes or a {111} plane intersecting with a {100} plane. Particles with intersecting {100} planes are not possible, because then apparent {110} bounding planes should be observed along $\langle 110 \rangle$ zones. Therefore {111} planes must be bounding planes, which means that the precipitates are octahedra or elongated octahedra.

Tetrahedra can also be constructed from {111} planes, but this shape has a surface area/volume ratio 25% larger than that of an octahedron of the same volume and is thus energetically less favorable. It could be that some octahedra have flattened vertices on {100} planes, but most particles were not truncated octahedra; these would appear as octagons along $\langle 100 \rangle$ zones, a shape which was never observed. In the Supplementary Materials file uploaded separately with the electronic version of this paper, a more detailed derivation of the shape of the particles is given based on all possible ways {111}, {100} and {110} planes can intersect.

Figure 2 shows an elongated octahedron as precipitate prototype, together with views of the shape along different $\langle 100 \rangle$ and $\langle 110 \rangle$ directions. The projections are the shapes of the precipitates expected to be observed. Also shown in the image are matching example precipitates discernible by their Moiré fringe contrast. The images were made not far from a $\langle 110 \rangle$ or $\langle 100 \rangle$ zone, but such that a (002) reflection was excited (so only the (002) fringes are visible). The projections of the prototype precipitate are consistent with the experimentally observed shapes. Therefore, all observations can be explained by precipitates which are regular or elongated octahedra bound by $\{111\}$ planes. In this interpretation, apparent $\{100\}$ bounding planes along $\langle 110 \rangle$ zones are bounding edges.

Due to the high lattice mismatch between the matrix and precipitating phase, the lattice surrounding the precipitate is deformed which results in blurry edges in the IFFT images. To improve the resolution and verify whether the conclusions hold for even the smallest particles, images of the precipitates under aberration-corrected HAADF STEM conditions were acquired.

Figure 3 shows several nanoprecipitates at the edge of the sample, viewed along the $[011]$ zone axis. They can be distinguished by Z-contrast. Having the precipitates at the edge of the thin foil reduces or removes overlap with the matrix, allowing the facets to be directly observed. The images show that even these small particles are faceted, and the facets appear to be primarily of the $\{111\}$ type and $\{100\}$ (which can be interpreted as edges) type. This supports the conclusions from the previous HRTEM images. Some particles have jagged sections on the interface, which were interpreted as steps on the faces of the particles.

3.2 Interface structure

Since the nanoprecipitates have a large mismatch with the austenite and share the cube-on-cube orientation relationship, a network of misfit dislocations must accommodate the difference in lattice spacing. The most efficient way to achieve this is with an array of pure edge dislocations in the interface plane. Unfortunately, the network of interface dislocations cannot be imaged by diffraction

contrast imaging as was done by Weatherly et al. on various interfaces [27], because the dislocations are too closely spaced.

Misfit dislocations can be observed edge-on by finding lattice plane discontinuities. This makes the Burgers vector and line direction identification ambiguous. Since both phases have the same crystal structure and share the cube-on-cube orientation relationship, any set of lattice planes can be selected to find the spacing between lattice plane discontinuities. Figure 4 shows three images from Figure 3 but overlaid with an IFFT using only the $(02\bar{2})$ planes from both phases. Yellow markers are placed on discontinuities between the planes near the matrix-precipitate interface, indicating the positions of misfit dislocations. The dislocations are spaced between 5 and 7 atomic planes apart, with one outlier at 9 atomic planes at the edge of the precipitate and the sample. The same treatment was performed on the HRTEM images from Figure 1, with similar results. The average dislocation spacing was 6.3 ± 0.1 lattice planes, the error accounting for the differences between particles. Using the lattice parameters $a_{TiC} = 4.326 \pm 0.002 \text{ \AA}$ [28] and $a_{matrix} = 3.589 \pm 0.001 \text{ \AA}$, an average spacing of 5.87 matrix planes is required between dislocations for complete relief of stress. The misfit dislocations are slightly more widely spaced, so the stress at the interface may not be completely relieved or the lattice parameter of the nanoprecipitates is less than that of pure TiC. If it is assumed the stress is completely relieved by the observed misfit dislocation spacing, the Ti-C precipitates will have a lattice parameter of $4.26 \pm 0.07 \text{ \AA}$. From the GPA maps in the last column of Figure 1, the Ti-C lattice corresponds to the Fe lattice dilated by $+16 \pm 2\%$, which corresponds to a lattice parameter of $4.16 \pm 0.07 \text{ \AA}$.

