On the Ti-Mo-Fe-C Atomic Clustering during Interphase Precipitation in the Ti-Mo Steel

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Abstract

Site-specific transmission electron microscopy (TEM) and atom probe tomography (APT) have been used to study the Ti-Mo-Fe-C atomic clustering during interphase precipitation at the early stages of austenite to ferrite transformation in a Fe-0.03C-1.5Mn-0.2Si-0.29Cr-0.22Mo-0.05Ti-0.025Al (in wt.%) steel. We observed: (i) the formation of only clusters at the beginning of austenite-to-ferrite transformation and co-existence of numerous clusters along with interphase nano-scale precipitates during development of the transformation, (ii) the nano-precipitates were formed via transient metastable precipitates, and (iii) a cluster-hardening mechanism was proposed based on hardness test and APT and TEM characterization. It was suggested that the rapid hardening reactions, due to the formation of solute clusters, can accompany the early stages of solid solution decomposition, which precede the formation of interphase precipitates.

Keywords: clusters, Ti-Mo interphase precipitation, site-specific transmission electron microscopy and atom probe tomography.

1. Introduction

The general trend to improve steels for the transport and construction sectors is to achieve higher strength while maintaining or improving other properties. JFE in Japan developed a steel with a strength of 780 MPa [1] and more recently 1200 MPa [2] through controlled precipitation hardening – the level of strength contribution from the precipitates being almost twice that obtained in conventional precipitation-hardened low-carbon steels. Extensive study of this steel [1-9] showed that extremely-fine, closely-spaced precipitates were formed during the austenite-to-ferrite (γ -to- α) phase transformation at the migrating γ/α interface in steels containing carbide-forming elements, such as Ti, Mo, V and Cr. These interphase precipitates are believed to be one of the most effective dispersion-strengthening particles [1-9]. Several mechanisms of interphase precipitation have been proposed: (i) the ledge mechanism, when the growth of ferrite into austenite occurs by lateral movement of small ledges and, as a result, planar sheets of interphase precipitates with regular sheet spacing are formed [3], (ii) the bowing mechanism when the curved sheets of interphase precipitates with regular sheet spacing are formed [10] or the quasi ledge mechanism, when the curved interphase precipitate sheets with irregular sheet spacing are formed [11, 12], (iii) the planar and curved ledge mechanism with the growth of incoherent ferrite/austenite interface [6], (iv) the structural ledges mechanism [13] and (v) the superledge mechanism [14].

The steels with additions of Ti and Mo showed good strength due to the formation of interphase precipitates with a nano-size of 2 to 5 nm in diameter [1, 2, 7]. It has been confirmed [15] that Mo controls the size of the precipitates by partially substituting Ti in the TiC lattice. Recent modelling [16] of the effect of Mo on the formation of interphase nano-precipitates in the advanced high strength steels containing Ti has suggested that the replacement of Ti by Mo might reduce the misfit between the nano-precipitates and ferrite

matrix leading to easier nucleation. At the same time, the substitution of Ti by Mo will reduce the equilibrium Ti concentration in the ferrite matrix during coarsening, which possibly retards the coarsening process of (Ti,Mo)C nano-precipitates [16]. Despite the high number of publications on the effect of Mo on the coarsening kinetics of (TiMo)C precipitates, its precise role is still unclear.

Our recent research [8] on thermomechanically-processed laboratory Ti-Mo steels by atom probe tomography (APT) and transmission electron microscopy (TEM) revealed co-existence of numerous *clusters* along with interphase nano-scale precipitates that can lead to the *cluster hardening* similar to that proposed for an Al-Cu-Mg alloy by Ringer et al. [17]. It was suggested by others that the formation of coherent *clusters* of solute atoms leads to the mismatch in size between the solvent and solute atoms and formation of the strain fields in the matrix, which retards the movement of dislocations [18-20]. However, it is uncertain if the same mechanism operates in Ti-Mo steel types.

The aim of the current research was to analyse the Ti-Mo-Fe-C atomic clustering during interphase precipitation at the early stages of austenite to ferrite transformation with a site-specific TEM and APT study.

