The Indirect Influence of the ω Phase on the Degree of Refinement of Distributions of the α Phase in Metastable β -Titanium Alloys

Yufeng Zheng¹, Robert E.A. Williams¹, John M. Sosa¹, Talukder Alam², Yunzhi Wang¹, Rajarshi Banerjee², Hamish L. Fraser^{1,*}

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

² Department of Materials Science and Engineering, University of North Texas, 3940 N. Elm, Denton, TX 76207, USA

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

Abstract

Non-conventional transformation pathways have been exploited to determine the degree of refinement of the microstructure of a metastable β -Ti alloy. This has involved a set of heat-treatments where samples, initially quenched to room temperature (RT) from above the β transus are slowly heated to 350°C, then isothermal annealed at 350°C for various times prior to up-quenching to 600°C and again isothermally annealed at that temperature, followed by quenching to RT. Interrupted treatments have also been performed so that the factors influencing the development of the final microstructure could be determined. Microstructures have been characterized by scanning and transmission electron microscopy, and atom probe tomography. It has been found that a distribution of the α phase may be formed whose scale is intermediate between the “super refined” and “refined” versions observed in previous research. The results are consistent with precursory isothermal ω precipitates playing an indirect role in the formation of the refined distribution of the α phase via a non-conventional transformation pathway.

Keywords: Titanium alloys; Phase transformations; Heterogeneous nucleation

Introduction

Metastable β Ti alloys, such as Ti-5Al-5Mo-5V-3Cr (Ti-5553), compositions in wt.%, have been the subject of considerable interest in the recent past. One of the characteristics that provokes this interest is the refinement in microstructure compared with that exhibited typically by the more commonly used α/β Ti alloys, for example, the alloy TIMETAL 6-4 (Ti-6Al-4V in wt. %). Here refinement refers specifically to the fine scale of the distribution of the α phase precipitated from β , that can be developed by varying heat-treatments following solution treatment above the β transus. There have been a number of assertions in the literature concerning factors that can influence the scale of the precipitation of α from β , generally invoking heterogeneous nucleation involving structural (e.g., the formation of the ω phase [1-9]) and compositional (e.g., phase separation of the β phase [10-12]) instabilities in these alloys. In general, these various proposed influences of instabilities involve phase transitions that follow non-conventional transformation pathways.

In recent work, the results of experiments performed on the metastable β alloy Ti-5553 show no phase separation in β , but that the ω phase does form on quenching to room temperature from β initially held at temperatures above the β transus. The first set of experiments involved step-quenching samples from above the β transus to temperatures above the stability range of the ω phase, i.e., where α forms from β in the absence of ω [13]. In these experiments, it was found that refined distributions of the α phase formed in samples quenched to temperatures $\leq 650^\circ\text{C}$, and it was concluded that the pseudo-spinodal mechanism, i.e., one involving a non-conventional transformation pathway, was responsible for the refined distributions of the α phase observed [13-16]. The second set of experiments involved precipitating α from β in samples that initially contained a distribution of the ω phase [17]. In these experiments, samples were solution treated above the β transus, and quenched to room temperature to effect a distribution of the ω phase (i.e., athermal ω). Subsequently, these samples were heated fairly rapidly (at rates $\geq 50^\circ\text{C}/\text{min}$) to 600°C , and it was found that the scale and distribution of α which resulted were similar to that formed by the pseudo-spinodal mechanism [13]. It was shown experimentally that the ω transformed back to β during the heating of samples to 600°C , and so the ω phase played no direct role in the nucleation of the α phase [17]. The third set of experiments followed the same

experimental scheme as in [17], but heating rates in the range 20°C/min to 1°C/min, i.e., relatively slow heating rates, were employed [18]. Under these conditions, extremely refined distributions of α were formed, termed “super-refined”, and based on results of both interrupted tests and phase field modeling, it was concluded that the ω phase did indeed influence markedly the precipitation of the α phase.

