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# $\omega$ phase strengthened 1.2GPa metastable $\beta$ titanium alloy with high ductility

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## Abstract

This paper provides a novel approach for exploiting  $\omega$  phase strengthening in a metastable  $\beta$  titanium alloy whilst retaining high ductility. The addition of 1wt% Fe into our previously designed Ti-7Mo-3Cr alloy can efficiently control the growth of  $\omega$  phase following air-cooling, resulting in a ultrahigh yield strength ( $R_{p0.2}$  of 1210 MPa) with large ductility ( $\epsilon_f$  of 0.15). Transmission electron microscopy of the annealed Ti-7Mo-3Cr-1Fe alloy revealed that the air-cooled Ti-7Mo-3Cr-1Fe exhibited extensive  $\omega$  precipitates 1-9nm in size, which were larger than that of its water-quenched counterpart (0.5-4 nm). EBSD and TEM results of deformed alloys showed that the growth of  $\omega$  phase in the air-cooled Ti-7Mo-3Cr-1Fe alloy modified the deformation mechanism from  $\{332\}$  twinning and dislocation slip, in the water-quenched alloy, to localized dislocation plasticity in  $\omega$ -void channels.

**Keywords:** Metastable beta titanium alloy;  $\omega$  phase; Strengthening; Yield strength

Metastable  $\beta$  titanium alloys with twinning and/or martensite transformation induced plasticity (TWIP and/or TRIP) have been exploited as biomedical and structural materials owing to their low elastic modulus, low biotoxicity, high strength and large uniform elongation [1-5]. Recently, promising mechanical properties (e.g. high ductility and high hardening rate) have been achieved in metastable  $\beta$  titanium alloys, such as Ti-12Mo[6], Ti-9Mo-6W[7, 8], Ti-10Cr[9] and Ti-7Mo-3Cr[10], with TRIP and/or TWIP effects (hereafter all the compositions are in mass %). However, the low yield strength (200 -500MPa) of these metastable  $\beta$  titanium alloys with TRIP and/or TWIP has been their “Achilles’s heel”, hindering their technological application. Although some metastable titanium alloys with high yield strength have been observed, such as gum metal [11], these alloys generally show a low work hardening rate and poor uniform elongation.

Depending on the chemical compositions and cooling rate, after solid solution heat treatment in the high temperature  $\beta$  phase region[3], the martensite transformation and secondary phase precipitation (e.g. alpha phase and  $\omega$  phase) can be activated separately or simultaneously, or the single-phase bcc structure retained. These different microstructures strongly influence the deformation mechanisms that occur upon loading. In the recent past, the influence of the  $\omega$  phase on the strengthening effect in metastable  $\beta$  titanium alloys has been the subject of considerable interest. For example, Liu et al. developed a series of spinal-support metastable  $\beta$  titanium alloys with changeable modulus via deformation induced  $\omega$  transformation [9, 12]. Moreover, Sun et al. [13] proposed that low-temperature flash aging of a Ti-12Mo alloy can effectively enhance the yield strength while preserving substantial elongation-to-failure, where the  $\omega$  embrittlement effect was successfully avoided by the accurate temperature and time control for suppressing of  $\omega$  growth and elemental partitioning. Lai et al.[14] also studied the effect  $\omega$  phase formation on the deformation mechanism of a metastable Ti-Nb-Ta-Zr alloy, and they reported that the formation of  $\omega$  phase enhanced the yield strength and shifted the deformation mechanisms from  $\{332\}$  twinning and martensite transformation, which were the main deformation mechanisms in the  $\omega$ -free counterpart, to localized dislocation plasticity in  $\omega$ -devoid channels.

In the current work, considering the formation of  $\omega$  phase is also dependent on  $\beta$  phase stability (i.e. the amount of  $\beta$  stabilizers present) and cooling rate, we proposed a new route to exploit the  $\omega$  phase strengthening effect while preserving high ductility. This led to a new metastable  $\beta$  titanium alloy, Ti-7Mo-3Cr-1Fe, optimised through  $\beta$  phase stability and cooling rate control. The Ti-7Mo-3Cr-1Fe alloy was developed based on our previously developed Ti-7Mo-3Cr alloy that had an initial deformation mechanisms of  $\{332\}$  and as  $\{112\}$  twinning and dislocation slip in water-quenched condition[10].