2. Experimental

A thermomechanical processing simulation of the investigated steel with composition of Fe–0.03C–1.5Mn–0.2Si–0.29Cr–0.22Mo–0.05Ti–0.025Al in wt.% (0.14C–1.5Mn–0.4Si–0.3Cr–0.125Mo–0.057Ti–0.02Al in at.%) was performed with the use of a computer-controlled servohydraulic thermomechanical simulator (Servotest - 500 kN machine). The original 40 mm-thick plate was reduced to 13 mm by hot rolling between 1200 and 1000 °C. Then cylindrical samples with a diameter of 10 mm and length of 15 mm were machined along the

transverse direction of the plate. Boron nitride lubricant was used to coat the specimens to minimize the friction between the contact surfaces of the specimen and the anvils during deformation. The samples were reheated to 1200 °C at a rate of 5 °Cs⁻¹ and held for 180 s (Fig. 1), which resulted in an average austenite grain size of $65 \pm 2 \mu\text{m}$. The precipitation dissolution temperature (A_{e3}) and equilibrium temperatures (A_{e1}) were calculated from the Thermo-Calc software with the TCFE3 database. Subsequently, the samples were cooled at a rate of 10 °Cs⁻¹ to 890 °C, and held for 10 s (Figure 1) followed by cooling at 30 °Cs⁻¹ to the coiling simulation temperature of 650 °C. The samples were then isothermally held for 1200, 1700 and 2200 s, and water quenched to study the precipitation kinetics during the ferrite transformation in partially transformed samples consisting of ferrite and martensite. The coiling temperature of 650 °C was selected based on the best hardness response of the samples after coiling simulations from 550 to 700 °C [21].

Struers DuraScan nano-hardness tests with a load of 0.098 N were performed on samples with different amounts of ferrite, with a minimum of 10 random indents from the ferrite grains and martensite islands. Optical microscopy examinations were performed with a reflected light Olympus DP 70 microscope. Image analysis software (ImagePro) was used to estimate the volume fraction of ferrite by area percentage as a ratio of the total detected phase area to the image frame. Transmission electron microscopy (TEM) for general microstructural study was performed with a Philips CM 20 microscope operated at 200 kV. TEM thin foils were prepared by twin jet electropolishing with a solution of 5% perchloric acid in methanol at -20 °C and a voltage of 50 V. Observations were made in both bright and dark field imaging modes.

The TEM and atom probe tomography (APT) samples for the site-specific study after isothermal holds of 1200 and 1700 s, near freshly-formed ferrite and martensite interfaces,

were cut by in-situ lift-out (INLO) technique in a focussed ion beam/scanning electron microscope (FIB/SEM), (Figure 2) [22]. TEM foils were prepared by FIB milling in a FEI dual-beam Quanta 3D FIB/SEM instrument with two different orientations (Figure 2b). Firstly, lamellae with nominal size of $10 \times 6 \times 1 \mu\text{m}$ were cut free from the area of interest with a 30 keV Ga^+ ion beam. After that, the samples were transferred to a copper TEM grid using a lift-out micromanipulator and then thinned at a reduced ion current at 30 keV to a thickness of ~ 100 nm or less. Further ion polishing at 5 keV and 2 keV was also used to minimize the thickness of the amorphous layer on both sides of the foil surface. Finally, TEM foils with a thin area of $\sim 6 \times 4 \mu\text{m}$ were made. The TEM samples prepared by INLO were studied with a JEOL JEM 2100F microscope operated at 200 kV.

