

Observation of a new B2 structured phase in Ti-15Mo (wt%)

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ARTICLE INFO

Keywords:

Titanium alloys
Phase transformation
Transmission electron microscopy
STEM HAADF
Electron spectroscopy

ABSTRACT

The formation of non-equilibrium and transient phases in metastable beta titanium alloys during low temperature thermal treatments is currently of great interest, as they provide a potential method of controlling the size and distribution of the equilibrium alpha phase and, hence, the resulting mechanical properties. Here, for the first time, we report on the formation of a new, B2 structured phase in the Ti-Mo system. The phase was observed in electron transparent material during *in situ*, and following *ex situ*, heat treatment at 300 °C. The B2 phase was enriched in Mo compared to the surrounding matrix material and formed in regular arrays of approximately square cross-section particles interspersed by thin beta channels. Electron diffraction indicated that the lattice parameter of this new phase was smaller than that of the parent phase, leading to significant strain in the beta channels. Critically, the B2 phase was only observed in material that had been electro-polished prior to heat treatment, and, therefore, it is hypothesised that this phase forms as a result of the preparation method and thin foil effects.

1. Introduction

Metastable beta (β) titanium alloys, which retain the high temperature bcc phase when quenched from the β phase field, are used in many high strength applications, including the landing gear of large civil aircraft [1–3]. One of the reasons for their utilisation is the ability to tailor the mechanical properties of these alloys through careful control of the microstructure during ageing heat treatments. The size, volume fraction and distribution of the reinforcing hexagonal alpha (α) phase ultimately determines the property balance of the material and, therefore, the ability to control the nucleation of the α phase is highly desirable [4–7].

Following rapid cooling from high temperature, the microstructures of these alloys are almost always found to contain nanoscale particles of the athermal omega (ω) phase in addition to the metastable β phase [8, 9]. This phase forms through the consecutive collapse of pairs of $\{111\}_{\beta}$ as a result of a soft phonon mode in the β phase and the particles are compositionally indistinct from the surrounding matrix [10, 11]. It is widely accepted that these particles can influence the nucleation of the α phase during subsequent heat treatments, thereby providing a method for microstructural control [12]. However, the exact mechanism by which this occurs remains under debate [13–16] and some of the most recent work has suggested that α phase nucleation may, in fact, be independent of the athermal ω phase [17].

Heat treatment at temperatures below that at which the α phase may form produces microstructures consisting of a β matrix and compositionally distinct precipitates with a similar crystal structure to that of athermal ω , commonly called isothermal ω [9]. These precipitates tend to have compositions that are rich in Ti, when compared to the matrix phase, and reject the alloying additions that stabilise the β phase [18, 19]. As these precipitates offer a potential route for microstructural control, understanding their development from a precursor microstructure of β and athermal ω is of great interest to the titanium community. As a result, several studies have looked at the microstructural evolution of different metastable β alloys during low temperature heat treatments [6, 20–26]. In the course of these studies, additional non-equilibrium phases have been observed, some of which are thought to be transient [27–36]. In the Ti-Mo system, transmission electron microscopy studies of relatively leanly stabilised alloys (with 6 and 8 wt% Mo) indicated that the orthorhombic martensite, present following quenching, spinodally decomposed during low temperature heat treatments [27, 28, 37]. This observation requires the existence of an orthorhombic phase with a composition intermediate to that of the equilibrium β and α phases. The occurrence of this phase is also supported by more recent X-ray diffraction data, where an orthorhombic structure was identified to form transiently prior to the equilibrium α phase in four different Mo containing commercial alloys: VT22 [32], Low Cost Beta [32], Ti-17 [33] and Ti-5Al-5Mo-5 V-3Cr [33]. Due to the

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<https://doi.org/10.1016/j.matchar.2018.06.017>

Received 15 March 2018; Received in revised form 5 June 2018; Accepted 10 June 2018

Available online 11 June 2018

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structure of this transient phase, it has been identified as the α'' martensite [32, 33]. However, this attribution seems unlikely as the orthorhombic phase observed formed during heat treatment, was compositionally distinct from its parent phase, and no α'' was identified following quenching from the β phase field [31]. As a result, the orthorhombic phase in Ti-5Al-5Mo-5V-3Cr has been studied in more detail using high-resolution electron microscopy and the results have indicated that the orthorhombic phase is, in fact, ordered and has a significantly larger unit cell than initially reported [29].

All of these studies highlight the need to develop a better understanding of the transformation sequences that can occur in metastable β titanium alloys during low temperature heat treatments, particularly with respect to transient transformations. Whilst there is an obvious attraction to studying commercial alloys, their inherent compositional complexity can make the interpretation of experimental data more challenging [11]. Consequently, data from simple binary systems can often provide more robust results. Therefore, in the current work, transmission electron microscopy was used to investigate the phase and microstructural evolution in a model binary metastable β alloy (Ti-15Mo wt%) during both *in situ* and *ex situ* thermal exposures at 300 °C.

