A Nano-scale Instability in the β Phase of Dilute Ti-Mo Alloys

Yufeng Zheng¹, Dipankar Banerjee² and Hamish L. Fraser^{1,*}

¹Center for the Accelerated Maturation of Materials and Department of Materials Science and Engineering, The Ohio State University, 1305 Kinnear Road, Columbus, OH 43212, USA.

²Department of Materials Engineering, Indian Institute of Science, C V Raman Ave, Bengaluru, Karnataka 560012, India

* Corresponding author: fraser.3@osu.edu, CEMAS, The Ohio State University, 1305 Kinnear Rd., Suite 100, Columbus, OH 43212-1177, USA

Abstract

A nano-scale instability in the β phase resulting in the formation of the disordered orthorhombic O' phase has been discovered in a fairly dilute binary Ti-Mo alloy, using selected area electron diffraction and high resolution scanning transmission electron microscopy. The O' phase is formed in the alloy when the Mo content exceeds a critical value. The instability occurs in β -solutionized samples that have been quenched to room temperature and is found to co-exist with athermal ω phase. Interestingly, this nano-scale instability, involving the $\{110\}\langle 1\bar{1}0\rangle$ soft-phonon shuffle, occurs in the β phase without deliberate additions of either interstitial or substitutional solutes.

Keywords: Titanium alloys; Phase transformations; High-resolution electron microscopy; Nano-scale instability; O' phase

In the recent past, metastable β titanium alloys have attracted considerable attention because of the refined nature of microstructures that can be effected by application of various thermal/mechanical processes [1, 2]. Usually, this refinement involves the precipitation of the intragranular α phase. In recent studies, it has been shown that the size, morphology and number density of these α precipitates in Ti-5Al-5Mo-5V-3Cr can be significantly influenced by the nano-scale structural and compositional instability present in parent β phase, in this alloy, the metastable isothermal ω phase [3-5]. In these latter studies, it was found that either the compositional and/or stress field associated with the isothermal ω phase may contribute to an increased driving force for α nucleation [5].

In addition to the well established ω phase, there have been reports of other instabilities that may occur in metastable β alloys. For example, it has been reported that the addition of interstitial oxygen to Ti-Nb based alloys can induce superelasticity and the temperature dependent shape memory effect, apparently due to the reversible transformation between the nano-sized modulated domains to long range α'' martensite during tensile deformation and heating [6-8]. The origin of the nano-sized modulated domains is proposed to be related to the local strain caused by the randomly distributed interstitial oxygen atoms in the matrix will suppress the long range α'' martensite formation [6, 7]. Such influence of oxygen on the suppression of α'' martensite has also been observed and introduced by Tane et al. [9, 10]. In a similar gum-type metal, Ti-23Nb-0.7Ta-2Zr-1.2O, the origin of

the Elinvar effect and low modulus is explained by the gradual formation of nano-size martensitic domains [11], undergoing a strain glass transition by random point defects [12, 13]. Recently, it has been discovered that substitutional additions to alloys may also promote structural instabilities. For example, Zr added to Ti-Nb, and Al added to Ti-Mo, alloys effect an instability in the β phase matrix involving the $\{110\}\langle 1\bar{1}0\rangle$ soft-phonon shuffle, resulting in the formation of the O' phase [14]. In this latter study, the role of the substitutional solutes appears to involve their negative influence on the stability of the ω phase. It appears then that in metastable β alloys, both interstitial and substitutional alloying additions may lead to the activation of structural instabilities in the β phase, and these may influence microstructural evolution during subsequent heat-treatment.

A question that is posed by the results of the studies discussed above is whether the various structural (and/or compositional) instabilities that have been identified occur only in concentrated alloys containing certain interstitial and/or substitutional solutes. The present study was motivated by this question and aims to establish whether instabilities may occur in simple binary alloys. Thus, two alloys have been the subject of study, namely Ti-12Mo and Ti-18Mo (compositions in wt.%) on the basis that their compositions are outside the range in which α' or α'' martensites have been reported [15]. The microstructures of β solutionized samples of these alloys, following quenching to room temperature, have been characterized using selected area electron diffraction (SAD) and high resolution scanning transmission electron microscopy, in the latter case using the high-angle annular dark-field (HAADF) imaging mode. The focus of the study is on the influence of binary solute content (Mo content) on instabilities in β phase, and as will be seen below, more specifically on its effect on the $\{110\}\langle 1\bar{1}0\rangle$ shuffle which results in the formation of the O' phase.