The Ti-7Mo-3Cr and Ti-7Mo-3Cr-1Fe alloys were arc melted from pure elements in a high-purity argon atmosphere. The ingots were homogenized at 1200°C for 3h under flowing argon and water quenched. It was then cold rolled from 6 to 2.4mm thickness and annealed at 850°C for 20 min under flowing argon, followed by water quenching or air cooling. X-ray diffraction was performed on a Siemens D5000 diffractometer fitted with a  $\text{CuK}\alpha$  radiation source, at a scan rate of 0.1°/min and a step size of 0.01°. Tensile samples with a gauge dimension of 3mm×12.5mm×1.5mm were cut along the rolling direction and polished from the plate after heat treatment. Tensile tests were performed on a Zwick/Roell Z050 with laser extensometer at a strain rate of  $4.0 \times 10^{-4} \text{ s}^{-1}$ . The annealed and tensile tested plate samples with 2.4mm

thickness were ground to  $\sim 100\mu\text{m}$  in thickness and punched to 3mm-diameter discs. Samples for EBSD imaging and TEM analysis were produced by twin-jet electropolished with a solution of 5% perchloric acid, 35% 2-butyoxyethanol and 60% methanol at  $-35^\circ\text{C}$ . In order to obtain a relatively flat region at magnification of  $500\times$  for EBSD mapping, the samples were electropolished for a short time (30-40 seconds) to remove the residual deformation surface layer induced by mechanical polishing. EBSD was performed using a field emission gun scanning electron microscope (FEI Inspect F50 FEG SEM) operated at 20kV with a step size of  $1\mu\text{m}$  for grain size analysis and  $0.15\mu\text{m}$  for twinning and phase analysis. A Tecnai T20 transmission electron microscope (TEM) operated at 200 kV was used to characterize the annealed and deformed samples. A double aberration corrected microscope JEM-Z3100F-R005 operated at 300 kV was also used to characterize the air-cooled Ti-7Mo-3Cr-1Fe alloy. A high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (JEOL 2100F) coupled with energy-dispersive spectroscopy (Oxford Instruments EDX detector) was used to investigate possible elemental partitioning with  $0.7\text{nm}$  spot size and  $15^\circ$  tilt toward EDX detector.

After annealing at  $850^\circ\text{C}$  for 20 min, a fully recrystallized microstructure with a broad grain size distribution (maximum  $205\mu\text{m}$ , minimum  $7\mu\text{m}$ ) was observed for air-cooled Ti-7Mo-3Cr-1Fe alloy, Supplementary Figure 1, which corresponds well with the grain size distribution of Ti-7Mo-3Cr alloy[10]. The EBSD map indicated a single phase microstructure free from annealing twins and second phases for both air-cooled and water-quenched alloys.

Supplementary Figure 2 shows the XRD profiles of Ti-7Mo-3Cr-1Fe and Ti-7Mo-3Cr alloys subjected to air cooling or water quenching after annealing at  $850^\circ\text{C}$  for 20 mins. For the water-quenched Ti-7Mo-3Cr-1Fe alloy, only peaks corresponding to  $\beta$  phase were identified, while both  $\beta$  phase and  $\omega$  phase were observed in the air-cooled Ti-7Mo-3Cr-1Fe alloy, suggesting that the slower cooling rate induced more  $\omega$  phase formation. For Ti-7Mo-3Cr alloy,  $\beta$  and  $\omega$  phases were observed in the both air-cooled and water-quenched alloys. This suggests that both cooling conditions and the addition of 1% Fe can tailor the formation of  $\omega$  phase.