3.3 Composition

Figure 5 shows clusters in the ion maps of the precipitate forming elements C, Ti and Mo in a heat treated sample. The composition of the clusters was estimated by defining an isosurface for Ti, C and C_3 ions which encompassed the clusters, then analyzing the ions contained by each surface individually using a peak decomposition algorithm [29]. Adjustment of the isosurface parameters was

done by plotting proxigrams. The proxigram shown in Figure 6 (a) resulted from setting the isosurface parameters so that the composition inflexion point was centered on 0. The left-hand side of the proxigram represents the matrix side of the isosurfaces, while the right hand side represents the precipitate side of the isosurfaces. The precipitates contain almost no Fe, which is consistent with earlier reports [30]. Hence, to estimate the precipitate composition, the isosurfaces were adjusted such that Fe content was minimized. The mass spectrum from all ions in the clusters combined is shown in Figure 6 (b). The average composition of the clusters with the sample standard deviation is shown in Table 2.

The results show that the precipitates are hypostoichiometric with respect to carbon (a stoichiometry of $MC_{0.5\pm0.1}$ can be inferred from the composition) and that they contain a large fraction of carbide formers other than Ti such as Cr, Mo and V. Contrary to earlier reports [21], no correlation was found between composition and the size of clusters, though the number of investigated clusters was small. In the Supplementary Materials file accompanying the electronic version of this paper, more details are given on the APT measurements and analyses, as well as APT results on the non-heat treated material.

Table 2 Composition of nanoprecipitates as estimated by defining an (Ti, C, C₃) isosurface in the sample heat treated for 2 h at 800 °C (shown in Figure 5(b)). The parameters of the isosurface were optimized such that the clusters contained as many ions as possible but contained a minimum amount of Fe. The ions enclosed in each isosurface were used to estimate the composition of each cluster. This table reports the mean and standard deviation of the composition of the 10 visible clusters.

Heat treatment	Clusters	Total ions considered	Element (at%)					
			Ti	Mo	Cr	V	Ni	C
800 °C, 2 h	10	3124	42±5	13±2	10±3	0.9±0.3	trace	34±6

3.4 Relationship with the matrix dislocations

As was reported in a previous publication by the present authors [8], precipitation of nanoprecipitates appeared to coincide with large scale dissociation of lattice dislocations. Figure 7 (a) shows limited dissociation in the as-received material (one dissociated dislocation is pointed out with an arrow), whereas after heat treatment most dislocations are clearly dissociated as evidenced by stacking fault fringes (Figure 7 (b)). Heat treatments at 500 °C below the precipitation temperature

showed similar dislocation structures as the as-received material. In the earlier work on dislocation dissociation upon heat treatment of Ti-stabilised austenitic steels, neither the nature (intrinsic vs. extrinsic) of the stacking fault nor the nature of the partials (Frank vs. Shockley) were determined [8]. Figure 7 (c) shows an HR HAADF STEM image of a nanoprecipitate sitting on a partial dislocation; as shown by the Burgers circuit, on the right of the precipitate a stacking fault can be seen, on the left there is no fault. The stacking order of the fault shows it to be intrinsic in nature. Together with Burgers circuit analysis, the partial dislocation must be of the Shockley type $\vec{b} = a/6\langle 211 \rangle$. This is consistent with regular dissociation of perfect $\vec{b} = \langle 110 \rangle$ dislocations into Shockleys and subsequent precipitation on the partials. Similar images were obtained for other precipitates. No evidence was found for extrinsic stacking faults or for Frank partials.