The alloys Ti-12Mo and Ti-18Mo used in current research were provided kindly by the TIMET Company. The oxygen contents of these alloys were measured by wet chemistry and are $\approx 0.25\text{wt}\%$ in both alloys. In order to improve the homogeneity, the as-received alloys were firstly homogenized in a vacuum furnace at 1100°C for 96 hours. Then, the bulk material was cut into $20\text{mm}\times 10\text{mm}\times 10\text{mm}$ small pieces using Electric Discharge Machining (EDM) for further heat treatment. The β solution treatment selected is the same as that used in [16]. Samples sectioned from the two alloys, wrapped with pure titanium foil, were solutionized at 1000°C for 30 minutes in a tube furnace and then quenched into water at room temperature. To remove the possible oxygen contaminated layer, small $5\text{mm}\times 5\text{mm}\times 5\text{mm}$ blocks were cut from the center part of the as-quenched samples. Thin foils for SAD and HAADF-STEM analysis were prepared from the center of the blocks, using the Dual-Beam Focused Ion Beam (DB-FIB) technique on an FEI Helios Nanolab 600 system, and any ion beam damage on the foil surfaces resulting from the DB-FIB was minimized using low voltage Ar^+ ion milling in a Fischione NanomillTM Model 1040. SAD patterns were recorded on a Philips CM200 transmission electron microscope operating at an accelerating voltage of 200kV, and HAADF-STEM images were recorded using a probe-corrected FEI Titan³TM 80-300 operated at 300kV, using a convergence semi-angle of 12 mrad and a collection semi-angle of 44 mrad, with an incident beam dwell-time of $4\mu\text{s}/\text{px}$ and a beam current of $\approx 90\text{pA}$.

SAD patterns from the as-quenched Ti-12Mo are shown in two different zone axes in Fig. 1(a and b). In Fig. 1(a), with the electron beam parallel to the $\langle 110 \rangle_\beta$ zone axis, ω reflections are observed clearly at $1/3$ and $2/3$ $\{112\}_\beta$ locations with examples highlighted by green circles. In Fig. 1(b), with the electron beam parallel to $\langle 100 \rangle_\beta$ zone axis, a zone axis for which no ω reflections are expected, there appears to be no minor intensity maxima at the positions corresponding to $1/2$ $\{310\}_\beta$, the locations where diffraction from the O' phase is expected [14]. This lack of a minor intensity maxima is confirmed in the intensity profile (from $\{200\}_\beta$ and $\{110\}_\beta$ highlighted by yellow dashed line) inset in the figure. SAD patterns from the as-quenched Ti-18Mo are shown in two different zone axes in Fig. 1(c and d). In Fig. 1(c), with the electron beam parallel to $\langle 110 \rangle_\beta$ zone axis, ω reflections are observed at $1/3$ and $2/3$ $\{112\}_\beta$ locations, again with examples highlighted by green circles, but their intensities are very much reduced compared with those in Fig. 1(a). In addition, there are diffuse intensity maxima observed at $1/2$ $\{112\}_\beta$ locations, highlighted in the figure by the arrows, and confirmed by the intensity profile inset in the figure. Compared with experimental and simulated diffraction patterns introduced in our early work [14], this set of reflections belongs to orthorhombic structure O' phase. In Fig. 1(d), with the electron beam parallel to $\langle 100 \rangle_\beta$ zone axis, diffuse intensity maxima are observed at the positions corresponding to $1/2$ $\{310\}_\beta$, confirmed in the intensity profiles inset in the figure. These latter locations are those for which diffraction from the O' phase is expected [14]. Finally, diffuse reflections may be observed at $1/2$ $\{110\}_\beta$ in Fig 1(d), but these are due to double diffraction, as detailed in [14]. The SAD patterns in Fig 1(a-d) show clearly that the athermal ω phase is formed in both as-quenched Ti-12Mo and Ti-18Mo, but the O' phase is only formed in the latter alloy.