2. Experimental Methods

An 8 mm diameter bar of Ti-15Mo (wt%), the actual composition of which is given in Table 1, was supplied by Rolls-Royce plc. A section of the bar was heat treated in an evacuated and argon backfilled quartz ampoule at 800 °C (~25 °C above the β transus temperature) for 1 h, followed by water quenching. From this material, four 0.4 mm thick slices were taken, perpendicular to the major axis, using a diamond impregnated sectioning wheel. A 3 mm diameter disc was subsequently removed from each slice through spark erosion. Three of these discs, A, C and D were immediately thinned to electron transparency via twin jet electropolishing with a 8% HClO₄ solution in CH₃OH at –35 °C and an applied voltage of 18 V, whilst Disc B was left at its original thickness. Disc A was studied in the as quenched condition, to provide a reference starting microstructure for all other samples. Disc B was heat treated in the un-thinned condition for 1 h at 300 °C in a Linkam TS1500V stage under flowing argon, before being thinned to electron transparency as described above. Disc C was studied *in situ*, during a heat treatment at 300 °C, using a JEOL 200CX transmission electron microscope (TEM). Whilst Disc D, which was pre-thinned, was subjected to an identical *ex situ* heat treatment to that of Disc B.

Bright-field (BF) images, dark-field (DF) images and selected area diffraction patterns (SADP) were obtained through conventional TEM in a JEOL 200CX and an FEI Tecnai Osiris both operated at 200 kV. Chemical information was obtained via energy dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS) in the FEI Tecnai Osiris operated in Scanning TEM mode (STEM) using an FEI Super-X system and a Gatan Enfium ER 977 spectrometer respectively. The Gatan Enfium spectrometer has dual EELS capability, where signal from two different energy ranges can be collected nearly simultaneously. For the EELS measurement, a collection angle of 100 mrad was used and the integrated energy evaluated over a 50 eV range. The corresponding ionisation cross-sections were taken from the standard Gatan database. High-resolution aberration corrected images, with sub-angstrom resolution, were acquired in an FEI Titan³ operated at 300 kV, using both high and low angle annular dark field detectors (HAADF and LAADF respectively). The inner collection angle used to acquire the HAADF images was 80 mrad, whilst a 25 mrad angle was

Table 1

Measured composition of the material studied (wt%).

Ti	Mo	Fe	O	C	N	H
84.26	15.56	0.01	0.13	0.01	0.01	0.02

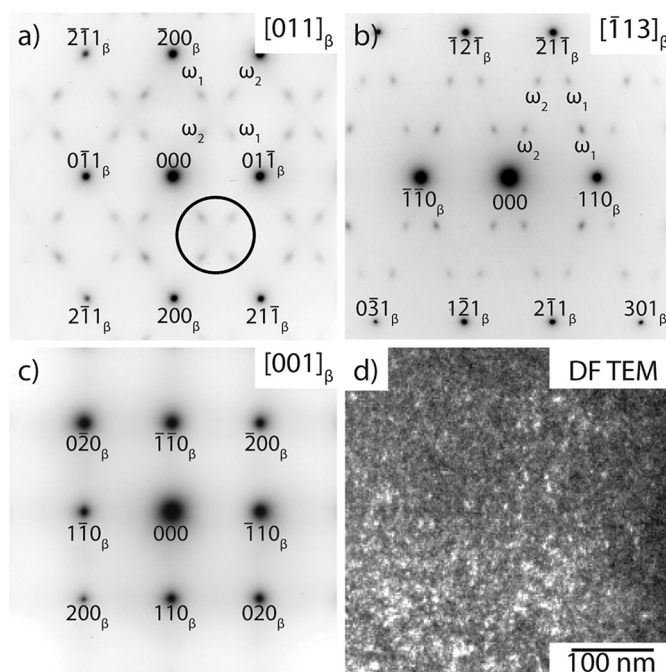


Fig. 1. Overview of selected area diffraction patterns (SADP) from Ti-15Mo (wt %) in the β solutioned and quenched condition, which contains reflections consistent with the presence of both β and athermal ω phases, acquired along a) $[011]_{\beta}$, b) $[113]_{\beta}$, c) $[001]_{\beta}$ and d) dark field image acquired using the four ω reflections indicated in part a).

used to acquire the LAADF images.

3. Results

SADPs from the as-quenched material, Disc A, viewed down a number of β zone axes are shown in Fig. 1. The patterns shown in Fig. 1a and b, which corresponded to the $[110]_{\beta}$ and the $[\bar{1}13]_{\beta}$ zones respectively, are typical of those reported for a metastable β alloy following quenching from the β phase field. They contain strong β reflections and weak, diffuse reflections at the $1/3$ and $2/3 < 112 >_{\beta}$ positions, consistent with the presence of the two different athermal ω phase variants visible in these β planes [38]. The diffraction pattern acquired along the $[001]_{\beta}$ exhibits no unique ω reflections, as the orientation relationship between the two phases results in identical interplanar spacings when viewed along this direction [31, 39]. A conventional DF image, acquired using the four ω reflections within the circle marked on Fig. 1a, is shown in Fig. 1d. As can be seen, imaging the athermal ω regions in this manner is extremely difficult and does not produce clear information as to the morphology or size of the phase. However, all of the data shown in Fig. 1 is consistent with recent high resolution studies on material in the same condition, which found no evidence of any other phase being present [11, 40].