Fig.1a shows a dark-field (DF) micrograph of the air-cooled alloy recorded using  $(\bar{1}010)_{\omega_1}$ , which shows the extensive formation of  $\omega$  precipitates with a size in range of 1 to 9nm. The inset in Fig.1a presents the selected-area electron diffraction (SAED) pattern recorded along  $[011]_{\beta}$  zone axis. Besides the distinct reflections from the  $\beta$  matrix, the pronounced diffraction intensity maxima at  $1/3$  and  $2/3 \{011\}_{\beta}$  positions provide further evidence of the extensive

formation of  $\omega$  precipitates. The DF image of the water-quenched alloy in Fig.1b also shows the extensive formation of  $\omega$  precipitates, but the size of these precipitates was much smaller, 0.5 to 4nm, than that of air-cooled alloy. This was in agreement with the SAED pattern in the inset of Fig.1b, where the diffraction intensity maxima corresponding to  $\omega$  phase were much weaker than that of  $\omega$  phase in air-cooled alloy, suggesting that of amount of  $\omega$  phase is smaller than that of air-cooled alloy. The DF micrographs of air-cooled and water-quenched Ti-7Mo-3Cr alloys are shown in Figs.1c and d. Insets in Figs.1c and d are their corresponding SAED patterns. In comparison with air-cooled and water-quenched Ti-7Mo-3Cr-1Fe alloys, the corresponding air-cooled and water-quenched Ti-7Mo-3Cr alloys exhibit larger  $\omega$  precipitates, suggesting the addition of 1% Fe can tailor the  $\omega$  precipitates size, instead of rapid growth of  $\omega$  precipitates observed in air-cooled Ti-7Mo-3Cr alloy.

The  $\omega$  phase in the air-cooled alloy was further characterized using HRTEM. Fig.2a shows the HRTEM image recorded along the  $[\bar{1}10]_{\beta}$  zone axis, confirming the extensive formation of  $\omega$  phase. Fig.2b shows the fast Fourier transform (FFT) pattern where both the  $\beta$ -associated and  $\omega$ -associated spots are observed, which are consistent with the SAED pattern in Fig.1b. The inverse FFT image obtained by masking the  $\omega$  spots (blue circles in Fig.2b) is shown in Fig.2c. Two  $\omega$  variants are observed in the inverse FFT image, termed as  $\omega_1$  and  $\omega_2$ . The size of  $\omega_1$  in the major and minor axis is 4.8nm and 4.1nm, respectively, while the size of  $\omega_2$  in the major and minor axis is 4.9nm and 3.8nm, which are consistent with Fig. 1a.

The STEM-HAADF image and corresponding EDX composition maps (Supplementary Figure 3) show no evidence of composition variation correlated with  $\omega$  in the air-cooled Ti-7Mo-3Cr-1Fe alloy. The EDX maps show a uniform K-shell X-ray intensity for Ti, Mo, Cr and Fe over the entire mapping area, which is consistent with the EDX composition maps of Ti-Nb alloy[15].

Fig.3 presents the tensile stress-strain curves of the Ti-7Mo-3Cr-1Fe alloy subjected to air-cooling or water-quenching after annealing at 850°C for 20 min. For comparison, the stress-strain curves of air-cooled and water-quenched Ti-7Mo-3Cr alloys are also shown. The water-quenched Ti-7Mo-3Cr-1Fe exhibits a yield strength,  $R_{p0.2}$  of 648MPa, ultimate tensile strength of 924MPa and strain to fracture of 0.25. Interestingly, air cooling substantially enhanced the yield strength ( $R_{p0.2}$  of 1210MPa) and ultimate tensile strength (1245MPa) of the Ti-7Mo-3Cr-1Fe alloy, while retaining a large strain to fracture of 0.15. Although the Ti-7Mo-3Cr alloy exhibited high strength and high ductility in the water-quenched condition[10], the air-cooled Ti-7Mo-3Cr alloy fractured without observable plasticity.

Supplementary Figure 4a shows that neither martensite transformation nor twinning was observed in the air-cooled alloy at 3% tensile strain, although several band structures (marked by white arrows in Supplementary Figure 4a) were occasionally observed within some grains. For the water-quenched alloy (Supplementary Figure 4b), extensive  $\{332\}\langle 113\rangle$  twins were observed, especially in relative large grains, where 2 or 3 twin variants activated. This corresponded well with our previous work in Ti-7Mo-3Cr alloy where the activation of twins was governed by both Schmid factor and grain size[10].

