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1 **Small-angle neutron scattering reveals the effect of Mo on interphase nano-precipitation**
2 **in Ti-Mo micro-alloyed steels**

3

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1 **Abstract**

2 Ti-containing micro-alloyed steels are often alloyed with molybdenum (Mo) to reduce nano-
3 precipitate coarsening, although the mechanism is still disputed. Using small angle neutron
4 scattering we characterised the precipitate composition and coarsening of Ti-alloyed and Ti-
5 Mo-alloyed steels. The results demonstrate ~25 at.% of Ti is substituted by Mo in the (Ti,
6 Mo)C precipitates, increasing both the precipitate volume percent and average size. Mo
7 alloying did not retard precipitation coarsening, but improved lattice misfit between
8 precipitate and matrix, contributing to better aging resistance of the Ti-Mo-alloyed steel. This
9 new understanding opens opportunities for designing aging-resistant micro-alloyed steels
10 with lean alloying elements.

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19 **Keywords:** Micro-alloyed steel, Interphase Precipitation, Small-Angle-Scattering.

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1 High-strength low-alloy steels strengthened through the interphase precipitation (IPP)
2 mechanism have seen a revival for automotive industry since the development of the
3 NANOHTEN steel which has tensile strength up to 780 MPa [1]. IPP is the phenomenon
4 that occurs upon the decomposition of austenite in steels containing strong carbide -forming
5 elements (such as Ti, Mo and V) and results in characteristic periodic planes of fine
6 precipitates [2, 3]. In low-carbon steel fine MC (M = Ti, Mo or V) IPP are encapsulated
7 within a soft ferritic matrix which is strengthened through the Orowan mechanism [4]
8 yielding a steel with high strength and formability [5].

9
10 However, these MC particles can coarsen during hot rolling or subsequent annealing heat
11 treatment, degrading the strength of the materials significantly. One possible solution
12 reported in the literature is the addition of molybdenum (Mo). Funakawa and Seto [6], and
13 later work conducted by others [7-10] found that steels with Mo additions showed that the
14 mechanical properties were retained longer during high-temperature ageing. These studies
15 were compared to the observed interphase precipitation in Ti-containing (~0.2wt%) and Ti-
16 Mo-containing (~0.1wt%Ti and ~0.2wt%Mo) low carbon steels with a fixed basic
17 composition ~0.04%C, 1.5%Mn, 0.2%Si in wt.%. It can be seen that in these studies, the
18 atomic ratio of Ti:C and (Ti+Mo):C were designed to be ~1:1. The most well-known
19 mechanism for this effect was reported by Jang et al. [8], who used first principles
20 calculations to propose that the Mo only participates during the early stages of precipitation
21 and becomes passive due to the energetic disadvantage during the subsequent growth and
22 coarsening stages. The coarsening of precipitates is mainly controlled by diffusion of Ti
23 atoms, therefore, the replacement of Ti by Mo reduces the Ti concentration in the ferrite
24 matrix, which decelerates the coarsening of (Ti, Mo)C precipitates [6, 8]. Moreover,
25 Funakawa *et al.* [6] observed that a decrease in Ti concentration from 0.2wt% to ~0.1wt%

1 without Mo additions in Ti-containing steel results in similar hardness of Ti-Mo-containing
2 one (~0.1wt%Ti and ~0.2wt%Mo). Jang *et al.*, [11] used CALPHAD and diffusion
3 simulations to show that the coarsening rate of TiC in Fe-Ti-C steels (fixed 0.04%C, wt%)
4 can be significantly retarded by decreasing the Ti/C ratio.

5

6 However, both the effect of Ti/C ratio and the Mo on the interphase precipitation have not
7 been well examined quantitatively, which leaves a question to the automotive industry
8 whether it is necessary to add Mo into Ti-containing steels. This is due to the widely used
9 techniques such as transmission electron microscopy (TEM) [12, 13] and atom probe
10 tomography (APT) [14-18] which have a limited capability to analyse statistically significant
11 numbers of precipitates. The size difference of precipitates in Ti and Ti-Mo steels presented in
12 the literature is so small (typically in the range of 1.6 nm to 10 nm [7-9]) that it is difficult to
13 statistically and accurately investigate the the role of Mo with TEM and APT.