4 Discussion

In this work, Ti-C nanoprecipitates that formed by ageing heat treatment in a 15-15Ti steel were studied in detail in order to gain a better understanding of their structure and composition. This may lead to an improved understanding of how these precipitates interact with point defects and matrix dislocations, and ultimately how these Ti-stabilized steels behave in operation.

The shape of the precipitates is determined by the bounding planes. In this study, the observed nanoprecipitates were consistent with octahedra and elongated octahedra bound by $\{111\}$ facets. The octahedral shape of the MX nanoprecipitates was demonstrated in a few studies in the past for Ti(N,C) in microalloyed austenitic steel by Liu et al. [11,31,32] and in a Mo containing austenitic steel by Wang et al. [33]. However, after prolonged ageing at higher temperatures (~ 900 °C) than explored in this study, large (50-70 nm) MX precipitates with truncated tetrahedral/tetra-kai-decahedral shapes with $\{100\}$ and $\{111\}$ bounding planes were found in austenite [34,35].

Yang et al. [36] showed that the chemical bonding energy between the matrix and the precipitates determines the shape of the precipitates, not the strain energy arising from the large misfit between

the phases. They treated the interfacial energy as the sum of a chemical contribution, calculated from nearest neighbor geometry and bonding energies, and a strain contribution, from a correlation by van der Merwe [37]. The chemical contribution γ_{chem} was highly orientation dependent, whereas the anisotropy of the strain contribution γ_{strain} was negligible. Their correlation showed that $\gamma_{\{111\}-Ti} < \gamma_{\{100\}} < \gamma_{\{110\}} < \gamma_{\{111\}-C}$; odd-index planes such as $\{111\}$ will be either Ti or C terminating, so two cases must be considered. Hence, the model predicts precipitates to be bound primarily by Ti-terminating $\{111\}$ facets. Using a Wulff construction, the model also predicts small $\{100\}$ facets when the C content is low, resulting in truncated octahedral shapes. The low C-content measured in this study should give rise to $\{100\}$ facets but convincing evidence for such facets were not observed. The large precipitates from earlier studies did show convincing evidence for $\{100\}$ facets [34,35], which may indicate a critical particle size must be surpassed before $\{100\}$ facets become stable.

In order for the particles to grow, $\{111\}$ layers of C and Ti must be added alternately, but $\{111\}$ C layers are high energy. A simple growth mechanism that avoids the creation of a Fe-C $\{111\}$ layer is proposed for the nanoprecipitates, and is shown pictorially in Figure 8. A new $\{111\}$ layer could nucleate by first growing a new $\{111\}$ layer of Ti on top of the Ti-C. The underlying $\{111\}$ C layer can be filled up afterwards, either by diffusion of C from the matrix or by redistribution of the C inside the Ti. This would circumvent building the high energy C layer between the austenite matrix and the Ti-C precipitate. Given that the nanoprecipitates were shown to be significantly hypostoichiometric with respect to C, a hypostoichiometric layer of Ti could potentially exist on top of the TiC without first forming a complete C layer. Also, the diffusion of C inside TiC is very rapid as compared to almost non-existent diffusion on the M lattice [38], and is even accelerated when impurities are introduced [39].

The measured composition of the precipitates is consistent with energy minimization arguments. The carbon hypostoichiometry of the phase is energetically favorable to reduce the lattice parameter and

thereby the misfit strain energy [21,40]. As shown by *ab initio* calculation, the increase in formation energy of TiC by the incorporation of Cr and Mo on the M sublattice is sufficiently compensated for by the decrease in strain energy due to further lattice parameter reduction [40]. In addition, C vacancy stability is enhanced by the introduction of other elements on the M lattice [39]. The lattice parameter for the Ti-C precipitates estimated from the GPA map and separately from the spacing of interface dislocations are both consistent with expected lattice parameter reductions [40–42].