In order to determine the initial deformation mechanism, TEM analysis was conducted on the air-cooled Ti-7Mo-3Cr-1Fe after 3% total strain (Fig.4). The BF image in Fig.4a shows that a high density of nano-band structures are observed. According to the  $\beta[110]$  zone axis SAED pattern in Fig.4b, only  $\beta$  phase and  $\omega$  phase are observed, indicating that these nano-band structures are not deformation twins or stress induced martensite. In order to identify these nano-band structures, DF images (Figs.4c and d) were obtained using  $\omega$  reflections marked by  $\omega_1$  and  $\omega_2$  in Fig.4b. The DF images (Figs.4c and d) show that these nano-band structures are poor in  $\omega$  phase, suggesting that these nano-band structures are  $\omega$ -void dislocation channels, as reported in a furnace-cooled Ti-Nb alloy[14].

It is well accepted that the isothermal  $\omega$  phase can cause embrittlement in metastable  $\beta$  titanium alloys. The growth of  $\omega$  phase leads a rapid increase of local elastic strains around the interface between  $\omega$  phase and  $\beta$  matrix, which act as obstacles for gliding dislocations[13]. The gliding dislocations are believed to cut through  $\omega$  phase on the  $\{112\}_\beta//\{\bar{1}100\}_\omega$  planes[14]. The growth of  $\omega$  phase increases the critical resolved shear stress for dislocation motion, resulting in a high yield strength and loss of ductility (embrittlement). In order to exploit the strengthening effect of  $\omega$  phase without significant loss of ductility, restricting the rapid  $\omega$  phase growth is necessary.

The growth of  $\omega$  phase in  $\beta$  titanium alloys is dependent on  $\beta$  stability (i.e. amount of  $\beta$  stabilizers) and cooling rate [1, 4, 14]. According to experimental knowledge and simulation work[1], Fe is one of the strongest  $\beta$  stabilizers among transition metals. The addition of Fe can greatly decreases the formation energy of  $\beta$  phase and meanwhile, Fe only has very limited effect on the formation energy of  $\omega$  phase, so Fe is also one of the most efficient elements suppressing  $\omega$  phase formation among the transition metals [1]. In the water-quenched Ti-Fe-Mo alloy [16, 17], very limited incommensurate  $\omega$  phase (1nm domains) was observed. The different mechanical behaviour between the air-cooled Ti-7Mo-3Cr and Ti-7Mo-3Cr-1Fe

alloys in Fig.3 and microstructural analysis in Figs.1 and 2 confirmed that the addition of 1wt% Fe successfully tailored the  $\omega$  precipitates size in the air-cooled Ti-7Mo-3Cr-1Fe alloy, leading to a superior combination of high strength and high ductility.