14

15 The present study utilizes Small-Angle-Neutron-Scattering (SANS) to study the precipitation
16 behaviour of two micro-alloyed steels aged at 650°C for various times. One steel (Fe-
17 0.079Ti-0.051C-1.63Mn-0.19Si-0.036Al-0,014P-0.006S-0.007N, wt%) contains Ti with a
18 Ti:C atomic ratio of 0.4. The second steel (Fe-0.07Ti-0.2Mo-0.044C-1.58Mn-0.19Si-
19 0.039Al-0,013P-0.005S-0.0046N, wt%) contains Ti and Mo with a (Ti+Mo):C atomic ratio
20 of ~1. The detailed characterization was undertaken using SANS, through analysis of both
21 the nuclear and magnetic signals, giving quantitative insight into the evolution of the average
22 precipitate size, volume percent, and precipitate chemistry in bulk samples, which are key
23 information to uncover the precipitation kinetics and hardening behaviour. The data obtained
24 is averaged over billions of precipitates and provides new insights not available from TEM or
25 APT where only tens to hundreds of precipitates are typically measured.

1 The alloys were vacuum induction melted, casted and then forged at about 1250 °C followed
2 by air cooling. Pieces 30×10×5 mm³ were sectioned and heat treated (See Supplementary Fig.
3 S1a). Firstly, the specimens were austenitized in a salt bath at 1250 °C for 300 s to dissolve
4 pre-existing precipitates and water quenched. Secondly, the specimens were austenitized at
5 950 °C for 120 s (to control the austenite grain size) then transferred directly to a salt bath at
6 650 °C for periods ranging from 0 to 36 ks and water quenched. Prolonged long-term ageing
7 for a further 144 ks was performed separately. The austenitization temperature of 950°C and
8 duration of 120 s were selected in order to balance the compromise between the austenite
9 grain size, the minimisation of carbide precipitation in austenite. Interphase precipitates can
10 only form at the advancing austenite/ferrite boundary and therefore, the majority of the Ti, Mo
11 and C must have remained in solution during austenization. The precipitation-time
12 temperature diagram obtained by Wang et al. [10] shows that the start times of carbide
13 precipitation in Ti-Mo (0.1%Ti-0.2Mo%) micro-alloyed steel exceeds 150 s at 950°C.

14

15 SANS experiments were performed on the SANS2d beamline at the ISIS Pulsed Neutron
16 Source, UK [19]. A magnetic field of 1.5 T was applied to saturate the ferritic matrix which
17 allows the separation of the magnetic and nuclear scattering. Specimens with dimension of ~9
18 mm×~9 mm× ~1 mm were cut from the heat treated samples for the SANS measurements.
19 The neutron beam size was 8mm in diameter and the measurement time was set to 60min.
20 The sample to detector distance was 4m which gave scattering vector, q , covered the range of
21 0.004 to 0.3 Å⁻¹. To avoid collecting scattering signal from multi-Bragg diffraction, only
22 neutrons with wavelengths, λ , from 4.5 to 16.5 Å were selected for data analysis [20]. One-
23 dimensional nuclear and “nuclear + magnetic” scattering intensity plots, I (intensity) versus q
24 were obtained by partial azimuthal averaging in 30 sectors around the horizontal and vertical
25 axes of the transmitted beam respectively using the software Mantidplot [21].