It has been noted that ω particles may influence precipitation of the α phase by providing additional driving forces for nucleation through either compositional and/or stress variations associated with the presence of the particles. In the case of the slow heating experiments discussed above [18], the compositional variations were measured directly, which were used subsequently with CALPHAD modeling to deduce contributions to the driving force from composition. The stresses associated with the ω particles were assessed using Khachaturyan’s microelasticity theory [19], and these have been used with the Burgers lattice correspondence [20] to determine an extra contribution to the driving force for nucleation from stress. It was not possible in that work to ascertain whether both of these factors made effective contributions to the increased driving force for nucleation, or whether one or the other is more dominant. Hence, the first aim of the present study was to determine the relative contributions of these two factors. The results of previous work [17, 18] are consistent with the ω phase either playing no role in, or in marked contrast having a direct influence on, the nucleation of the α phase. To understand the role of ω fully, it is important to determine whether ω forming during heat-treatment of these metastable β alloys can play an *indirect* role in effecting refined distributions of the α phase. Hence, the second aim of the present research was to determine under what conditions an indirect role might be played by this metastable phase.

Experimental procedure

The alloy studied in this research was Ti-5553 which was kindly supplied by the TIMET Company. The composition of this material has been measured using wet chemistry, and reported previously as Ti-5.67Al-5.00Mo-4.92V-3.04Cr-0.48Fe-0.18O-0.002N [18]. Bars were cut using electrical discharge machining from the Ti-5553 (subscale: 1.5mm×3mm×40mm) for heat-treatment studies. The heat-treatments were performed in Electrical-Thermal-Mechanical-

Tester (ETMT) in vacuum. All samples were β solution heat-treated at 1000°C for 30 minutes and subsequently fast cooled to room temperature.

After the β -solution treatment, two sets of experiments were performed. In the first set, samples were heated to 350°C at a rate of 5°C/min, and subsequently up-quenched to 600°C and isothermally held for various lengths of time at that temperature before being fast cooled to room temperature. The second set of experiments involved samples being heated to 350°C at a rate of 5°C/min, and subsequently held isothermally at 350°C for various lengths of time before being up-quenched to 600°C. In both sets of experiments, interrupted tests were performed to permit the evolution of microstructure as a function of heat-treatment to be determined.

The microstructures of the various samples were first characterized using scanning electron microscopy (SEM), mainly using an FEI Sirion SEM operating at an accelerating voltage of 12kV and mostly recording backscattered electron (BSE) images. Backscattered SEM images were analyzed quantitatively with a custom-developed image processing package, MIPAR™[21]. The aerial number density of particles in given images was determined using a watershed routine for feature; the accuracy of these determinations is about $\pm 10\%$. For finer scale microstructural characterization, site-specific TEM foils were prepared using the Focused Ion Beam (FIB) technique, employing an FEI Helios Nanolab 600 system. Foils were “polished” subsequently at low voltage using a Fischione Model 1040 Nanomill. TEM dark-field images and diffraction patterns were obtained on a Philips CM200 microscope at 200kV and energy dispersive x-ray spectroscopy (XEDS) analyses were performed in an aberration-corrected (S)TEM, equipped with a SuperX (FEI) four-quadrant silicon drift detector, FEI Titan3™ G2 60-300 S/TEM at 300kV. Atom probe needles were prepared using the FEI Nova 200 NanoLab. These needles were used in a local electrode atom probe (LEAP™) system from Imago Scientific Instruments, using the voltage mode at a temperature of 60K, with an evaporation rate 0.2—1.0% and a voltage pulse fraction at 20% of steady-state applied voltage, for 3D atom probe (3DAP) tomography.

Results and Discussion

Two sets of experiments have been performed. In both sets, samples were first solution treated above the β transus, and then quenched to room temperature. In this way, all the various

experiments described below began with samples that contained a fine homogeneous distribution of athermal ω precipitates (as shown previously in [18]).

Experiment set #1: Slow-heating to 350°C, immediate up-quenching to 600°C

The first set of experiments involved heating samples slowly, at 5°C/min, to 350°C in order to promote the transformation from athermal to isothermal ω , and, because of solute redistribution accompanying the development of this latter phase, effect compositional variations in the samples. Upon reaching 350°C, samples were up-quenched to 600°C, the temperature where previously refined distributions of the α phase in this particular alloy have been effected, and held isothermally for various times, as depicted in the schematic diagram in Fig. 1(a). In this way, it was hoped that the α phase would form in the presence of the compositional variations resulting from the isothermal ω phase, but not in the presence of the phase itself. The resulting distributions of the α precipitates would then be compared with the “super refined” observed previously [18].