The investigation of the structure of nano-scale O' phase in Ti-18Mo using HAADF-STEM imaging is shown in Fig. 2. The fast Fourier transformation (FFT) inset in Fig. 2(a) implies the co-existence of athermal ω phase with the O' phase, the corresponding spatial frequencies being highlighted using the green and blue dashed circles, respectively. Fig. 2(b) shows a magnified view of the nano-scale O' phase (dashed yellow circle in the figure), with the electron beam parallel to the $\langle 110 \rangle_\beta$ zone axis. The inset shows the intensity profile along the yellow color dotted line, revealing the periodic small displacements of every other atomic column from the *bcc* lattice in the O' phase. The apparent displacement of atoms is consistent with structure of O' phase first imaged in [14] and is corresponding to the extra spatial frequencies present at $1/2$ $\{112\}_\beta$ in the FFT. To the author's knowledge, this experimental result is the first to observe and image the activation of the $\{110\}\langle 1\bar{1}0 \rangle$ shuffle mechanism in a dilute binary alloy.

The structure of athermal ω phase in both alloys was investigated using HAADF-STEM, shown in Fig. 3. In both alloys, a collapse of $\{111\}_\beta$ planes along their normal $\langle 111 \rangle_\beta$ direction is observed, which is consistent with the reported formation mechanism of athermal ω phase [16-20]. However, a careful comparison of the HAADF images from the structures of the athermal ω in the two alloys, Fig. 3(a and c), when viewed along $\langle 110 \rangle_\beta$ shows clear differences in the arrangements of the atomic columns. These differences are due to the variations in the degree of collapse of the $\{111\}_\beta$ planes. Thus, consider the higher magnification image of athermal ω in a quenched sample of Ti-12Mo

shown in Fig. 3(b). The red rectangle in the figure outlines the structural motif of the ω phase, and, as can be seen, the two atomic columns within that rectangle lie on the blue line that joins the mid-points of the short edges of the rectangle. This corresponds to the fully collapsed state of the athermal ω phase. In contrast, in as-quenched Ti-18Mo, shown in Fig 3(d), the blue line through the two atomic columns within the red rectangle is inclined significantly to that shown in Fig. 3(b), indicating that the atom shuffle (or atom plane collapse) has occurred only partially. It appears that the increase in Mo content in the Ti-18Mo alloy has caused a suppression of the degree of atom collapse. These results are consistent with the density function theory calculations in [17] that show for ω particles containing significant concentrations of Mo, the partially collapsed structure of athermal ω is energetically more favorable over a fully collapsed one.

It was noted above that in Fig. 1(c), in the quenched Ti-18Mo sample, ω reflections are observed at $1/3$ and $2/3$ $\{112\}_\beta$ locations, but their intensities are very much reduced compared with those from the as-quenched sample of the Ti-12Mo alloy (Fig. 1(a)). This is consistent with the increased Mo content reducing the thermodynamic stability of the ω phase. It has also been discovered that increasing the Mo content effectively stabilizes the $\{110\}\langle 1\bar{1}0\rangle$ shuffle leading to the formation of the nano-scale O' phase in Ti-18Mo; in this quenched alloy, it is observed that the O' phase co-exists with athermal ω phase.

These results lead us to speculate in Fig. 4 on the relative stability of the O' phase. Fig. 4(a) shows a conventional phase diagram that includes various metastable phases. We have not distinguished in the diagram between the α' and α'' martensite on the grounds that these originate from the same shear + shuffle mechanism that operates to different degrees in the two martensites [21]. In Fig. 4(b) we show schematically various instabilities and their composition and temperature dependences that lead to these metastable phase. Thus the martensite is related to the operation of the shear+shuffle modes, while the O' phase forms from the $\{110\}\langle 1\bar{1}0\rangle$ shuffle in binary alloys and is promoted by α phase stabilizing alloying additions such as Al and O.