The APT samples were also fabricated by INLO method from site-specific locations, i.e., similar to the ferrite grain near ferrite/martensite interphase used for TEM sample preparation (Figure 2). The APT samples were prepared by FIB milling using a FEI dual-beam Nova 200 FIB/SEM at the Oak Ridge National Laboratory. The APT study was performed at Oak Ridge National Laboratory with a CAMECA Instruments LEAP 4000X HR Local Electrode Atom Probe, which was operated in the voltage-pulsed mode with a specimen temperature of 60 K, a pulse repetition rate of 200 kHz, and a pulse fraction of 0.2. The maximum separation envelope method was used to isolate the solute-enriched clusters and precipitates from the matrix and measure their radius of gyration and local solute contents [22, 23]. The parameters used were a maximum separation distance between carbon atoms of 0.75 nm, and a 0.1 nm grid spacing. Precipitates containing less than 50 atoms were ignored to eliminate the effect of random solute fluctuations in the matrix. The Guinier radii (r_G) of the clusters and precipitates were calculated from the radii of gyration (l_g) data by the standard equation [22, 23]: $r_G = \sqrt{(5/3)l_g}$.

3. Results

The aim of the interrupted experiments with isothermal holding times of 1200, 1700 and 2200 s at a temperature of 650 °C was to monitor the changes in size, composition and distribution of interphase nano-precipitates during austenite-to-ferrite transformation. In order to achieve this, the newly-formed ferrite grains near martensite islands were locally studied by INLO high-resolution TEM (HRTEM) and APT after the different isothermal holding times.

The microstructure after holding times of 1200, 1700 and 2200 s consisted of martensite accompanied by ferrite fractions of 17 ± 1.5 , 45 ± 1 and 75 ± 1 %, respectively (Figure 3). The ferrite grain size varied between 1.5 and 10 μm for all the isothermal time conditions. The nano-hardness tests were performed on the ferrite grains near the ferrite/martensite interface and on martensite blocks in the samples after all isothermal treatments. The nano-indentations were placed inside the ferrite grain to avoid grain boundary strengthening effect and at a distance of approximately 1 μm from the martensite/ferrite interface in the ferrite grain interior to avoid the effect of an increased dislocation density in ferrite near the interface as a result of martensite transformation. The nano-hardness of ferrite changed from 301 ± 10 to 322 ± 10 and 271 ± 10 after 1200, 1700 and 2200 s of isothermal holding times, respectively (Figure 3). The hardness of martensite was almost similar for all the isothermal holding conditions with an average hardness level of 380 ± 20 .

TEM and APT analyses of microstructure after 1200 s were performed on the samples prepared by INLO from site-specific locations, i.e., from a ferrite grain near the ferrite/martensite interface (Figure 2). The bright and dark field HRTEM images analysis of the INLO TEM samples from this particular ferrite grain did not reveal the formation of nano-precipitates, an additional diffraction pattern study showed only the reflections from the

[111] $_{\alpha}$ ferrite matrix in this selected zone (Figure 4a). It should be noted here that recently the formation of interphase precipitates has been reported after shorter isothermal transformation time [24, 25]. However, the composition and/or the thermomechanical processing schedules reported in those literatures are significantly different than in the present work. The HRTEM of the same ferrite grain revealed that the [111] $_{\alpha}$ lattice structure arrangement was locally disrupted in several parts of the matrix (shown by the black arrow in Figure 4b) possibly due to a nucleation of new “nano-phase” with the size of $\sim 1\text{-}2$ nm in thickness and up to ~ 5 nm in length (Figure 4b). It was suggested that these are clusters formed in the ferrite matrix. However, it was extremely hard to identify the individual characteristics of these ultrafine features by HREM as part of the cluster showed a distinct crystal structure (outlined in Figure 4b) and the formation of an interface between the cluster and the ferrite matrix, whereas the crystallography of the remaining part of the cluster was governed by the ferrite matrix (Figure 4b). The clusters are defined here as solute rich groupings of atoms without any regular atomic arrangement, which may appear with a shape, composition and crystallography governed by the matrix, whereas the precipitates are formed by the nucleation of a new phase with a specific crystal structure, which includes the formation of an interface. APT analysis of the samples after holding for 1200 s from the similar ferrite grain as that studied using TEM (see Figure 2), confirmed the presence of a uniform distribution of numerous C and Ti clusters containing less than 50 solute atoms in the C and Ti atom maps (Figure 5a). It is important to highlight that Mo did not participate in the initial formation process of the clusters (Figures 5a and b). The cluster composition varied from 37 ± 10 to 73 ± 9 at.% C and 24 ± 8 to 53 ± 9 at.% Ti with the balance of Fe (Figure 5b). The Guinier radius of clusters varied between 1.35 and 1.75 nm (Figure 5b). Careful rotation of the atom map from the area outlined in Figure 5b revealed that clusters in this area were formed along nearly parallel rows with a separation distance of 10 ± 0.2 nm (Figure 5c), whereas in other areas of the map,