1 The microstructures of polished and 2% Nital etched samples were examined using scanning
2 electron microscopy (SEM) via an FEI Quanta 650 FEG-SEM operated at a voltage of 20 kV.
3 Detailed microstructures of the (Ti,Mo)C precipitates were examined using a JEOL 2100
4 TEM. Thin foil specimens were mechanically polished to ~30 μm in thickness followed by
5 ion beam milling to electron transparency. The microhardness (Hv) of ferrite grains in heat
6 treated samples was measured using a microhardness tester with a load of 0.1 kgf. 20
7 measurements were conducted for each sample.

8
9 Fig.1a shows the mean value of Hv versus age time at 650 $^{\circ}\text{C}$ for both Ti and Ti-Mo
10 containing steels and the error-bar represents one standard deviation. The Ti-Mo containing
11 steels show slightly higher hardness and better ageing-resistance compared to the steel with
12 only Ti additions. As shown in Figs. 1b and 1c, the γ to α transformation in both steels occurs
13 rapidly and both reached ~90% completion in a similar duration of 60 s. This agrees with the
14 dilatometry results (Supplementary Fig. S1b). Figs. 1b, 1c, 1d and 1e also show that
15 decreasingly small regions of bainite formed during quenching with increasing isothermal
16 holding. Both SEM and dilatometry measurements reveal that Mo has a small effect on the γ
17 to α transformation. Bright field TEM images of the Ti and Ti-Mo containing samples
18 transformed at 650 $^{\circ}\text{C}$ for 36 ks are shown in Figs. 2(e) and (f). In both alloys, characteristic
19 periodic planes of nanoscale precipitates are observed, indicative of interphase precipitation.

20
21 Fig. 2 shows the one dimensional nuclear and magnetic SANS data in the form of Iq^2 versus
22 scattering vector (q) (left hand axis) for the selected isothermally transformed (60 s, 36 ks
23 and 180 ks) alloys. The results for the water quenched sample and the remaining isothermally
24 transformed (0.3ks, 3.6 ks and 18 ks) samples are shown in Supplementary Figs. S2 and S3.
25 The ratio of magnetic scattering ($I_{mag}(q)$) to nuclear scattering ($I_{nuc}(q)$) intensity, $R(q)$,

1 which is related to the precipitate composition, is shown on the left-hand axis. If all
2 precipitates have the same composition then the value of $R(q)$ would be constant. On the
3 other hand, $R(q)$ would vary if either there were more than one type of precipitate present of
4 differing size or the precipitate composition is size dependent [22]. Clearly, there were two
5 types of particles with significant difference in both size and composition formed in both
6 steels revealed by two different $R(q)$ values of ~ 3 and ~ 1 at low (0.004 to $\sim 0.01 \text{ \AA}^{-1}$) and
7 high (0.02 to $\sim 0.1 \text{ \AA}^{-1}$) q region respectively. A low number density of large ($> 500 \text{ nm}$),
8 cube-shaped TiN precipitates can be formed during casting process and could remain
9 undissolved during the experimental solution treatment [10]. These large TiN precipitates
10 only contribute to the Porod scattering at low q region $< 0.001 \text{ \AA}^{-1}$ and has negligible
11 influence on the scattering signal at q region $> 0.01 \text{ \AA}^{-1}$.

12

13 In the low q region, $R(q)$ increases due to the presence of large iron carbides and this is seen
14 to exist in the Ti-containing steels up to 180 ks. In the Ti-Mo containing steels, there is less
15 evidence for an increase in $R(q)$ at low q suggesting less iron carbide forms in this steel. The
16 scattering from large scale iron carbides also reveals itself in the form of a Porod Law slope
17 of approximately q^{-2} on the plot of Iq^2 versus q at the low q region. These large iron
18 carbides (Figs. 1b and 1c), make only a small contribution to the nuclear scattering signal
19 (because of their small contrast factor) but a significant contribution to the magnetic
20 scattering signal. This causes to a marked difference between these two signals at low q as
21 revealed by an increase in the $R(q)$ value. In the samples isothermally held for 180 ks, the
22 matrix phase transformation was completed so iron carbides did not form following
23 quenching resulting in a smaller difference between the nuclear and magnetic signals across
24 the entire range of q . At high q region, it is the fine IPP that contribute to the nuclear and
25 magnetic signals and so $R(q)$ plateaus from which the chemical composition of the IPP can

1 be estimated. A low number density of large (> 500 nm), cube-shaped TiN precipitates can be
2 formed during casting process and could remain undissolved during the experimental solution
3 treatment [1]. These large TiN precipitates only contribute to the Porod scattering at low q
4 region $< 0.001 \text{ \AA}^{-1}$ and has negligible influence on the scattering signal at q region $> 0.01 \text{ \AA}^{-1}$.