The burgers and line vectors of the interface dislocations cannot be directly measured from the images in Figure 1, Figure 3 or Figure 4. In the literature [36,43], it was assumed that the interface dislocations between TiC and austenite formed a network of edge dislocations with the shortest lattice vector in the lowest energy arrangement. On a {111} plane, this would be a hexagonal network with $\vec{b} = a/2 \langle 110 \rangle$ and line vectors along $\langle 112 \rangle$ directions, as was observed on low angle grain boundaries in FCC and BCC crystals [44] as well as on large FCC precipitates with small mismatch [27]. However, such a network is highly unlikely in the highly misfitting TiC/austenite interface. In Figure 8 a) and b), two (111) layers of the Ti M-sublattice of a hypothetical precipitate are shown and on top is a non-relaxed (111) layer of steel matrix (Fe for simplicity). The two Ti layers are shown in different colors so that the different types of stacking in the Fe layer are highlighted. In the non-relaxed layer of Fe, there are regions of good fit where the Fe continues the FCC stacking (ABC) of the underlying Ti layers (inside the blue circles), regions of faulted fit (ABA) where the Fe is stacked directly above the first Ti layer (inside the green circles), and regions of bad fit (ABB) where the Fe is stacked directly above the second Ti layer (inside the red circles).

Molecular dynamics simulations in the context of FCC bi-metal {111} interfaces have shown that the atoms at the interface relax to maximize areas with ABC and ABA stacking, while minimizing the area of ABB stacking [17,45,46]. The result is that interface dislocations form to divide the regions of ABC and ABA stacking along $\langle 110 \rangle$ directions and with burgers vector $a/6 \langle 211 \rangle$. The dislocations intersect on nodes located on the centers of worst fit. While this paper considers a metal-ceramic

interface, the principles from the metal-metal interfaces should remain valid. Figure 9(c) shows this network together with the hexagonal network. The hexagonal network is very unlikely because regions of bad fit and regions of faulted fit are treated identically, whereas it was shown that ABA stacking is a significantly lower energy configuration than ABB [17].

While direct observation of this network is not possible because the interface is buried, an indirect confirmation was obtained from the GPA strain field near the experimentally observed misfit dislocations. This strain field was compared to an analytical model by van der Merwe [37] describing the strain field of an infinite array of pure edge dislocations on the interface between two semi-infinite misfitting lattices. The experimental mean dilatation map overlaid on the HRTEM image is shown in Figure 10 (a); it is an enlargement of part of the image in the last column of Figure 1(a) marked with an arrow. A different color map was used than in Figure 1. The mean dilatation according to the model is shown in Figure 10 (b). Inputs to the equations are the lattice parameters, the burgers vector and elastic constants (which are assumed equal for both materials). The burgers vector in the model was assumed to be of the $a/6 \langle 211 \rangle$ type. Since GPA can't detect when the matrix ends and Ti-C begins, it assumes one lattice type in the strain calculation. Therefore, the larger lattice parameter of Ti-C compared to austenite manifests itself as a region under tension. To facilitate comparison with the experiment, 0.16 dilatation was added to the Ti-C half of the model image; this accounts for the difference in lattice parameter across the boundary which can't be automatically detected by GPA. Despite the simplicity of the model, the match with the experiment is good, both showing similar features and feature sizes. Near the misfit dislocations the matrix is severely compressed while the Ti-C is under tension. Between the misfit dislocations, the matrix is slightly under tension, while the Ti-C is slightly under compression. The good match between model and experiment suggests that the interface dislocation likely have burgers vector $a/6 \langle 211 \rangle$. Full details concerning the implementation of the van der Merwe model are given in the Supplementary Materials file accompanying the electronic version of this paper.