An *ex situ* heat treatment, expected to form isothermal ω , was performed on Disc B, which was thinned after thermal exposure. SADPs from this sample acquired down the $[001]_{\beta}$ and $[011]_{\beta}$ are shown in Fig. 2a and b respectively. In the $[001]_{\beta}$ SADP, Fig. 2a, only reflections corresponding to the β phase are apparent, whereas the presence of the ω phase is clearly visible in the SADP acquired along the $[011]_{\beta}$, Fig. 2b, where there is strong intensity at $1/3$ and $2/3 < 112 >_{\beta}$. In addition to these strong independent ω reflections, weaker reflections were also observed at $1/3$ and $2/3 < 110 >_{\beta}$ and $< 200 >_{\beta}$, labelled by the letter d. However, these reflections were not seen in the $[001]_{\beta}$ SADP, Fig. 2a, despite both the $< 110 >_{\beta}$ and $< 200 >_{\beta}$ being contained within the $\{001\}_{\beta}$. This suggested that the weaker spots, observed in Fig. 2b, were a result of double diffraction, which was

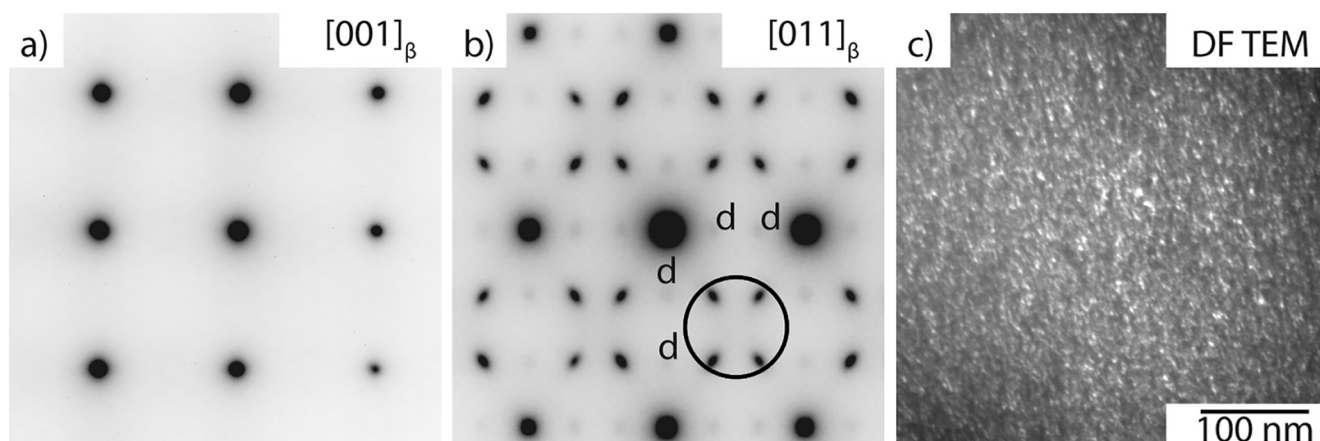


Fig. 2. Ti-15Mo (wt%) heat treated at 300 °C for 1 h followed by electropolishing to a thin section, a) SADP down the $[001]_{\beta}$, b) SADP down the $[011]_{\beta}$, and c) DF image of the isothermal ω precipitates generated using the encircled reflections in b). The intensity maxima demarked d in part b are a result of double diffraction.

confirmed through their disappearance when the sample was subjected to small tilts away from the zone axis. A DF image of the isothermal ω precipitates, produced using the four reflections encircled in Fig. 2b, is shown in Fig. 2c. It can be seen that the precipitates are fine scale (< 10 nm) ellipsoids and homogeneously distributed within the parent β matrix, consistent with previous reports using both TEM [41, 42] and atom probe tomography [18, 19, 25, 43].

To elucidate the transition of the ω phase from the athermal to the isothermal state, an *in situ* TEM heating experiment was performed. Disc C, which was already thinned to electron transparency, was heated to 300 °C in a double tilt holder. Prior to heating, the sample was aligned to the $[001]_{\beta}$ zone axis and an SADP and corresponding BF image of the microstructure acquired, Fig. 3a and b respectively. The same region of the sample was observed during heating and realigned to $[001]_{\beta}$ once the temperature had reached 300 °C. An SADP and corresponding BF image were acquired after a 15 min exposure at the target temperature and are shown in Fig. 3c and d. The SADP along the

$[001]_{\beta}$ following thermal exposure, Fig. 3c, was markedly different to that acquired at room temperature, Fig. 3a. The reflections visible at room temperature were circular, whereas the same reflection positions at elevated temperature were asymmetric with an outward skew away from the transmitted beam (*i.e.* smaller d-spacings). In addition, new reflections were observed at positions of approximately $1/2 < 200 >_{\beta}$, which do not correspond to either the β or ω structures. Therefore, these reflections indicated the presence of a new phase. The corresponding BF image, shown in Fig. 3d, also exhibited a significant change from the equivalent room temperature image, Fig. 3b, and showed the presence of a regular array of fine scale features with an approximately square cross-section.