The result of heat-treating a sample in this manner with an isothermal hold of 2 hours is shown in Fig. 1(b). As can be seen, a refined distribution of α plates in the β matrix result. The scale of the distribution appears to be very similar to that formed either by step-quenching to 600°C from above the β transus [13], or by heating solution-treated and quenched samples rapidly ($\geq 50^\circ\text{C}/\text{min}$) to 600°C [17]. This is confirmed by applying routines in MIPAR™ to determine the aerial number density of α plates, $\approx 11 \text{ plates}/\mu\text{m}^2$, a value slightly higher than those determined for both the step-quenched and rapidly heated samples (typically $\approx 6 \text{ plates}/\mu\text{m}^2$), but much less than the super-refined distribution reported in [18], where typical values are $\approx 35 \text{ plates}/\mu\text{m}^2$.

To assist in developing an understanding of the influence of the heat-treatment described in Fig. 1, a sample was heated slowly (5°C/min) to 350°C, up-quenched to 600°C, and then immediately (after ≈ 1 sec) quenched to room temperature. The resulting microstructure is shown in Fig. 2(a), where, when considering the diffraction pattern shown in Fig. 2(b), it is evident that the sample consists of a distribution of athermal ω in a β matrix. It appears that the isothermal ω developed during slow heating to 350°C (shown previously in [18] and also here in Fig. 6(b) below) transformed to β during the up-quenching to 600°C, and as a result of rapid cooling to

room temperature from 600°C, a distribution of athermal ω has formed. This result shows that the ω phase is not present during the subsequent nucleation of α in samples isothermally held at 600°C, for example, such as shown in Fig. 1. Although the phase itself may not be present, as noted above, there is a possibility that compositional variations introduced from the isothermal ω precipitates, which would have developed during slow heating to 350°C, may persist in these samples following the structural transformation of ω back to β , and in this case, such compositional variations may influence the nucleation of α . To establish whether, or not, such compositional fluctuations are present in samples heat-treated such as the one in Fig. 2, two different methods of compositional analysis have been employed. In the first, energy dispersive x-ray spectroscopy (XEDS) of thin foils in an aberration-corrected (S)TEM, equipped with a SuperX (FEI) four-quadrant silicon drift detector has been used to ascertain whether compositional fluctuations occur. The results are shown in Fig. 3, where XEDS compositional maps are shown for the major elemental components in the alloy. As can be seen, the compositions appear to be fairly uniform. The second attempt to determine if compositional fluctuations are present in samples heat-treated as that in Fig. 2 has involved the application of atom probe tomography (APT). A typical result is shown in Fig. 4. Fig. 4(a) displays an APT compositional map showing a fairly uniform composition (blue: 100% Al; red: 100% V, Mo, Cr and Fe). Fig. 4(b) shows a plot of the distribution of Ti atoms (termed “observed” in the figure), compared with a binomial distribution that would be expected from an homogeneous random solid solution. The data in both Fig. 4(a and b) are consistent with the XEDS data, showing a fairly uniform distribution of the elemental species, i.e., not showing compositional fluctuations. In this case, the α phase forming during the heat-treatment described in Fig. 1 nucleated without any influence from the ω phase (i.e., with contributions from neither stress nor composition). Based on the similarity in scale of the resulting distribution of α precipitates, it is reasonable to conclude that the nucleation involved the pseudo-spinodal mechanism as in the case of samples step-quenched from above the β transus [13], as well as in samples, initially containing a distribution of athermal ω , rapidly heated ($\geq 50^\circ\text{C}/\text{min}$) from room temperature to 600°C [17].

Experiment set #2: Slow-heating to 350°C, isothermally holding prior to up-quenching to 600°C

The results of experiment set #1 show that in samples slowly heated to 350°C and subsequently up-quenched to 600°C, the ω phase transforms to β , with very small, if any, compositional fluctuations persisting in the β matrix. The second set of experiments is designed to investigate whether heat-treatments may be varied to *promote* the compositional variations associated with ω , such that they might persist during up-quenching and so may influence nucleation of the α phase. Thus, samples initially containing a distribution of athermal ω were heated slowly (5°C/min) to 350°C, and then held isothermally at that temperature for various periods of time prior to being up-quenched to 600°C. This heat-treatment is depicted in the schematic diagram in Fig. 5(a). When this heat-treatment is performed with an isothermal hold of three hours at 350°C, the resulting microstructure is shown in Fig. 5 (b and c), exhibiting an SEM/BSE image and a High Angle Annular Dark Field (HAADF) STEM image, respectively. The α distribution appears to be rather refined, especially compared with that shown in Fig. 1(b). When processed using MIPAR™ routines, the segmentation being shown in Fig. 5(d), it is determined that the aerial number density of precipitates is typically ≈ 24 laths/ μm^2 , compared with values of ≈ 5 -10 laths/ μm^2 for the “refined” distributions [13, 17], as in Fig. 1(b), and ≈ 35 laths/ μm^2 for the “super refined” distributions discussed in [18]. The present distribution (Fig. 5(b)) is termed “more refined.”