they were randomly distributed in the ferrite matrix. The distance between the clusters within the rows was 6.5 ± 0.5 nm. The number density of the *clusters* was $2.5 \pm 0.3 \times 10^{22} \text{ m}^{-3}$. The formation of clusters in high strength steels has been recently confirmed by M. Kapoor et al. [26].

The precipitation in a ferrite grain situated near the ferrite/martensite interface, formed after 1700 s of isothermal holding at 650 °C, was also investigated by TEM and APT on the samples prepared by INLO. Precipitates, aligned along the interphase lines parallel to the interface between martensite and ferrite, were observed by HRTEM (Figure 6a). This technique clearly revealed the formation of nano-precipitates with a specific crystal structure and an interface between the particle and the matrix (Figure 6b). HRTEM confirmed that the nano-precipitates had a spheroidal shape, with a radius of 2 ± 0.5 nm and that the orientation relationship between the particles and matrix was $[0\bar{1}1]_{\alpha\text{-Fe}} // [011]_{(\text{TiMo})\text{C}}$ (Figures 6a and b), which corresponds to the Baker-Nutting relationship [27]. Based on the TEM micrographs and APT data, the average distance between the interphase rows was 17 ± 1 nm and the average distance between the nano-precipitates was 5.5 ± 1 nm. It is also important to highlight here that conventional TEM study showed randomly distributed nano-precipitates within the ferrite grains situated far from the interface (Figure 6c) similar as was reported in [24]. APT from INLO samples taken from the same ferrite grain as for HRTEM also showed the presence of spheroidal nano-precipitates, arranged along parallel lines, as well as clusters. The average composition of nano-particles/clusters was 56 ± 5 C, 17 ± 5 Mo and 24 ± 8 Ti (at.%) with the balance of Fe and the corresponding average Guinier radius was 1.95 ± 0.14 nm (Figure 6d), i.e., after this isothermal holding time, Mo had partitioned to the nano-precipitates/clusters (Figure 6d). The presence of randomly redistributed nano-precipitates was also evident from APT data. The number density of the *nano-precipitates/clusters* was $3.0 \pm 0.2 \times 10^{22} \text{ m}^{-3}$.

TEM performed after isothermal holding time of 2200 s at the temperature of 650 °C confirmed that all ferrite grains have nano-precipitates formed along interphase rows or randomly redistributed (Figure 7a). Moreover, coarse precipitates formed along the grain boundary were also observed, as indicated by the black arrows in Figure 7a. The average distance between the interphase precipitate rows calculated from TEM images and APT maps was 18 ± 1 nm and the average distance between the precipitate was 5.1 ± 0.7 nm. APT analysis from the ferrite grains located far from the martensite phase confirmed the formation of the nano-precipitates and clusters (Figure 7b). Importantly, the smaller nano-particles/clusters with the Guinier radius range of 1.3 – 2 nm showed a broader compositional range (Table 1, Figure 7c), i.e. 26-79 C, 10-30 Mo and 10-52 Ti (at.%) with the balance of Fe, whereas the larger nano-particles with the Guinier radius of 2 - 3.5 nm revealed the composition of 41-52 C, 8-14 Mo, 24-33 Ti at.% with the balance of Fe (Table 1, Figure 7c). The number density of the *nano-precipitates/clusters* was $3.5 \pm 0.1 \times 10^{22} \text{ m}^{-3}$.