5

6 To isolate the scattering signal only from nano-sized TiC or (Ti, Mo)C precipitates the Porod
7 Law region at low q and the incoherent background in both the nuclear and magnetic SANS
8 signals were subtracted. Fig. 3 shows the mean values of $R(q)$, which were calculated by
9 taking the average of $R(q)$ values in the q range from ~ 0.0194 to $\sim 0.0775 \text{ \AA}^{-1}$ (for samples
10 aged for 60s to 3.6 ks) and ~ 0.0097 to $\sim 0.0664 \text{ \AA}^{-1}$ (for samples aged from 18 ks to 180 ks).
11 The error in Fig. 3 is given as one standard deviation. The results show that the mean values
12 of $R(q)$ for isothermally transformed Ti and Ti-Mo alloys were ~ 0.70 and ~ 0.95 respectively.
13 The ageing time did not change the mean values of $R(q)$ significantly. The theoretical $R(q)$
14 values of ~ 0.64 and ~ 1 represent the average chemical composition of the precipitates in Ti
15 and Ti-Mo containing steels are TiC and $\text{Ti}_{0.75}\text{Mo}_{0.25}\text{C}$ respectively [21], as shown by the red
16 and blue horizontal lines in Fig. 3. The substitution of Ti with Mo in the precipitates is in
17 excellent agreement with results obtained from APT [18, 23-24] and extraction [25] in similar
18 micro-alloyed steels (e.g. 0.05% to 0.2% Ti-0.20%Mo-0.045% C, wt%).

19

20 The volume percent (f_v) of TiC and (Ti, Mo)C were calculated from the invariant, Q , of the
21 magnetic SANS signal using the equation $Q = \int_0^\infty I(q)q^2 dq = 2\pi^2 (\rho_p - \rho_m)^2 f_v(1-f_v)$ [21, 26].
22 where ρ_p and ρ_m are the magnetic scattering length densities of precipitate and matrix. The
23 use of magnetic SANS signal ensures that the volume percent calculation is independent of
24 the chemical composition of the precipitates. Fig. 4a shows that the volume percent of TiC in
25 Ti steels and (Ti, Mo)C in TiMo steels were $\sim 0.10\%$ and $\sim 0.13\%$ respectively and invariant

1 with isothermal holding. The equilibrium volume percent of 0.156 vol% (TiC phase fraction)
2 and 0.157 vol% ((Ti, Mo)C phase fraction) at 650 °C calculated using Thermo-Calc and the
3 TCFE7 database. In the Ti-Mo steel, the equilibrium atomic ratio of Ti to Mo in (Ti, Mo)C
4 precipitates is predicted to be ~9:1, which indicates the Mo is not strong stabiliser for MC-
5 type carbide.