It is important to perform interrupted experiments to determine the evolution of microstructure during the heat-treatment depicted in Fig. 5(a). These experiments are detailed in Fig. 6(a), and involve four heat-treatments: one to the point of the blue circle, also labeled (b) in the figure, followed by immediate quenching to room temperature; one to the point of the green circle, marked (c) in the figure, followed by immediate quenching to room temperature; one to the point of the purple circle, marked (d) in the figure, followed by immediate quenching to room temperature, and finally, heat-treating to the brown circle, marked (e) in the figure, again followed by immediate quenching to room temperature. The result of the first interrupted experiment (heat-treated to the blue circle (b) in Fig. 6(a)) is shown in Fig. 6(b), and this has been characterized by TEM, from which the microstructure is shown to consist of a distribution of isothermal ω precipitates in a β matrix. When performing the heat-treatment to the point of the green circle (c) in Fig. 6(a), the resulting microstructure is shown in Fig. 6(c), and, on the basis of selected area diffraction patterns (not shown here), consists of a refined distribution of α laths. Evidently, the distribution of isothermal ω is replaced by a refined distribution of the α phase

during the isothermal anneal at 350°C. When performing the heat-treatment to the point of the purple circle (d) in Fig. 6(a), a refined distribution of α laths is observed in the dark-field TEM image shown in Fig. 6(d). The fourth interrupted experiment involves executing the heat-treatment depicted in Fig. 6(a) to the point of the brown circle, marked (e) in the figure, followed by immediate quenching to room temperature. The result of this experiment is presented in Fig. 6(e), showing athermal ω precipitates and an α platelet (the latter feature is a very rare observation). It appears that almost all of the α phase shown in Fig. 6(d) has transformed back to the β phase, and the β matrix now contains a distribution of athermal ω precipitates resulting from the quench from 600°C to room temperature. This is, at first, a somewhat unexpected result as the composition of the up-quenched α precipitates would still be in the two phase ($\alpha + \beta$) phase field, and their composition might approach equilibrium (at 600°C) by diffusion of solute. This phenomenon is discussed below. From these experiments, it is evident that the ω phase itself does not play a direct role in the formation of the “more refined” distribution of the α phase as in Fig. 5(b). A question remains whether the isothermal ω present at 350°C influences the nucleation of the α phase at that temperature (Fig. 6(c and d)), which in turn may influence formation of the “more refined” α distribution at 600°C (Fig. 5(b)). This is also discussed in the following.

From the results discussed above, it appears that during the heat-treatment depicted in Fig. 5(a), the following transformations occur: Initially, the sample consists of a refined distribution of athermal ω precipitates in the β matrix. Upon heating slowly to 350°C, the athermal ω is replaced by isothermal ω , which coarsens in scale presumably accompanied by solute partitioning. During isothermal annealing at 350°C, a very refined distribution of the α phase forms, replacing the ω phase. The scales of the distributions after holding for 90 min and 3 hours at 350°C, shown in Fig. 6(c and d), respectively, may be compared with that in Fig. 5(c) in [18], this latter distribution being the precursor to the “super refined” α distribution. This comparison has been done using the routines in MIPAR™, the results shown in Fig. 7, where the number density of the distribution in Fig. 7 (a) (the distribution exhibited in Fig 5(c) in [18]), ≈ 7000 laths/ μm^2 , in Fig. 7 (b) the number density is ≈ 6700 laths/ μm^2 , and in Fig. 7(c), the number density is ≈ 4000 laths/ μm^2 .