4. Discussion

The formation of Ti-(Mo)-(Fe)-C solute clusters, along with interphase nano-precipitates in the Mo-Ti microalloyed steels formed during austenite-to-ferrite transformation, has recently been extensively studied by the current authors with APT [7, 8, 21]. We have found [21] that clusters co-exist with nano-precipitates during all stages of interphase precipitation and have various morphologies such as: (i) “diffused” clusters with a small number of atoms (~20), (ii) single-atomic layer clusters with the disc morphology and higher number of atoms, and (iii) multi-layer clusters with the disc morphology. It was also shown that the clusters display a wide scatter in composition with a different amounts of Ti, Mo and Fe. Nevertheless, when the size of the cluster increased, the composition range became narrower; reducing the residual Fe and, finally, the cluster composition approached that of the MC carbide i.e. B1-

type of carbide, where M is Ti and Mo [8]. The composition of clusters and nano-precipitates is a critical issue in their size control, since if the atomic concentration ratio of Ti/Mo in solution increases, so does the size of the interphase clusters/particles [9]. However, it is still unclear how the development of austenite-to-ferrite transformation affects the composition of clusters/nano-precipitates. In the current study, we have attempted to undertake a more systematic study with the aim to establish the individual characteristics of clusters and nano-precipitates during earlier stages of austenite-to-ferrite transformation. In order to achieve this goal, the experimental program of interrupted isothermal treatments at 650 °C for 1200, 1700 and 2200 s in combination with the site specific TEM and APT samples preparation was designed.

Firstly, it is worth to mentioning here that it was assumed that the interphase precipitates were formed by the ledge mechanism [10], where the planar interphase precipitation occurs in sequence along the migrating ferrite ledges parallel to a coherent interface. The height of ledges differs depending on transformation conditions and usually equals to an intersheet spacing of particles rows. In this case, precipitates nucleate at the terraces of ledges and grow within ferrite after being overrun by the next ledge [10].

Only clusters were observed within the newly formed ferrite grain at the beginning of transformation after 1200 s (Figs. 4, 5). However, the clusters were not randomly distributed within the ferrite matrix but aligned along parallel lines with a regular spacing of 10 ± 0.2 nm between the lines and a distance between the clusters in the row of 6.5 ± 0.5 nm (Table 2). The clusters appear to lack an identifiable crystal structure. The nano-precipitates along with the clusters were observed at later stages of precipitation after 1700 s of transformation. Moreover, some nano-particles were aligned parallel to the interphase lines whereas others were randomly distributed within the ferrite matrix. It is believed that the formation of clusters or clusters/nano-precipitates in the ferrite grain depends on the mobility of interface

and transformation temperature. At austenite-to-ferrite transformation temperature of 650 °C, the transformation of austenite to ferrite is accelerated at the beginning of transformation because of a large driving force, i.e., the ledge mobility is high, whereas at the late stages, the transformation is retarded [8]. The migration of the γ/α phase boundary is driven by the concentration gradient of carbon in the adjacent austenite where the para-equilibrium condition exists [6, 15]. It has been proposed that the γ/α interphase boundary during its migration absorbs metallic solutes atoms, which, in turn, apply a drag force to finally stop the boundary and precipitate nucleation takes place on the boundary [6, 15]. It seems plausible to suggest that, since the mobility of the interface within first 1200 s of isothermal hold at 650 °C is expected to be fast, there is no time for the growth of the interphase nano-precipitates and only formation of clusters at the interface occurs. However, the formation of clusters enables creating the favourable concentration gradient ahead of the γ/α interface to move the interface ahead. When the mobility of the interface slowed down with an increase in isothermal time to 1700 s, the formation of interphase nano-precipitates took place along with the clusters.

The composition of clusters varied between 37 – 73 C and 24 - 53 Ti at.% (Figure 5b, Table 1) after 1200 s of isothermal hold. It is important to highlight here, that Mo did not participate in the composition of clusters after this isothermal treatment. It has been reported [17] that Mo participated at the initial stage of precipitation, when the contribution of interfacial energy is critical to encourage the nucleation, since a contraction of the lattice parameter of TiC is desirable for better coherency with ferrite. Moreover, the partial replacement of Ti by Mo during the formation of TiC particles can help to decrease the strain energy and keep the interface coherent with the Baker Nutting orientation relationship [16]. However, in this study, we observed only formation of clusters after 1200 s of isothermal hold, i.e., the solute atoms which have the same crystal structure as the solvent phase, so the interfacial energy

between cluster and the matrix does not seem to be critical. The clusters appeared to be the multi-layers clusters with the disc morphology (Figure 5d).