6

7 Figs. 4b, 4c and 4d show the Kratky radius (R_{max}), Guinier radius (R) and thickness (T)
8 (disk morphology [24]) of particles obtained from both nuclear and magnetic SANS
9 scattering signs. The Kratky radius is calculated by $R_{max} = \sqrt{3}/q_{max}$ (the “pseudo-Guinier
10 radius”), where the q_{max} determined from the the Kratky plot (Iq^2 vs q) [27]. Alternatively, a
11 radius of gyration, R_{g1} , is extracted from the Guinier plot (which takes the form of $\ln(I)$ vs q^2)
12 using a self-consistent method with $1 < qR_{g1} < 2$. Considering a distribution of monodisperse
13 thin discs of thickness, T , and radius, R , the relationship between T , R and R_{g1} is given by
14 $R_{g1}^2 = T^2/12 + R^2/2$ [28]. A second Guinier plot of $\ln[q^2(I)]$ vs q^2 is known to give a radius of
15 gyration, R_{g2} , that is related to the disc thickness, $R_{g2} = (T^2/12)^{0.5}$. Fig. 4b shows that the
16 average size of the TiC and (Ti, Mo)C interphase precipitates increased from ~6.5nm after
17 60s to ~10nm after 3.6ks, but exhibit minimal growth during the further ageing up to 180ks at
18 650°C. The average Guiner radius (Fig. 4c) of disk precipitates has been found ~2nm smaller
19 than Kratky radius, but followed very similar tendency as kratkey radius. Fig. 4d indicated
20 that the average Gunier thicknesses of TiC and (Ti,Mo)C were ~5.5nm and ~6.5nm
21 respectively and both exhibit insignificant evolution (<1.5nm) during isothermal ageing.
22 Hence, the hypothesis that the Mo can retard the growth and coarsening of (Ti,Mo)C
23 interphase precipitation is not supported by our results, which show the average precipitate
24 size in aged Ti-containing steels were even slightly smaller than in aged Ti-Mo-containing
25 steels.

1
2 The precipitates coarsening rates in both alloys were extremely low. In Ti-containing steels it
3 is known that a low Ti/C ratio (0.4) causes the concentration of Ti at the precipitate-ferrite
4 interface to become small and therefore the diffusion gradients which drive coarsening
5 become shallow and slow [11]. While in Ti-Mo added steels, although the Ti+Mo/C=1 and
6 Mo incorporated into the precipitates at nucleation, the subsequent growth of precipitates is
7 controlled by the diffusion of Ti atoms rather than Mo. We can conclude that the addition of
8 Mo slightly improved the ageing-resistance of the steels (Fig. 1a) is due to (Ti,Mo)C having a
9 reduced misfit strain between the carbide and ferrite matrix than TiC [8, 29], rather than Mo
10 retarding coarsening of the precipitates. Seol et al. [30] and Wang et al. [31-32] indicated that
11 Mo can segregate at precipitate's outer to form a core-shell structure with Ti-rich core and
12 Mo-rich shell. Mo layer inhibiting the diffusion of Ti, and V from the matrix into the
13 precipitates, which impedes particle coarsening. Whether this mechanism exists in Ti-Mo
14 added steels needs future investigation. The current work only shows the Mo did not retard
15 the global growth and coarsening of (Ti,Mo)C in 0.07%Ti-0.2%Mo (wt%) micro-alloyed
16 steels.

17
18 The addition of Mo also slightly increased the hardness of the steels (Fig. 1a). This is due to
19 the higher volume percent of interphase precipitates rather than a decreased average size of
20 precipitate. Approximately 25 at.% Mo co-precipitates as (Mo,Ti)C at the early stage of
21 precipitation and this increased the volume percent of these precipitates from ~0.1% to
22 ~0.13%. This yields ~7% improvement in the precipitation strengthening effect based on the
23 Ashby-Orowan equation $\Delta\sigma_{ppt} = \frac{0.538Gb f_v^{0.5}}{2R} \ln\left(\frac{R}{b}\right)$ [9, 33, 34]. Where, $\Delta\sigma_{ppt}$ is the increase in
24 yield strength, G is the shear modulus, b is the Burgers vector, f_v is the carbide volume
25 fraction and R is the mean carbide radius.