Care must be taken when considering TEM data obtained from an *in situ* heat treatment as diffuse scattering increases and thermal drift reduces the quality of the image. In addition, it was not possible to obtain diffraction data from other zones, as the heating stage had limited tilting capabilities. To overcome these issues, Disc D, which had already been thinned to electron transparency, was heat-treated *ex situ* under identical conditions to Disc B. SADPs from the $[001]_{\beta}$ and $[011]_{\beta}$ of Disc D are shown in Fig. 4, along with a BF image of the microstructure. The additional reflections located at $\sim 1/2 < 200 >_{\beta}$, which were seen in Fig. 3c, were also observed in the material heat treated *ex situ*, Fig. 4a. Similar additional reflections were observed at the same locations in the $[011]_{\beta}$ SADP of the *ex situ* heat treated sample, Fig. 4b, along with reflections at $1/3$ and $2/3 < 112 >_{\beta}$ corresponding to the ω phase. The presence of additional diffracted intensity at locations that are consistent with the forbidden reflections of a bcc lattice, suggested that the sample contained a primitive cubic structure with a unit cell similar in size to that of the parent β phase. Interestingly, although both the $[001]_{\beta}$ and $[011]_{\beta}$ SADPs showed a cube-cube orientation relationship existed between the two phases, the alignment of the square cross-sectioned features seen in Fig. 4c indicated that the faces of these features were along the $\{110\}_{\beta}$ rather than along the $\{100\}_{\beta}$.

Based on the evidence from the SADPs it seems likely that the additional reflections corresponded to the B2 structure, but this intermetallic phase has not been reported in the Ti-Mo binary system. Crucially, the formation of this phase would nominally require a 1:1 ratio between Ti:Mo and, therefore, significant local compositional changes would have had to occur during the short thermal exposure. To investigate whether such changes had occurred, material aged *ex situ*, Disc D, was studied in an STEM instrument equipped with both EDX and EELS detectors. An annular dark field (ADF) image of the microstructure is shown in Fig. 5a. Significant intensity variations can be seen within the material with approximately square features, similar to those observed from the same area under conventional bright field TEM conditions, Fig. 4c. When imaging in ADF mode, intensity variations are

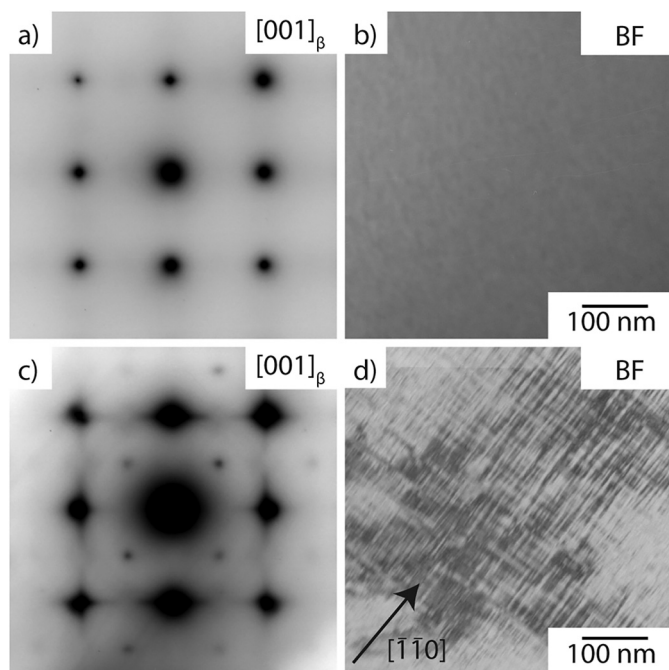


Fig. 3. Ti-15Mo (wt%) prior to and following *in situ* heat treatment at 300 °C in the TEM a) SADP down the $[001]_{\beta}$ prior to heating, b) corresponding BF image of the microstructure, c) SADP down the $[001]_{\beta}$ following 15 min at 300 °C and d) corresponding BF image of the microstructure.