HRTEM and INLO APT after of 1700 s of isothermal hold (Figure 6) confirmed the formation of not only clusters but also nano-precipitates. The nano-precipitates/clusters were aligned along the parallel lines with a regular spacing of 17 ± 1 nm, which is a larger distance than that observed after 1200 s. The formation of interphase nano-precipitates with a larger distance between the rows is the indirect evidence that during further 500 s after 1200 s of isothermal hold (i.e., after 1700 s) the transformation of austenite to ferrite was retarded so that nano-precipitates, not only clusters, can be formed and the velocity of interface was slowed down so that the distance between the nano-precipitate rows became greater. The newly formed nano-precipitates followed the Baker-Nutting crystallographic orientation relationship with the ferrite matrix (Figure 6b) leading to the greater coherency that precipitates adopt with ferrite when they form at the ferrite/austenite interface [5]. The composition of the nano-precipitates/clusters after this interrupted experiment contained 17 ± 5 Mo as well as 56 ± 5 C, 24 ± 8 Ti at.%, i.e., it appears that Ti was partially replaced by Mo. The presence of Mo in the composition of interphase nano-precipitates can contribute to decelerating the ripening kinetics of fine (Ti,Mo)C precipitates [16] and, as mentioned above, to a decrease in the interface energy caused by a reduction in strain energy at the interface due to the partial replacement of Ti by Mo. What needs to be emphasized here that the size of the clusters and nano-precipitates was quite similar after 1200 and 1700 s and only slightly increased after 2200 s of isothermal hold. This appears that the interface velocity or ledge mobility does not affect the size of interface precipitation carbides.

It appears that after the isothermal hold of 2200 s, the transformation was almost completed, as only 17 % of martensite was observed (Figure 3). The nano-precipitates showed the tendency for coarsening with the maximum radius of gyration of 3.5 nm compared to the

shorter isothermal treatments (Figure 7). The distance between the interphase particle rows and that between the particles in the row was 18 ± 1 nm and 5.1 ± 0.7 nm, respectively, i.e., similar to those after 1700 s (Table 1). Moreover, all Ti-C clusters and nano-precipitates contained Mo in their composition after 1700 and 2200 s of isothermal hold. It seems that mobility of the interface was similar for both isothermal treatments allowing Mo to participate in the composition of nano-particles/clusters. The composition of the clusters after 2200 s varied significantly depending on the size of the clusters (Table 1). It appears that the clusters with the size of 1.3-2 nm have a wide variety of compositions whereas the nano-precipitates with a larger size have a tendency to reach the MC equilibrium composition. All nano-particles and clusters after all the isothermal conditions used showed Fe as balance in their composition. The level of Fe varied depending on the level of C, Ti and Mo. Thus, it seems that the Ti-Mo-C precipitates were formed via a cascade of metastabilities, i.e., the formation of solute clusters and/or transient metastable precipitates that have a composition and structure different from the stoichiometric equilibrium phase [17, 28]. We have proposed [17] that even Ti-Mo-C clusters can grow with compositional changes and the presence of Fe is to simplify the nucleation by lowering the lattice misfit, which leads to a reduction in the nucleation barrier.

The average hardness of ferrite after 1200 s, when only clusters were observed, and after 1700 s with interphase precipitates and some clusters were almost similar and decreased after 2200 s, as a result of precipitate coarsening. It appears that the presence of the clusters, namely the strain fields in the matrix surrounding the coherent clusters, provide strength similar to that associated with the interphase precipitation strengthening. The hardness of ferrite could be also affected by the distance between the interphase precipitation rows [29]. We would also like to highlight that the hardness of ferrite after 1200 and 1700 s was close to that of martensite, which enables to improve stretch-flangeability of steel.