Interestingly, the O' phase reported in the present study (and in [14]) yields the same diffraction patterns as observed in [11], but where in that latter study, it was assumed that the phase formed was the nano-sized martensitic domain (nano-size α'' domain). O' phase and α'' phase both exhibit orthorhombic structure and Cmc_m symmetry, but there are significant differences between the two phases. Most importantly, these two phases are transformed from β phase by different mechanisms. The orthorhombic structure of the O' phase is transformed from the *bcc* lattice only by a $\{110\}\langle 1\bar{1}0\rangle$ shuffle, which is indicated in Fig 2(c), that atoms on every the other $\{110\}_\beta$ planes will shuffle in the $\langle 1\bar{1}0\rangle_\beta$ direction. But in contrast, the transformation from the *bcc* lattice to the α'' phase is composed of two necessary components, one is the $\{11\bar{2}\}\langle 111\rangle$ shear and the other is the $\{110\}\langle 1\bar{1}0\rangle$ shuffle. It is tempting to speculate that the present O' phase and the nano-size disordered orthorhombic phase, termed nano-scale martensitic domain in [11], have, in fact, the same identity.

In summary, the current research has shown that the nano-scale O' phase is the result of a structural instability in the β phase in titanium alloys. Thus, while it has been claimed that such nano-scale domains form in solute rich, oxygen containing, alloys such as materials with compositions similar to that of gum metal [6-8, 11], the present study has established that the instability may be active in alloys with far simpler compositions. It appears that a necessary condition that must be met in order for the $\{110\}\langle 1\bar{1}0\rangle$ shuffle to be activated is that the β composition be such that the stability of the ω phase is sufficiently reduced. Thus, although the alloys in the present study (Ti-12Mo and Ti-18Mo) contain similar amounts of oxygen as in the alloys studied in [6], the instability occurs only when the Mo content is such that the stability of the ω phase is sufficiently reduced. The behavior of Ti-Nb alloys with additions of Zr also suggests that the effect of alloying additions including O will change the relative temperatures at which these instabilities occur as a function of composition so as to promote O' in favor of both martensite and ω phase [14]. Indeed, the requirement may be met in a variety of metastable β titanium alloys, providing the possibility that unique properties, such as superelasticity and the shape memory effect, may be found in a much wider range of titanium alloys than has been currently established.

Acknowledgement

The support of this research by the National Science Foundation, under grant DMR-1309270, is very gratefully acknowledged. One the authors, DB, is grateful for the award of a JC Bose Fellowship of the Department of Science and Technology, Govt of India.

References

- [1] D. Banerjee, J.C. Williams, *Acta Mater.*, 61 (2013) 844-879.
- [2] J.D. Cotton, R.D. Briggs, R.R. Boyer, S. Tamirisakandala, P. Russo, N. Shchetnikov, J.C. Fanning, *JOM*, 67 (2015) 1281-1303.
- [3] Y. Zheng, R.E.A. Williams, J.M. Sosa, Y. Wang, R. Banerjee, H.L. Fraser, *Scripta Mater.*, 111 (2016) 81-84.
- [4] Y. Zheng, R.E.A. Williams, J.M. Sosa, T. Alam, Y. Wang, R. Banerjee, H.L. Fraser, *Acta Mater*, 103 (2016) 165-173.
- [5] Y. Zheng, R.E.A. Williams, D. Wang, R. Shi, S. Nag, P. Kami, J.M. Sosa, R. Banerjee, Y. Wang, H.L. Fraser, *Acta Mater*, 103 (2016) 850-858.
- [6] M. Tahara, H.Y. Kim, T. Inamura, H. Hosoda, S. Miyazaki, *Acta Mater*, 59 (2011) 6208-6218.
- [7] M. Tahara, T. Kanaya, H.Y. Kim, T. Inamura, H. Hosoda, S. Miyazaki, *Acta Mater.*, 80 (2014) 317-326.
- [8] H.Y. Kim, L. Wei, S. Kobayashi, M. Tahara, S. Miyazaki, *Acta Mater.*, 61 (2013) 4874-4886.
- [9] M. Tane, T. Nakano, S. Kuramoto, M. Hara, M. Niinomi, N. Takesue, T. Yano, H. Nakajima, *Acta Mater.*, 59 (2011) 6975-6988.
- [10] M. Tane, T. Nakano, S. Kuramoto, M. Niinomi, N. Takesue, H. Nakajima, *Acta Mater.*, 61 (2013) 139-150.
- [11] Y. Wang, J. Gao, H. Wu, S. Yang, X. Ding, D. Wang, X. Ren, Y. Wang, X. Song, J. Gao, *Scientific Reports*, 4 (2014).
- [12] D. Wang, Y. Wang, Z. Zhang, X. Ren, *Phys. Rev. Lett.*, 105 (2010) 205702.