1

2 In summary, our SANS results (nuclear and magnetic scattering signals) reveal Mo does not
3 play a role in retarding nano-precipitate coarsening, which is in contrary to existing literature.
4 Instead, our results show that approximately 25 at.% Mo replaced Ti in the (Mo,Ti)C
5 precipitates, increasing both the precipitate volume percent and average size, and changing
6 the lattice spacing, altering the coherency. Ti-Mo-alloyed steel has higher volume fraction of
7 nano-precipitates than Ti-alloyed steel hence higher hardness. The better ageing-resistance of
8 the Ti-Mo steels than Ti only steels is mainly due to the decrease in misfit between the
9 carbide and matrix leading to coherency being maintained at longer aging times in Ti-Mo
10 alloyed steel. This new understanding opens opportunities for design of ageing-resistant
11 micro-alloyed steels with significantly less amount of Mo.

12

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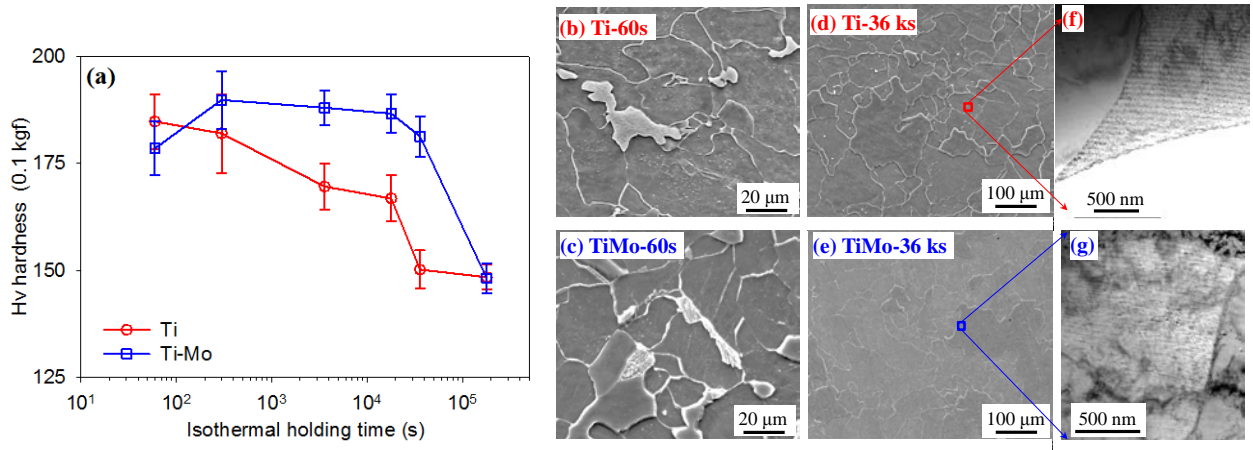
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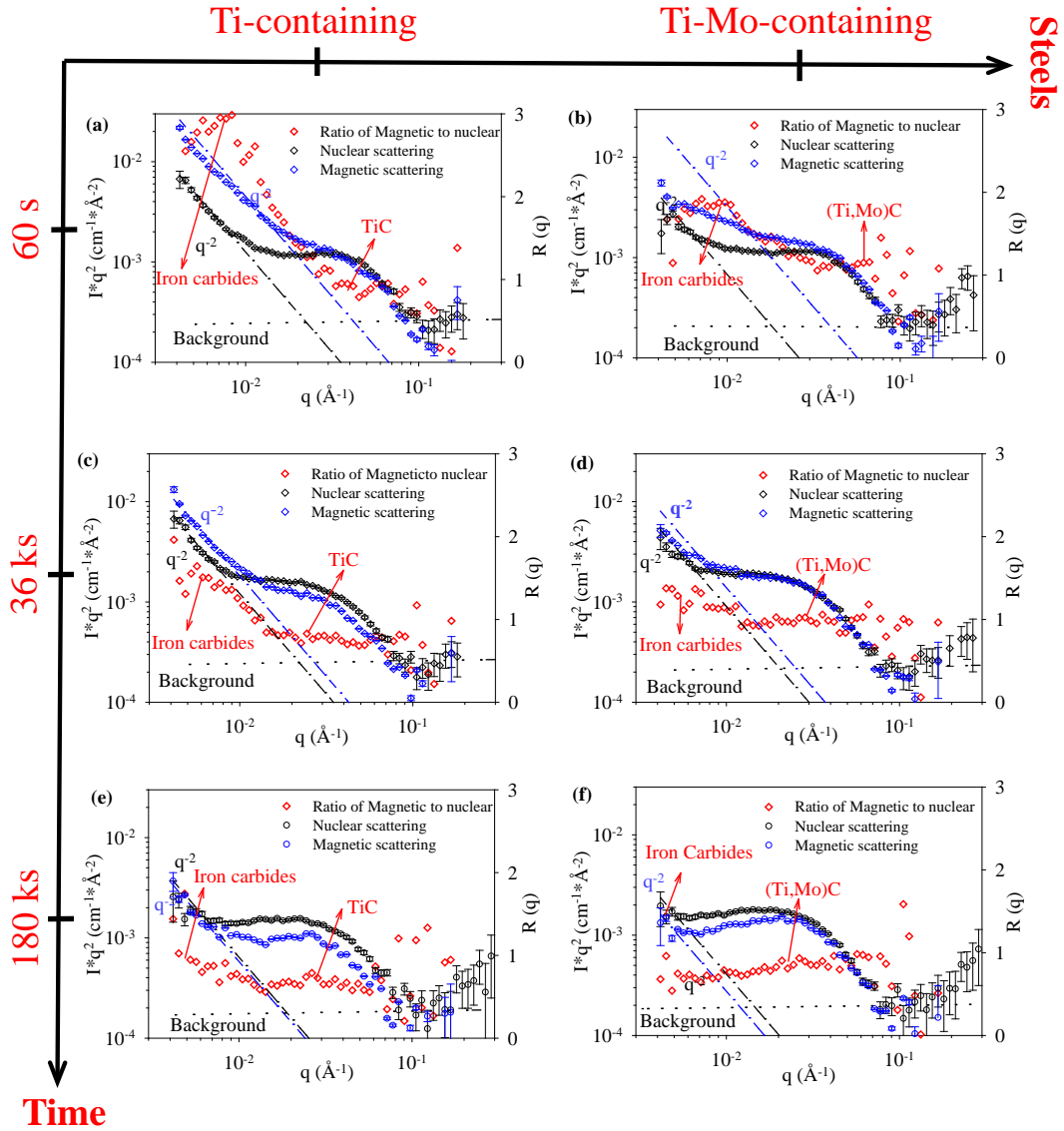
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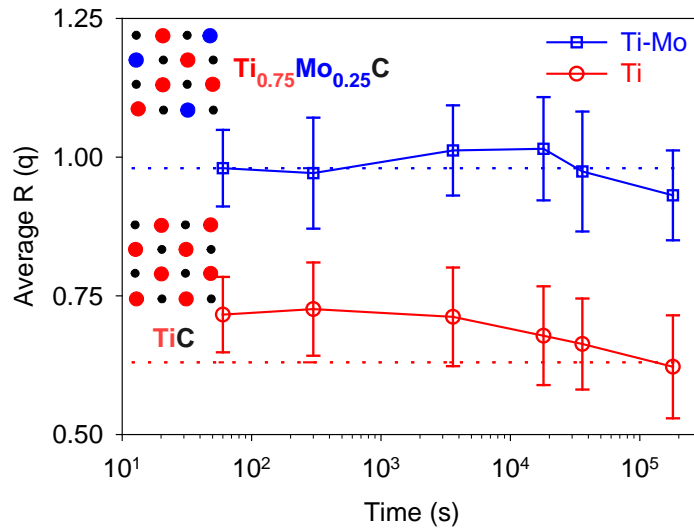
7 Fig. 1. (a) Effect of isothermal holding time, t , on measured microhardness, H_v , of the Ti and
8 Ti-Mo steels held at 650 °C. Error bars in H_v correspond to one standard deviation from the
9 mean. (b) to (e) SEM images of the Ti (b and c) and TiMo (d and e) samples isothermally
10 transformed for 60 s and 36 ks. (f) and (g) Bright field TEM images of the Ti and TiMo steels
11 respectively after ageing for 36 ks showing interphase precipitation.