Mantri et al. reported that, after annealing at 475 °C for 48h, the partitioning of Mo induced by the precipitation of  $\omega$  phase in Ti-12Mo significantly stabilized the  $\beta$  matrix, resulting in a change of deformation mechanism from TWIP and TRIP to dislocation slip[18]. In this work, the change in the deformation mechanism in the air-cooled Ti-7Mo-3Cr-1Fe alloy was attributed to the growth of  $\omega$  phase that acts as a strong barrier for  $\{1\bar{1}0\}_\beta\langle 110\rangle_\beta$  atomic movements[14]. In metastable  $\beta$  titanium alloys, the shuffling of  $\{1\bar{1}0\}_\beta$  planes along the  $\langle 110\rangle_\beta$  direction is involved in the martensite transformation and twinning [14, 19]. In order to determine the effect of  $\omega$  phase on the suppression of martensite transformation and twinning, Lai et al. calculated the shear modulus along  $\{11\bar{2}0\}_\omega$  as this is parallel to  $\{1\bar{1}0\}_\beta$  [14]. The shear modulus along  $\{11\bar{2}0\}_\omega$  was calculated to be 39.55GPa, which was much larger than that of  $\{1\bar{1}0\}_\beta$ , <18GPa[14]. Therefore, it was the formation of a high density of larger  $\omega$  precipitates in air-cooled Ti-7Mo-3Cr-1Fe alloy that acted as strong local barriers to  $\{1\bar{1}0\}_\beta\langle 110\rangle_\beta$  atomic movements, which completely suppressed  $\{332\}\langle 113\rangle$  twinning. As deformation twinning was completely suppressed in the air-cooled Ti-7Mo-3Cr-1Fe alloy, the plastic deformation of this alloy relied on localized dislocation slip in the nano-sized  $\omega$ -devoid dislocation channels (Fig.4). The formation of the  $\omega$ -devoid dislocation channels is attributed to the gliding of dislocations on the  $\{112\}_\beta$  slip plane cutting through  $\omega$  precipitates via the prismatic slip plane  $\{\bar{1}100\}_\omega$  of the  $\omega$  phase, which is parallel to the  $\{112\}_\beta$  slip plane, and so promoted transformation of  $\omega$  to  $\beta$  [20].

In summary, we report a new route to exploit the  $\omega$  phase strengthening to obtain a superior combination of strength and ductility in a Ti-7Mo-3Cr-1Fe beta titanium alloy. The addition of 1wt% Fe in Ti-7Mo-3Cr alloy efficiently controlled the rapid growth of  $\omega$  phase in the air-cooled condition, leading to an ultra-high yielding strength ( $R_{p0.2}$  of 1210MPa) and large strain to failure (15%). We believe that much more substantial improvements can be achieved by further composition and cooling rate optimization.

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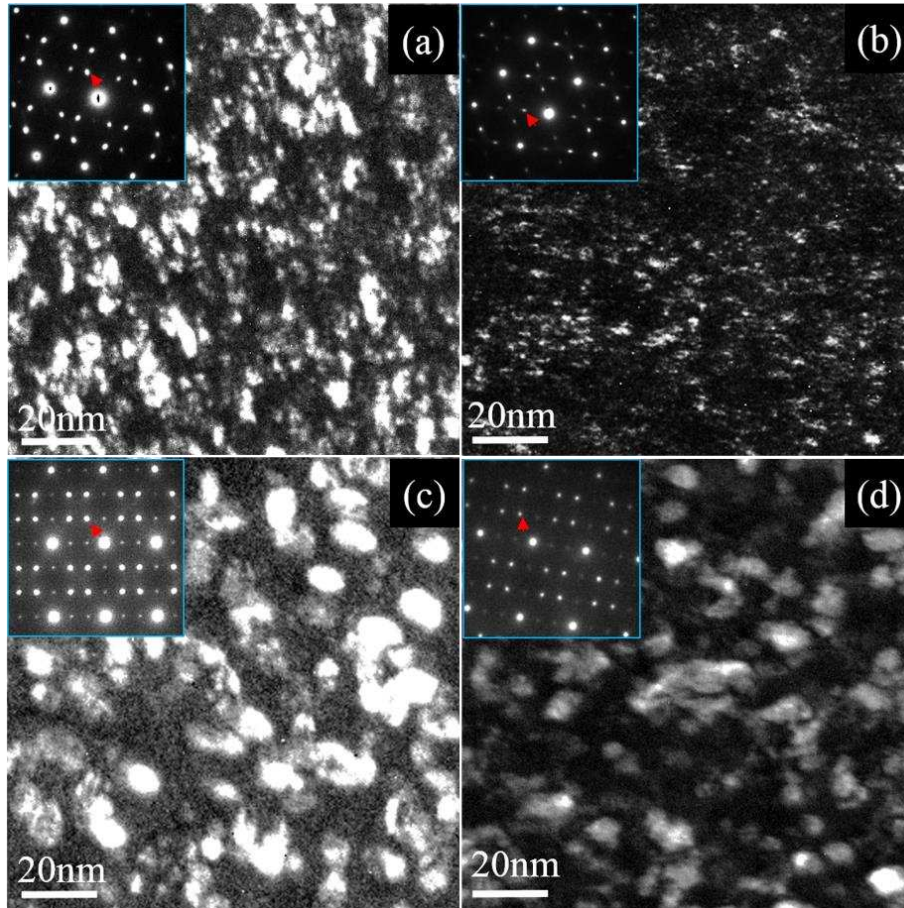