5. Conclusions

The current work has investigated key aspects of the evolution of precipitation in the Ti-Mo steel during isothermal treatment at 650 °C from the formation of clusters to the formation of nano-precipitates. In the current work it was demonstrated that:

1. The Ti-(Mo)-(Fe)-C clusters co-existed with nano-precipitates in all studied ferrite grains;
2. Only Ti-C clusters aligned along parallel lines were formed at the beginning of austenite to ferrite transformation, whereas the development of the transformation led to the formation of the nano-precipitates;
3. The clusters had the same crystal structure as the solvent phase and a wide range of compositions;
4. The Ti-Mo-C nano-precipitates were formed through transition of solute clusters and/or metastable precipitates that have a composition and structure different from the stoichiometric equilibrium phase.

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Table 1. The interphase nano-particles/clusters characteristics after different isothermal treatments at 650 °C.

Isothermal holding time, (s)	Guinier Radius, (nm)	Distance between interphase rows, (nm)	Distance between nano-particles/clusters, (nm)	Composition of nano-particles/clusters, with the balance of Fe, (at.%),
1200	1.35 - 1.75	10±0.2	6.5±0.5	37 – 73 C, 24 - 53 Ti
1700	1.95±0.14	17±1	5.5±1	56 ± 5 C, 17 ± 5 Mo, 24 ± 8 Ti
2200	1.3-2	18±1	5.1±0.7	26-79 C, 10-30Mo, 10-52Ti
	2-3.5	18±1	5.1±0.7	41-52 C, 8-14 Mo, 24-33 Ti

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Figure Captions:

Figure 1. Thermomechanical processing schedule.

Figure. 2. Representative SEM micrographs of the: (a) partially-transformed sample with formation of polygonal ferrite (PF) and martensite (M), analysed area is outlined by dash line and also shown is the schematic position of the in-situ lift-out (INLO) samples used for APT and HRTEM study near interface, and (b) position of the INLO, TEM and APT samples (shown by the arrows) from the ferrite grain near the ferrite/martensite interface shown in (a).

Figure. 3. Optical micrographs and the nano-hardness values as a function of volume fraction of ferrite, after 1200, 1700 and 2200 s of isothermal hold at 650 °C.

Figure. 4. TEM of the INLO sample after isothermal hold for 1200 s at 650 °C: (a) TEM micrograph and diffraction pattern (the inset) with a zone axis of $[111]_{\alpha}$ from ferrite grain near ferrite/martensite interface, and (b) HRTEM of a cluster in the ferrite matrix.

Figure. 5. APT of the INLO samples after isothermal hold for 1200 s at 650 °C: (a) representative APT 2 at. % C+Ti concentration isosurface of the clusters, (b) solute concentration of the clusters as a function of the Guinier radius, (c) selected atom maps from the volume outlined in Fig. 5a, showing interfacial formation of clusters, and (d) selected atom map of the multi-layer cluster, the matrix atoms were suppressed with the maximum separation method with $d_{\max} = 0.75$ nm.

Figure 6. TEM (a-c) and APT (d) of the INLO samples after isothermal hold for 1700 s at 650 °C: (a) HRTEM image showing the interphase precipitation in ferrite near the ferrite/martensite interface, (b) bright field image and diffraction pattern from the nano-precipitate (the zone axes are $[0\bar{1}1]_{\alpha\text{-Fe}} // [011]_{(\text{TiMo})\text{C}}$), (c) bright and dark TEM images of randomly distributed precipitates with the corresponding diffraction pattern shown in the inset, the zone axis of ferrite is $[111]_{\alpha}$ and the zone axis of carbide is $[\bar{1}10]_c$ and (d) C-Mo-Ti, 2 at.% of concentration isosurface of the nano-precipitates.