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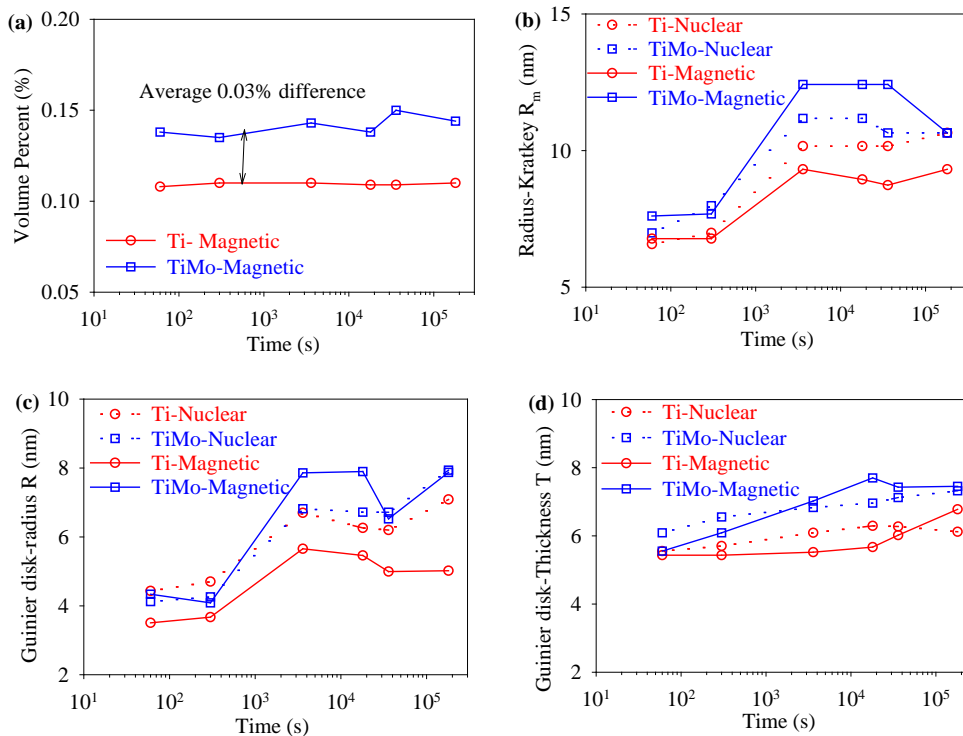
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2 Fig. 2. One-dimensional nuclear and magnetic SANS patterns of Iq^2 (left hand axis) and $R(q)$
 3 (right hand) axis versus scattering vector, q , obtained from the (a, c and e) Ti and (b, d, and f)
 4 TiMo samples isothermally transformed at 650 °C for (a and b) 60 s, (c and f) 36 ks, (e and f)
 5 180 ks respectively.
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Fig. 3. Plot of the mean value of $R(q)$ as a function of scattering vector, q , calculated from the scattering curves in Fig. 2. $R(q)$ is the ratio of magnetic to nuclear scattering intensity. Theoretical values for TiC and for $Ti_{0.75}Mo_{0.25}C$ are shown by the horizontal lines.



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Fig. 4. Graphs to show the effect of isothermal holding time, t on carbide particle volume fraction and particle dimensions in Ti and TiMo alloys aged at 650 °C. (a) Particle volume percent calculated from analysis of the invariant, Q , of the magnetic SANS data. Particle dimensions obtained from (b) Kratky radius, R_{max} , assuming spherical-shaped particles and (c and d) Guinier analysis assuming disk-shaped particles. (c) shows the disk radius, R , versus ageing time, t , and (d) shows disk thickness, T , versus time, t .