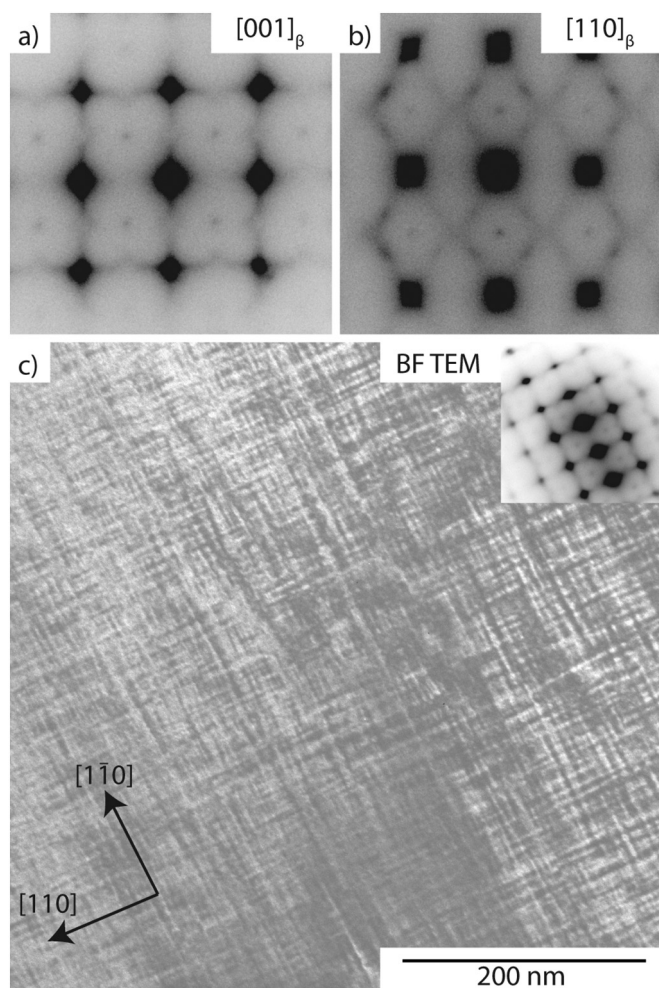


Fig. 4. Pre-thinned Ti-15Mo (wt%) following an *ex situ* heat treatment at 300 °C for 1 h a) SADP down the $[001]_{\beta}$, b) SADP down the $[011]_{\beta}$ and c) BF image of the microstructure viewed along the $[001]_{\beta}$.

a result of both chemical and strain inhomogeneities within the sample. EDX generated elemental distribution maps, acquired from the area within the box drawn on Fig. 5a, are shown in Fig. 5b and c for Ti and Mo respectively. The distribution map for Ti, Fig. 5b, indicated the presence of compositional variation within the material, which corresponded to the features observed in the ADF image, Fig. 5a. The narrow

channels of bright contrast within the ADF image are enriched in Ti and surround approximately square cross-section regions that have a lower Ti concentration. However, the inverse trend was not observed in the Mo distribution map, Fig. 5c, which did not show any significant variations in signal above the noise. The distribution maps for Fe and O were also considered but neither showed any appreciable variations that could be associated with the microstructural features.

Another method of studying compositional variation in a STEM is to use electron energy loss spectroscopy. However, the large difference between the edge energies of Ti and Mo make single detector measurement challenging, except at low energies (e.g. 200–700 eV). Unfortunately, within this energy range, the Mo $M_{4,5}$ edge has a delayed edge onset and low signal above background. In addition, the close proximity of this Mo edge to the C K edge makes the accurate determination of the peak area difficult, even using advanced analysis techniques [11]. To overcome these issues, two independent EELS energy ranges were used to make near simultaneous measurements over different energy ranges. One range covered 200 to 700 eV, which encompassed the sharp Ti $L_{2,3}$ edges, whilst the second, set between 2000 and 2700 eV, captured the Mo $L_{2,3}$. One of the most significant advantages of an EELS measurement with a binary alloy is the ability to quantify the compositions without reference to an external standard. The ratio of the post edge areas can be directly related to composition through the use of cross section analysis [44]. This analysis approach also suppresses the influence of sample thickness variations. An ADF image of Disc D is shown in Fig. 6a, corresponding to the area from which EELS data was acquired. The resulting dataset was processed using *k* factor analysis and the compositional profile of the line drawn on Fig. 6a is shown in Fig. 6b. The error in the calculated composition, indicated by the error bar on the first data point, was taken as the standard deviation in the entire EELS dataset. The compositional profile, determined from both the Ti and Mo EELS data, showed variations across the microstructural features well in excess of the error. The darker contrast square features in the ADF image, Fig. 6a, appeared to have an elevated Mo content, whilst the brighter contrast channels were Ti rich, in line with STEM EDX data, Fig. 5b. However, exact correspondence between the ADF image and the EELS dataset is unlikely given the effect of beam drift and drilling at this length scale.

As mentioned previously, the contrast observed in ADF images is generated by both compositional variation and strain. In both Figs. 5a and 6a, the Ti rich channels appeared brighter in contrast than the Mo rich phase. This would suggest that the signal is being dominated by strain, as the inverse contrast would be expected from the elemental partitioning. To establish this observation more conclusively, high and low angle annular dark field images were acquired, in which the contrast variation is dominated by composition and strain respectively.