Fig. 1. TEM analysis of the annealed Ti-7Mo-3Cr-1Fe and Ti-7Mo-3Cr alloys subjected to air cooling or water quenching. (a) and (b) DF micrographs of Ti-7Mo-3Cr-1Fe alloy subjected to air cooling and water quenching respectively; (c) and (d) DF micrographs of Ti-7Mo-3Cr alloy subjected to air cooling and water quenching respectively. DF images were recorded using  $(\bar{1}010)_{\omega_1}$ , marked by red arrow in the SAED patterns (Insets). SAED patterns were recorded with beam//[011] $_{\beta}$ .

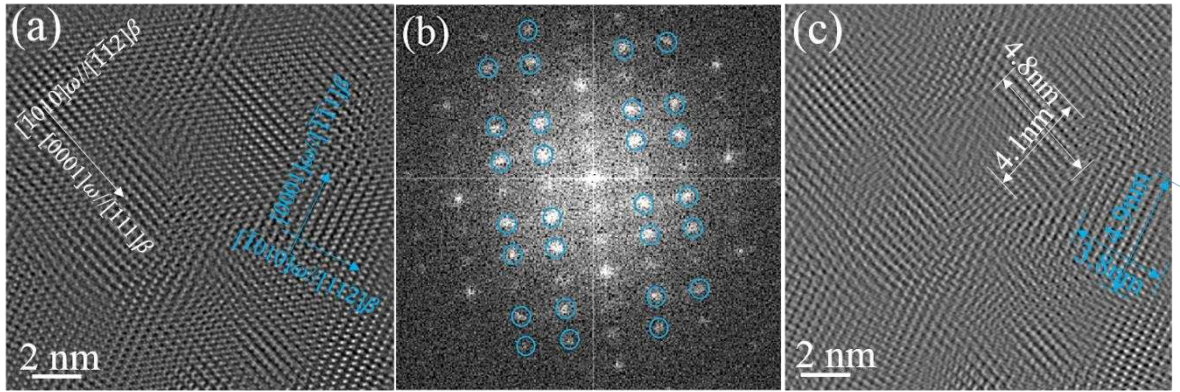


Fig.2.HRTEM study of the annealed Ti-7Mo-3Cr-1Fe alloy subjected to air cooling. (a) HRTEM image recorded along the  $[\bar{1}10]_{\beta}$  zone axis,(b) corresponding FFT pattern, (c) inverse FFT image by masking the  $\omega$  spots (blue circles) in (b).

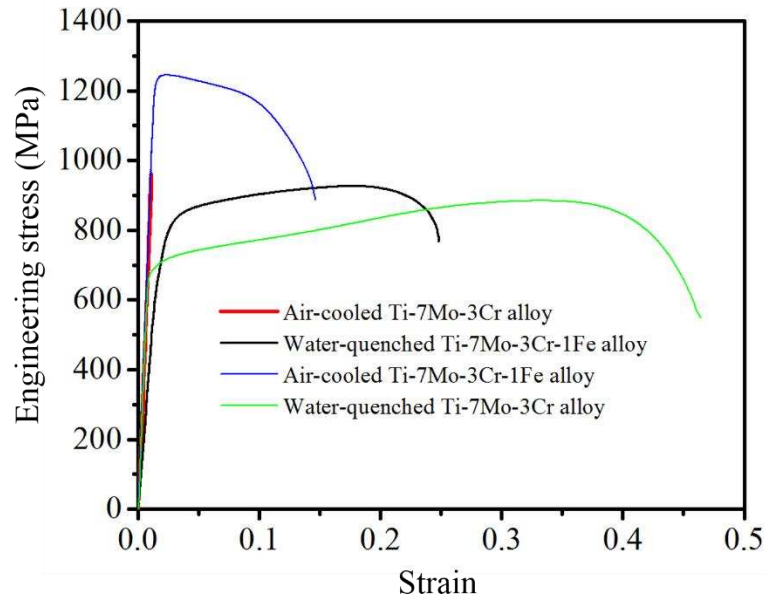


Fig.3. Tensile engineering stress-strain tensile curves of Ti-7Mo-3Cr and Ti-7Mo-3Cr-1Fe alloys subjected to air cooling or water quenching after annealing.