Figure. 7. TEM (a) and APT (b, c) of the samples after isothermal hold for 2200s at 650°C: (a) representative TEM image of interphase precipitation and precipitates formed along grain boundary, the latter are shown by the black arrows (the inset is the enlarged view of interphase precipitation), (b) C-Mo-Ti, 2 at. % concentration isosurface of the nano-particles and the selected box represents the area of interest, dashed lines show suggested interface lines, the matrix atoms were suppressed using the maximum separation method with $d_{\max} = 0.75$ nm, (c) solute concentration of the nano-particles as a function of the Guinier radius.

Table 1. The interphase nano-particles/clusters characteristics after different isothermal treatments at 650 °C.

Isothermal holding time, (s)	Guinier Radius, (nm)	Distance between interphase rows, (nm)	Distance between nano-particles/clusters, (nm)	Composition of nano-particles/clusters, with the balance of Fe, (at.%),
1200	1.35 - 1.75	10±0.2	6.5±0.5	37 – 73 C, 24 - 53 Ti
1700	1.95±0.14	17±1	5.5±1	56 ± 5 C, 17 ± 5 Mo, 24 ± 8 Ti
2200	1.3-2	18±1	5.1±0.7	26-79 C, 10-30Mo, 10-52Ti
	2-3.5	18±1	5.1±0.7	41-52 C, 8-14 Mo, 24-33 Ti

Figure 1. Thermomechanical processing schedule.

Figure. 2. Representative SEM micrographs of the: (a) partially-transformed sample with formation of polygonal ferrite (PF) and martensite (M), analysed area is outlined by dash line and also shown is the schematic position of the in-situ lift-out (INLO) samples used for APT and HRTEM study near interface, and (b) position of the INLO, TEM and APT samples (shown by the arrows) from the ferrite grain near the ferrite/martensite interface shown in (a).

Figure. 5. APT of the INLO samples after isothermal hold for 1200 s at 650 °C: (a) representative APT 2 at. % C+Ti concentration isosurface of the clusters, (b) solute concentration of the clusters as a function of the Guinier radius, (c) selected atom maps from the volume outlined in Fig. 5a, showing interfacial formation of clusters, and (d) selected atom map of the multi-layer cluster, the matrix atoms were suppressed with the maximum separation method with $d_{\max} = 0.75$ nm.

Figure 3

Figure. 3. Optical micrographs and the nano-hardness values as a function of volume fraction of ferrite, after 1200, 1700 and 2200 s of isothermal hold at 650 °C.

Figure 4

Figure. 4. TEM of the INLO sample after isothermal hold for 1200 s at 650 °C: (a) TEM micrograph and diffraction pattern (the inset) with a zone axis of $[111]_{\alpha}$ from ferrite grain near ferrite/martensite interface, and (b) HRTEM of a cluster in the ferrite matrix.

Figure 6

Figure 6. TEM (a-c) and APT (d) of the INLO samples after isothermal hold for 1700 s at 650 °C: (a) HRTEM image showing the interphase precipitation in ferrite near the ferrite/martensite interface, (b) bright field image and diffraction pattern from the nano-precipitate (the zone axes are $[0\bar{1}1]_{\alpha\text{Fe}} // [011]_{(\text{TiMo})\text{C}}$), (c) bright and dark TEM images of randomly distributed precipitates with the corresponding diffraction pattern shown in the inset, the zone axis of ferrite is $[111]_{\alpha}$ and the zone axis of carbide is $[\bar{1}10]_{\text{C}}$ and (d) C-Mo-Ti, 2 at.% of concentration isosurface of the nano-precipitates.

Figure 7

Figure. 7. TEM (a) and APT (b, c) of the samples after isothermal hold for 2200s at 650°C: (a) representative TEM image of interphase precipitation and precipitates formed along grain boundary, the latter are shown by the black arrows (the inset is the enlarged view of interphase precipitation), (b) C-Mo-Ti, 2 at. % concentration isosurface of the nano-particles and the selected box represents the area of interest, dashed lines show suggested interface lines, the matrix atoms were suppressed using the maximum separation method with $d_{\max} = 0.75$ nm, (c) solute concentration of the nano-particles as a function of the Guinier radius.

clusters

precipitates