- [13] D. Wang, Z. Zhang, J. Zhang, Y. Zhou, Y. Wang, X. Ding, Y. Wang, X. Ren, *Acta Mater.*, 58 (2010) 6206-6215.
- [14] Y. Zheng, R.E.A. Williams, S. Nag, R. Banerjee, H.L. Fraser, D. Banerjee, *Scripta Mater.*, doi:10.1016/j.scriptamat.2016.01.024
- [15] R. Davis, H.M. Flower, D.R.F. West, *Acta Metall.*, 27 (1979) 1041-1052.
- [16] A. Devaraj, S. Nag, R. Srinivasan, R.E.A. Williams, S. Banerjee, R. Banerjee, H.L. Fraser, *Acta Mater.*, 60 (2012) 596-609.
- [17] S. Nag, A. Devaraj, R. Srinivasan, R.E.A. Williams, N. Gupta, G.B. Viswanathan, J.S. Tiley, S. Banerjee, S.G. Srinivasan, H.L. Fraser, R. Banerjee, *Phys. Rev. Lett.*, 106 (2011) 245701.
- [18] F. Sun, F. Prima, T. Gloriant, *Mater. Sci. and Eng.: A*, (2010).
- [19] J.C. Williams, M.J. Blackburn, *Trans. of the Metall. Soc. of Aime*, 245 (1969) 2352-2355.
- [20] J.C. Williams, Defontaine, D., N.E. Paton, *Metall. Trans.*, 4 (1973) 2701-2708.
- [21] G. Lütjering, J. Williams, *Titanium (Engineering Materials and Processes)*, Springer, Berlin Heidelberg, 2007.

Figure Captions:

Fig. 1. TEM SAD patterns from as-quenched Ti-12Mo and Ti-18Mo: (a) SAD pattern with the electron beam parallel to the $\langle 110 \rangle_{\beta}$ zone axis showing the presence of athermal ω phase in Ti-12Mo; (b) $\langle 100 \rangle_{\beta}$ zone axis SAD showing the absence of O' phase in Ti-12Mo; (c) $\langle 110 \rangle_{\beta}$ zone axis SAD showing the co-existence of athermal ω phase and O' phase in Ti-18Mo; (d) $\langle 100 \rangle_{\beta}$ zone axis SAD showing the presence of O' phase in Ti-18Mo.

Fig. 2. HAADF-STEM images showing the co-existence of athermal ω phase and O' phase in Ti-18Mo: (a) low magnification HAADF-STEM image with its FFT (inset) showing the co-existence of athermal ω phase and O' phase in β matrix; (b) higher magnification image showing $\{110\}\langle 1\bar{1}0 \rangle$ shuffle in the center of O' phase; (c) schematic figure showing the $\{110\}\langle 1\bar{1}0 \rangle$ shuffle to transform *bcc* structure β phase to orthorhombic structure O' phase.

Fig. 3. HAADF-STEM images showing the degree of $\{111\}_{\beta}$ collapse in as-quenched Ti-12Mo and Ti-18Mo: (a) and (b) full $\{111\}_{\beta}$ collapse from the center of athermal ω particle in Ti-12Mo; (c) and (d) partial $\{111\}_{\beta}$ collapse from the center of athermal ω particle in Ti-18Mo.

Fig. 4. Schematic figure showing various instabilities in the postulated pseudo-binary phase diagram of titanium alloys, without (a) and with (b) the O' phase

Figure 1

Figure 2

Figure 3

Figure 4

Graphical Abstract