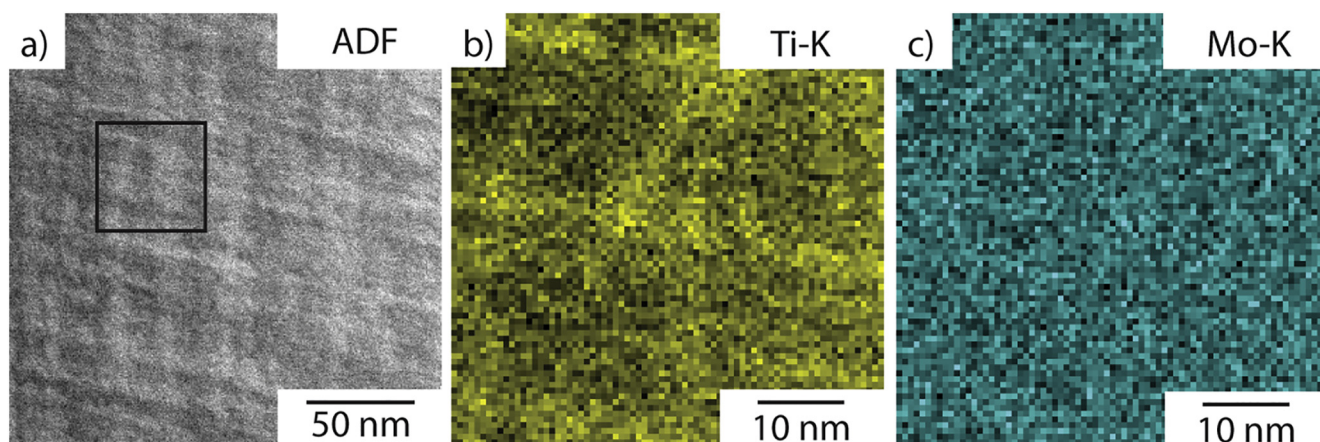


Fig. 5. STEM analysis of Disc D a) ADF image from the same region as that shown in Fig. 4 showing an significant intensity variation within the microstructure and STEM-EDX maps acquired from the area within the box shown in a) for b) Ti and c) Mo.

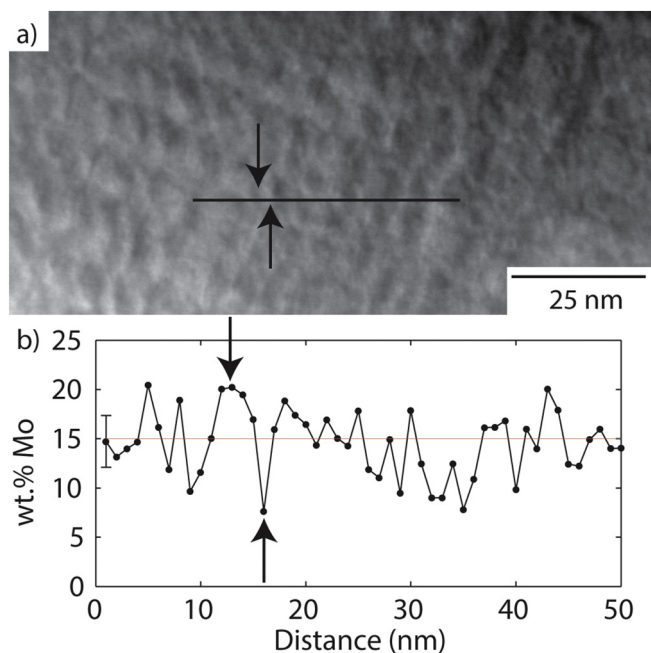


Fig. 6. a) Annular dark field image of Ti-15Mo (wt%) following an *ex situ* heat treatment of 1 h at 300 °C and b) composition variation along the line shown in part a) determined through cross section analysis of EELS data. The arrows indicate the data corresponding to a Mo-rich B2 region and a Mo lean matrix region respectively.

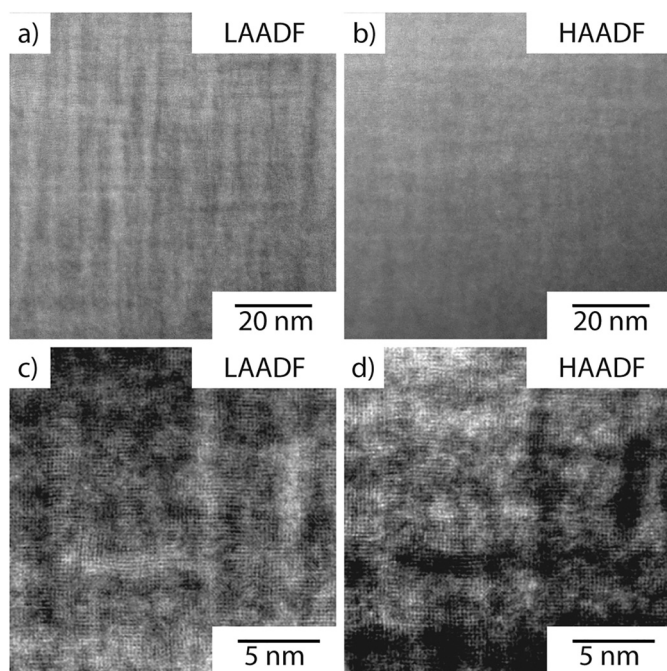


Fig. 7. a & c) Low and b & d) high angle annular dark field images of the microstructure of Ti-15Mo (wt%) following an *ex situ* heat treatment of 1 h at 300 °C.

Raw LAADF and HAADF images, acquired simultaneously down the $[001]_{\beta}$, are shown in Fig. 7a and b. It is immediately obvious that greater contrast variation exists in the LAADF image than the HAADF image, in line with the other ADF images. Higher magnification, contrast enhanced, images from both modes are shown in Fig. 7c and d. Both images contain perpendicular features with inverse contrast between the two modes. The HAADF image, which is dominated by

composition, shows darker contrast channels between brighter, square-like areas, suggesting Ti rich channels and Mo rich square regions, in agreement with the spectroscopy data. The corresponding features in the LAADF image, which is strain dominated, indicate that the channel regions contain more strain than the new phase.