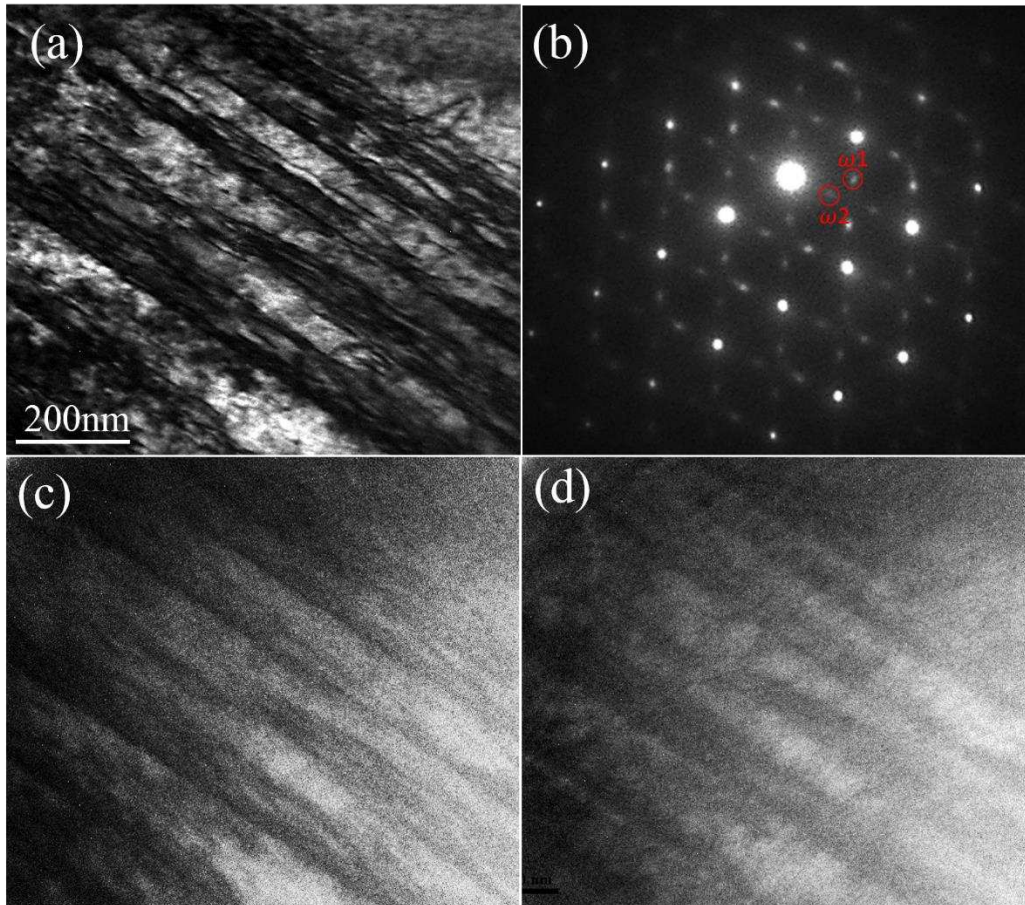


Fig.4. TEM analysis of the tensile-tested air-cooled Ti-7Mo-3Cr-1Fe alloy after 3% total strain. (a) BF image and its indexed  $\beta[110]$  zone axis SAED pattern (b). (c) and (d) corresponding DF images acquired using  $\omega$  reflections marked by  $\omega_1$ (c) and  $\omega_2$  (d) in (b).