These results are interpreted as follows. It has been concluded previously that the nucleation of the α phase in the distribution shown in Fig. 7 (a), which results in the super-refined distribution of α when continuously heated slowly to 600°C [18], is influenced by both the stress and compositional components associated with the presence of isothermal ω precipitates. Because the refinement of the α in the distribution shown in Fig. 7(b) is essentially the same as that in Fig. 7 (a), and it is known that when the sample reaches 350°C, there is a distribution of isothermal ω present, it is reasonable to conclude that this ω influences nucleation of the α phase in the same way, i.e., by both stress and compositional components. Continuous aging at 350°C for a further 90 min (i.e., 3 hours in total), leads to some coarsening of the α distribution, as would be expected by Ostwald Ripening (Fig. 7(c and f), i.e., ≈ 4000 laths/ μm^2).

Factors influencing formation of the “more refined” microstructure

A most surprising result involves the immediate structural transformation of the α precipitates, present following heat treatment to the purple circle, marked (d), in Fig. 6(a), to β upon up-quenching to 600°C. To understand this phenomenon, it is important at first to estimate the compositional changes that are occurring with heat-treatment. This has been attempted using APT, and the results of compositional analyses are shown in Figs. 8 and 9. In Fig. 8, compositional profiles across α and β phases in samples heat-treated to the purple circle, marked (d), in Fig. 6(a) are presented. The general trends in compositional changes between the two phases appear to be as expected, i.e., the β -stabilizing elements Mo, V, Cr and Fe have low concentrations in the α phase. The relatively small difference in the Al content between the two phases is somewhat surprising, and possibly indicates that the composition of the α phase is not at equilibrium. Rather interestingly, after annealing at 350°C for 3hrs, while the slower diffusing, β stabilizing solute elements, Mo, V, Cr, and Fe, are rejected from the α precipitates, the faster diffusing Al does not partition to any significant degree (based on the APT composition profiles shown in Fig. 8). While this observation is difficult to explain, it should be noted that the equilibrium compositions of α and β phases in such a multi-component system have not been calculated, especially at low temperatures such as 350°C. For samples heat-treated to the brown circle, marked (e), in Fig. 6(a), and immediately quenched to room temperature, the results of compositional analyses using APT are presented in Fig. 9. In Fig 9(a), the distribution of the Ti

and Al atoms are plotted, and it is difficult to assess, simply based on the visual appearance of the reconstruction, whether small compositional fluctuations exist. Following conventional atom probe practice, the frequency distribution of Ti atoms as a function of composition is plotted, together with a fitted binomial distribution, the latter corresponding to a homogeneous uniform composition within the β matrix, Fig. 9(b). As can be seen, there appears to be a relatively significant deviation between the experimental curve and the binomial, especially when compared with the same comparison shown previously in Fig. 4(b). Attempts have been made to model the experimental curve shown in Fig. 9(b), using two Gaussians, and while it has been found that there is no unique fit (i.e., “best” fit using the conventional R^2 values), a number of reasonable fits are found indicating the presence of compositional fluctuations. Based on the significant difference in experimental results (i.e., comparing the experimental curves in Figs. 4(b) and 9(b)), it is reasonable to assume that there are real compositional fluctuations present in these samples (i.e., after being heat-treated to the point (e), brown circle, in Fig. 6(a)), although the exact compositional differences cannot be determined uniquely.

The partial transformation of the α precipitates that exist after heat-treatment to the purple circle, marked (d) in Fig. 6(a), to the β phase indicates that the α phase formed at 350°C becomes unstable at 600°C. This would imply that at the lower temperature (T_1), the composition of the phase occurs on the solute lean side of the $c_0(T)$ point, whereas this composition would lie on the solute rich side of $c_0(T)$ at the higher temperature (T_2), as indicated schematically in the diagrams in Fig. 10 (it should be noted that in the figure, the composition of the α phase at the lower temperature (350°C), $c_{\alpha}(T_1)$, has been assumed to be of a non-equilibrium value, because of the slow rates of diffusion expected at that temperature). If this is in fact the case, then at 600°C, the α phase would transform congruently to the β phase, driven by the free energy reduction indicated by the green arrow in Fig. 10(a). This refined distribution of compositional pockets, having a lower local concentration of β stabilizers at T_2 , as compared with the surrounding matrix, would provide preferred nucleation sites for the precipitation of the equilibrium α phase at this temperature. As the distribution of these pockets would be similar to that of the original α distribution prior to up-quenching, the re-precipitating α particles would be distributed on a similarly fine scale, i.e., a distribution of the α phase that would be somewhat coarser than that in the “super-refined” α (comparing the α distributions in Figs. 7(c and d), i.e.,

≈ 7000 laths/ μm^2 vs. ≈ 4000 laths/ μm^2) such that the “more refined” distribution of α is formed. The fact that the “more refined” α is finer than the “refined” α would indicate that the scale of the “more refined” version is dictated by the scale of the α precipitates after annealing at 350°C for 3 hours, whereas the scale of the “refined” α is determined by local compositional fluctuations at 600°C , as per the pseudo-spinodal model [13].