The Fourier transform of a high resolution STEM image produces a frequency map of the periodicities in the original image, equivalent to an SADP. Fig. 8a is a raw high resolution HAADF image of Disc D along the $[001]_{\beta}$ and the corresponding frequency map is shown in Fig. 8b. Despite the contrast variations in the raw HAADF image being relatively faint, the fast Fourier transform of the atom columns provide evidence of the B2 phase similar to the conventional SADPs presented in Fig. 4a. Whilst the eye is unable to distinguish the extra frequencies within Fig. 8b, the additional maxima become clear when plotting the intensities within the two boxes as a function of position, Fig. 8c. Within profile 1, which corresponds to a $[200]_{\beta}$, extra intensity is observed approximately half way between the central point and the $\{200\}_{\beta}$. In addition, the $\{200\}_{\beta}$ frequencies appear to be separating into two distinct maxima. Similarly, this effect was also observed within profile 2, where the $\{110\}_{\beta}$ peak had clearly split into two components, which are symmetric around the central point. These observations are also consistent with the asymmetry of the SADP reflections in Fig. 3c. Thus, within the HAADF image both the β and B2 phases are present. Comparing the d-spacing of the $\{002\}$ peaks with that of the $\{001\}_{B2}$ indicated that the B2 phase had a slightly smaller lattice parameter than the β phase. This observation is consistent with the reported influence of Mo concentration on the lattice parameter of the β phase.

To examine the relationship and interface between these two phases in more detail, annular dark field images of the same region but at different magnifications were considered. As an orientation, Fig. 9a presents a relatively low magnification LAADF image of the studied area viewed down a $\langle 100 \rangle_{\beta}$ zone axis. The bright contrast strained channels, which were presented in Fig. 7a, are clearly visible and are aligned with the $\langle 110 \rangle_{\beta}$. The material within region b was studied at higher magnification and the corresponding frequency map is shown in Fig. 9b, which is essentially identical to that presented in Fig. 8b. By selecting only the frequencies that correspond to the atom periodicities of the two crystal structures, a Fourier filtered image can be produced that suppresses background noise. The mask used in the present work is overlain on Fig. 9b and was used to filter an atomic resolution HAADF image acquired from region c, Fig. 9c. The individual atom columns are clearly visible within the image and variations in their intensity, and therefore average atomic number, can be observed. To show this variation more clearly, the intensity of the entire row of atoms within the black box is plotted in Fig. 9d. Moving from left to right, the atom column intensity changes from approximately even to showing a periodic brighter – darker variation. This change in intensity marks the boundary between the solid solution β phase and the ordered B2 structure, as shown by the schematic unit cells in Fig. 9c. Interestingly, it is clear that the interface plane between the two phases is $\{100\}_{\beta}$, which corresponds to the expected cube-cube orientation relationship between the β matrix and B2 precipitates, and not the $\langle 110 \rangle_{\beta}$ alignment of the channels.

4. Discussion

The elements that stabilise the β phase are commonly separated into two categories based upon their binary phase diagrams. Elements such as Mo, Nb, Ta and V, which form continuous body centered cubic solid solutions with Ti, are referred to as isomorphous additions, whilst elements such as Fe, Co and Ni, which form intermetallics with Ti, are known as eutectoid formers [45]. The intermetallic phase in these eutectoid systems is often a B2 structured phase but its formation in binary isomorphous element alloys has not been reported previously. Thus, the evidence presented in Fig. 3 to Fig. 9, all of which indicates the presence of a B2 structured phase, is surprising.

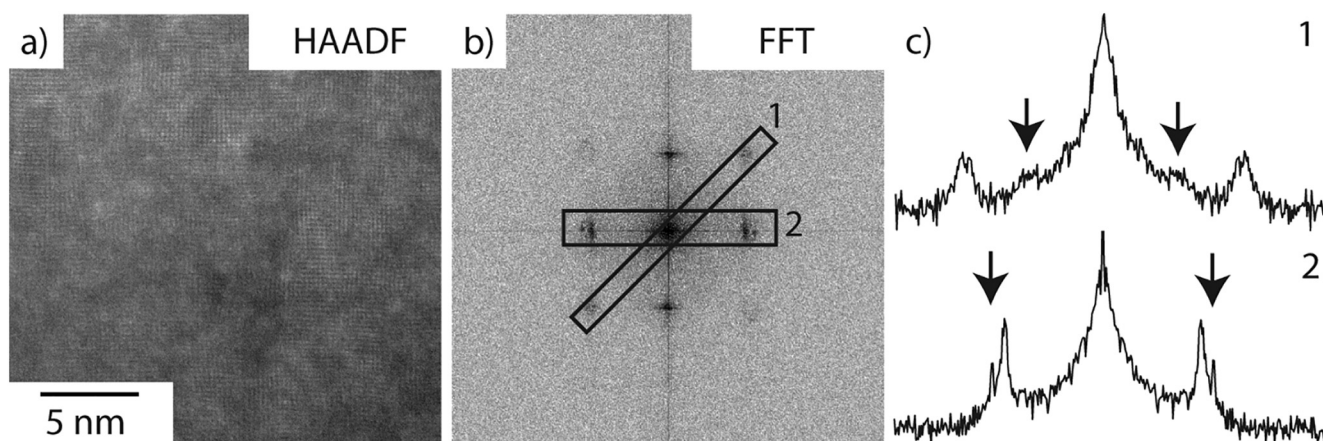


Fig. 8. a) Raw high angle annular dark field image acquired down the $[001]_{\beta}$ from Ti-15Mo (wt%) following an *ex situ* heat treatment of 1 h at 300 °C, b) reduced fast Fourier transform of part a, and c) intensity profiles taken from the corresponding boxes in part b. The arrows in c) highlight the presence of the additional B2 phase reflections.