The structure of the nodes cannot be resolved by microscopy, but their role can be especially important in the interaction of point defects with the interface [47]. Shao et al. have shown that the structure of nodes on the {111} interface between two dissimilar FCC metals can be especially complex and varied [17,45,46]. In general, a reduction in distance between nodes below 2 nm resulted in compact nodes leading to local high stress concentrations. The node distance for the austenite Ti-C case is around 1.5 nm. How well this model for the nodes extends to metal-carbide interfaces remains speculative.

Precipitation occurred simultaneously with dissociation of dislocations, which we reported on in an earlier publication [8]. In this paper, we found that most precipitates observed by HR HAADF STEM were associated with either a Shockley partial dislocation or a twin boundary. This contrasts earlier reports. Silcock et al. [4,5] reported that precipitates grew only from Frank partials. Though they studied NbC, this phase has a similar lattice parameter and should behave similarly to TiC in austenite. Kesternich et al. [48] reported that Ti-C nanoprecipitates grew on perfect dislocations, though it is likely they did not detect the dissociation of dislocations. To explain the sluggish coarsening kinetics, Kesternich et al. proposed nanoprecipitates nucleate when climbing dislocations interact causing local supersaturations. The fact that the nanoprecipitates are located on partial dislocations makes this mechanism very unlikely, because dissociated dislocations are much less mobile than perfect dislocations. Recent work has shown that slow coarsening kinetics could be explained by precipitates showing a core-shell structure that stabilizes the interface [35].

Dislocation dissociation after ageing could have multiple explanations. Ageing could result in local chemistry changes around dislocations that lower the stacking fault energy (SFE), thereby promoting dislocation dissociation into two Shockley partials. Possibly, enrichment of Ti near dislocations before precipitation reduces the SFE. However, to our knowledge, no composition-SFE correlation for steels from literature captures the effect of Ti, so its effect remains speculative. A second explanation is that increased dislocation dissociation is simply the result of recovery. As dislocations are annealed

out, longer segments of dislocations will be free to dissociate to equilibrium length. In the tight dislocation network of the as-received material, the dislocations are more constrained. Because recovery and precipitation happen in the same temperature/time window, it is not possible to deconvolute the factors contributing to dissociation. After dissociation, the precipitates grow on the partial dislocations, thereby pinning them.

5 Conclusion

In this paper, the structure and composition of Ti-C nanoprecipitates were studied by TEM, HR STEM and APT. Special attention was devoted to studying the relationship between the precipitates and the matrix, including the bounding facets of the precipitates, the structure of the misfit dislocation network and the relationship with matrix dislocations. We found that:

- Precipitates were faceted on {111} planes yielding octahedral and elongated octahedral shapes. This is consistent with an interfacial energy model if the precipitates grow by adding {111} layers of Ti to the surface with the C diffusing in to fill the sub lattice afterwards.
- The network of misfit dislocations was proposed to be triangulated, with dislocation lines along $\langle 110 \rangle$ directions and burgers vectors $a/6 \langle 211 \rangle$. A simple model of the strain field around an array of misfit dislocations with this burgers vector was consistent with the measured strain field around misfit dislocations.
- The misfit dislocations were spaced slightly more widely than expected from the lattice parameters of the matrix and TiC. APT revealed the precipitates contained about 25 at% of Mo, Cr and V. Also, the precipitates were hypostoichiometric with respect to C. These effects both reduce the lattice parameter of the precipitate (in comparison with pure TiC) thus yielding a smaller misfit and more widely spaced misfit dislocations.
- Precipitation and matrix dislocation dissociation occurred simultaneously. Most precipitates were found on Shockley partial dislocations. Dissociation could be promoted due to local

chemistry changes near dislocations or due to recovery. After dissociation, the partials are pinned by precipitates.

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7 References

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