The diagrams presented in Fig. 10 are, of course, schematic and hence notional. To assess whether they have any basis in fact, CALPHAD calculations have been performed using the software package Thermo-Calc, for the case of the Ti-Mo binary system. The results are shown in Fig. 11 (a and b) for 350°C and 600°C , respectively. The average composition of the Ti-5553 alloy using its Mo-equivalency value (the approximate nature and limitations of which have been discussed elsewhere [13]) is $\approx 9\%$, and this is shown on the diagrams by the vertical lines. While the composition of the α precipitates forming at 350°C , is expected to lie marginally to the left (solute lean side) of the lines marked in Fig. 11, the de-stabilization of these α precipitates at 600°C , and consequent formation of solute (β stabilizer) depleted pockets, can be rationalized based on these CALPHAD assessments and these appear to be consistent with the present hypothesis.

The present results are consistent with the notion that the most refined distribution of the α phase forms when both the stress and compositional variations associated with isothermal ω are present during the nucleation of the α , yielding the “super-refined” distribution. It has not been possible to determine whether one of these contributing factors, stress and composition, provides a more significant contribution to the increased driving force for nucleation. The coarser distribution, “more-refined”, forms by a very different pathway. In this latter case, at first, a super-refined distribution of α is produced because of the influence of isothermal ω , involving stress and compositional components associated with the fine metastable particulate. This super-refined α distribution coarsens by Ostwald Ripening during continued aging at 350°C until the sample is up-quenched to 600°C , when the α phase transforms congruently to β , leaving compositional pockets in the β matrix on the scale of the coarsened prior α distribution. Upon continued aging at 600°C , the α re-precipitates on these compositional pockets having the maximum degree of supersaturation on the coarser scale dictated by the distribution from the isothermal anneal at 350°C , yielding a distribution of similar scale, i.e., the “more-refined” α . In

this latter case, ω does not play a direct role *but* rather influences the scale of the final α distribution by influencing the scale of the α phase forming on aging at intermediate temperatures (in this case, 350°C), i.e., an *indirect* role.

Conclusions

This research has involved two aims, the first being to determine the relative contributions of stress and composition associated with isothermal ω particles when this phase plays a *direct* role in nucleation of α (i.e., in the production of “super-refined” α distributions). Although it was hoped that the applied heat-treatments would permit an assessment of the relative influences of these two factors, this was found not to be the case. The second aim of the present research was to determine under what conditions an *indirect* role might be played by the ω phase. It was found that the scale of the final α distribution formed in the heat-treatments described above was indeed influenced by the ω phase, but in an indirect way. Thus, the isothermal ω precipitates developed during the initial heat-treatment influence directly the scale of the intermediate α distribution, and subsequently, this latter distribution influences the scale of the final distribution of α precipitates. It is concluded that the ω phase may play both direct and indirect roles in the development of refined distributions of the α phase in metastable β -Ti alloys.

Acknowledgement

The support of this research by the National Science Foundation, under grant DMR-1309270 and DMREF grant DMR-1435483, is very gratefully acknowledged.

References

- [1] M.J. Blackburn, J.C. Williams. Phase Transformations in Ti-Mo and Ti-V Alloys, *Trans. Met. Soc. AIME* 242 (1968) 2461-2469.
- [2] J.C. Williams, M.J. Blackburn. The Influence of Misfit on the Morphology and Stability of the Omega Phase in Titanium--Transition Metal Alloys, *Trans. Met. Soc. AIME* 245 (1969) 2352-2355.
- [3] C.G. Rhodes, J.C. Williams. Precipitation of Alpha-phase in Metastable Beta-phase Ti Alloys, *Metall. Trans. A* 6 (1975) 2103-2114.
- [4] G.M. Pennock, H.M. Flower, D.R.F. West. *Titanium' 80: Science and Technology* (1980) 1343-1351.

- [5] Y. Ohmori, T. Ogo, K. Nakai, S. Kobayashi. Effects of Omega-Phase Precipitation on Beta $\rightarrow$ Alpha, Alpha" Transformations in a Metastable Beta Titanium Alloy, *Mater. Sci. Eng. A* 312 (2001) 182-188.
- [6] F. Prima, P. Vermaut, G. Texier, D. Ansel, T. Gloriant. Evidence of Alpha-Nanophase Heterogeneous Nucleation from Omega Particles in a Beta-Metastable Ti-Based Alloy by High-Resolution Electron Microscopy, *Scripta Mater.* 54 (2006) 645-648.
- [7] S. Nag, R. Banerjee, R. Srinivasan, J.Y. Hwang, M. Harper, H.L. Fraser. Omega-Assisted Nucleation and Growth of Alpha Precipitates in the Ti-5Al-5Mo-5V-3Cr-0.5Fe Beta Titanium Alloy, *Acta Mater.* 57 (2009) 2136-2147.
- [8] S. Azimzadeh, H.J. Rack. Phase Transformations in Ti-6.8Mo-4.5Fe-1.5Al, *Metall. Mater. Trans. A* 29 (1998) 2455-2467.
- [9] T. Li, J.M. Cairney, D. Kent, M.S. Dargusch, D. Kent, G. Sha. The Mechanism of Omega-assisted Alpha Phase Formation in Near Beta-Ti Alloys, *Scripta Mater.* (2015).
- [10] G. Narayanan, T. Archbold. Decomposition of the Metastable Beta Phase in the All-Beta Alloy Ti-13V-11Cr-3Al, *Metall. Trans. A* 1 (1970) 2281-2290.
- [11] G.H. Narayanan, T.S. Luhman, T.F. Archbold, R. Taggart, D.H. Polonis. A Phase Separation Reaction in a Binary Titanium-Chromium Alloy, *Metallography* 4 (1971) 343-358.
- [12] A. Devaraj, S. Nag, R. Banerjee. Alpha Phase Precipitation from Phase-separated Beta Phase in a Model Ti-Mo-Al Alloy Studied by Direct Coupling of Transmission Electron Microscopy and Atom Probe Tomography, *Scripta Mater.* 69 (2013) 513-516.
- [13] S. Nag, Y. Zheng, R.E.A. Williams, A. Devaraj, A. Boyne, Y. Wang, P.C. Collins, G.B. Viswanathan, J.S. Tiley, B.C. Muddle, R. Banerjee, H.L. Fraser. Non-Classical Homogeneous Precipitation Mediated by Compositional Fluctuations in Titanium Alloys, *Acta Mater.* 60 (2012) 6247-6256.
- [14] A. Boyne, D. Wang, R.P. Shi, Y. Zheng, A. Behera, S. Nag, J.S. Tiley, H.L. Fraser, R. Banerjee, Y. Wang. Pseudospinodal Mechanism for Fine Alpha/Beta Microstructures in Beta-Ti Alloys, *Acta Mater.* 64 (2014) 188-197.
- [15] Y. Ni, A.G. Khachaturyan. From Chessboard Tweed to Chessboard Nanowire Structure during Pseudospinodal Decomposition, *Nature Mater.* 8 (2009) 410-414.
- [16] Y. Ni, W. Rao, A.G. Khachaturyan. Pseudospinodal Mode of Decomposition in Films and Formation of Chessboard-Like Nanostructure, *Nano Lett.* 9 (2009) 3275-3281.
- [17] Y. Zheng, J.S. Sosa, R.E.A. Williams, Y. Wang, R. Banerjee, H.L. Fraser. The Role of Omega Phase in Non-Classical Homogeneous Precipitation of the Alpha Phase in Beta-Titanium Alloys, *Scripta Mater.* (Under review).
- [18] Y. Zheng, R.E.A. Williams, D. Wang, R. Shi, S. Nag, P. Kami, J.M. Sosa, R. Banerjee, Y. Wang, H.L. Fraser. The Role of Omega Phase in the Formation of Extremely Refined Distributions of Alpha Phase in Titanium Alloys, *Acta Mater.* (Under review).
- [19] A.G. Khachaturian. *Theory of Structural Transformations in Solids*, Wiley, New York, 1983.
- [20] W.G. Burgers. On the Process of Transition of the Cubic-body-centered Modification into the Hexagonal-close-packed Modification of Zirconium, *Physica.* 1 (1934) 561-586.
- [21] J.M. Sosa, D.E. Huber, B. Welk, H.L. Fraser. Development and Application of MIPAR: a Novel Software Package for Two- and Three-Dimensional Microstructural Characterization, *Integr. Mater. Manuf. Innov.* 3 (2014) 10.

Figure Captions:

Figure 1. (a) Heat-treatment scheme for experiment set #1. (b) Microstructure of Ti-5553 following the heat-treatment shown schematically in (a), i.e., slow heating to 350°C, up-quenching to 600°C, and isothermally held at 600°C for 2 hours.

Figure 2. Microstructure of a sample that, following solution treatment and being quenched to room temperature, had been slowly heated (5°C/min) to 350°C, up-quenched to 600°C, and then immediately quenched to room temperature. (a) TEM dark-field image, formed using reflections from athermal ω , shown in the selected area diffraction pattern (electron beam direction parallel to $\langle 110 \rangle_{\beta}$, in (b).

Figure 3. XEDS compositional maps (for the elements given on each map) of sample heat-treated as in figure 2.

Figure 4. Atom probe analysis of sample heat-treated as in figure 2. (a) a 3DAP compositional map showing a fairly uniform composition (blue: 100% Al; red: 100% V, Mo, Cr and Fe). (b) The comparison of observed distribution of Ti atoms with a binomial distribution.

Figure 5. Heat-treatment scheme for experiment set #2: Microstructure of a sample that, following solution treatment and being quenched to room temperature, had been slowly heated (5°C/min) to 350°C, and then held at 350°C for 3 hours, before being up-quenched to 600°C, and held at 600°C for 2 hours prior to being quenched to room temperature. (a) Schematic diagram depicting the heat-treatment. (b) and (c) SEM (BSE) and HAADF/STEM, respectively, of the resulting α distribution. (d) Image processing (see text) to yield a number density of ≈ 24 laths/ μm^2 ; this is a higher number density than measured for the “refined distribution”, but smaller than that of the “super-refined” distribution.

Figure 6. Determination of the development of microstructure during the heat-treatment depicted in the schematic diagram in (a). (b) Microstructure of a sample heated at 5°C/min to 350°C, and then quenched to room temperature. (c) Microstructure of a sample heated at 5°C/min to 350°C, held at that temperature for 90 minutes, and then rapidly cooled to room temperature. (d) Microstructure of a sample heated at 5°C/min to 350°C, held at that temperature for 3 hours prior to being rapidly cooled to room temperature: TEM dark-field image formed using a diffraction maximum from the α phase. (e) Microstructure of a sample heated at 5°C/min to 350°C, held at that temperature for 3 hours, followed by up-quenching to 600°C, and then immediately (≈ 1 sec) rapidly cooled to room temperature: TEM dark-field image formed using reflections from both the athermal ω phase and the α phase.

Figure 7. (a) TEM dark-field image recorded using a diffraction maximum from the α phase in a sample heated at 5°C/min to 400°C and immediately quenched to room temperature [18]. (b) TEM dark-field image recorded using a diffraction maximum from the α phase in a sample heated at 5°C/min to 350°C, held at that temperature for 90 minutes, and then quenched to room temperature. (c) Same as in (b) except the sample is held at 350°C for 3 hours prior to quenching to room temperature. (d-f) Processed images of the experimental ones in (a-c), respectively, which yield quantitative information for the two different heat-treatments, see text for details.

Figure 8. Profiles recorded using APT showing the compositional variations in the α and β phases in a sample heat-treated as in Fig. 6(d).

Figure 9. Atom probe analysis of sample heat-treated as in Fig. 6(e). (a) an ATP compositional map (5% Ti and 10% Al atoms) showing a fairly uniform composition. (b) The comparison of observed distribution of Ti atoms and the binomial distribution.

Figure 10. Schematic diagrams showing the possible variations in free energy curves that would be consistent with the experimental results shown in Fig. 6(e). $c_0(T)$ is the c_0 composition at

temperature T ; c is the average initial composition; $c_{\alpha}(T_1)$ is the non-equilibrium composition of α precipitates at the lower (T_1) temperature.

Figure 11. Gibbs free energy curves for the Ti-Mo system. The vertical lines are drawn at a composition of $\approx 9\text{wt\%Mo}$, the Mo-equivalency value for the alloy Ti-5553. (a) 350°C ; (b) 600°C .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 6 (cont)

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11.

Graphical Abstract

more-refined α microstructure