Within the Ti-Mo binary system, several other phases are known to form, including the equilibrium α phase and two martensite phases, α' and α'' . However, all of these phases have lower symmetry crystal structures and markedly different lattice parameters, which are inconsistent with the data presented. For the same reason, the additional reflection seen in the SADPs from Discs C and D, Fig. 3 and Fig. 4, cannot correspond to the ω phase, as clearly shown in Fig. 2a.

The Ti-Mo binary system has been reported to contain a miscibility gap, which suggests that alloys of a certain concentration would undergo a phase separation [46–48]. Recently, this concept has been adapted to develop the mixed-mode transformation mechanism in Ti-Mo alloy and used to explain the decomposition of the β phase into $\beta + \omega$ [48]. However, this mechanism would not lead to the formation of a B2 phase and at no point during the present work has any evidence been found to suggest the co-existence of two bcc phases, required for a spinodal decomposition. In addition, if a phase separation was responsible for the occurrence of the B2 phase, it is unclear why this should not also have occurred in the bulk specimen, Disc B.

The fact that the B2 phase was only observed in the thin foils suggests that the material underwent a change in structure as a result of the electro-polishing step. It is not uncommon for thin foils to show different phase and behaviour to bulk material [36, 49–51]. During thinning, and despite the low temperature, it is possible the material may have taken up hydrogen, which has significant solubility in the β phase. It has been suggested that this hydrogen could be retained following electro-polishing if a sufficiently thick oxide layer exists on the sample [36]. The presence of hydrogen within the material during thermal exposure would either stabilise the β phase, or if present in significant concentration could result in the precipitation of hydride phases [52]. If hydrides were assumed to form, then they would be expected to exist as either the face centered cubic, δ , or in a tetragonally distorted form, depending on the exact hydrogen concentration [36, 52, 53]. However, when considering typical lattice parameters for these phases in the Ti-Mo system, ~ 4.431 Å for the δ phase and ~ 3.186 & ~ 4.107 Å for the tetragonal phase [53], there are no allowed reflections that have interplanar spacings consistent with the $1/2 < 200 >_{\beta}$ positions observed in the present work. As a result, hydride formation cannot account for the observed features in the experimental diffraction patterns.

Hydrogen is a potent β stabilising element and has significant solubility within the β phase, up to ~ 1.5 at.% [52] but it exhibits no appreciable solubility in Mo [54]. As a result, an uptake of H during electro-polishing could have altered the thermodynamics of the system prior to heat treatment. Given the immiscibility of H in Mo it is possible that the presence of H in the thinned samples could have promoted

some form of β phase separation, leading to the formation a B2 phase, that would not be observed in a bulk specimen. However, the assessment of local hydrogen concentration is extremely complicated and beyond the scope of the EDX and EELS techniques employed in this work. Thus, at present, the role of hydrogen in mediating the formation of the B2 phase is unestablished.

The production of a thin foil also reduces the local constraint on the specimen, which would have been previously imparted by the surrounding material. This alteration could also affect the local thermodynamics of the system, as the strain contribution to the Gibbs energy is lessened. Since the B2 phase was found to possess a smaller lattice parameter than the β phase, Fig. 8, its precipitation in the β matrix would create a surrounding strain field, as shown in Fig. 7. Without the presence of a free surface the magnitude of these strains within the β phase could be higher and may inhibit the formation of the B2 phase. Thus, it is conceivable that the Gibbs energy of the B2 phase may only offer the lowest energy state in a thin foil. However, without further investigation, the relative contributions of these different effects cannot be established and so the precise reason why the B2 phase only appears to form in thin foils remains unclear.

Whilst, the results presented here are the first direct evidence of a B2 structure existing in the Ti-Mo system, similar microstructures comprising different phases have been reported before in Ti-Mo alloys with lower Mo concentrations. Cellular microstructures on the same length scale to those reported here, have been observed in Ti-(4–8)Mo (wt%) alloys following thermal exposure at temperatures between 450 and 550 °C [27]. Outside of the Ti-Mo system, tweed microstructures containing a B2 structure have been observed in Ti-Al-Nb alloys [55]. In addition to the similar appearance of the tweed to the square-cross section features reported here, the same $< 110 >_{B2}$ directionality was observed. It is thought that the tweed microstructures in these systems are a precursor to the martensite transformation and is caused by the softening of $< 110 >$ phonon modes [55]. In theory, the martensite transformation could be triggered by a strain energy gradient analogous to the role of composition in traditional spinodal decomposition [56]. This “strain spinodal”, containing regions of high and low strain, might explain the nature of the tweed microstructures and the $< 110 >_{\beta}$ square cross sections shown here. Interestingly, it is argued that thin material, which includes effects from two surfaces, may be sufficient to place the free energy density as a function of strain close to a strain spinodal [45]. Therefore, it is possible that the B2 phase observed here could be the result of a complex interaction between $< 110 >$ phonon softening and thin foil effects during transient phase formation.

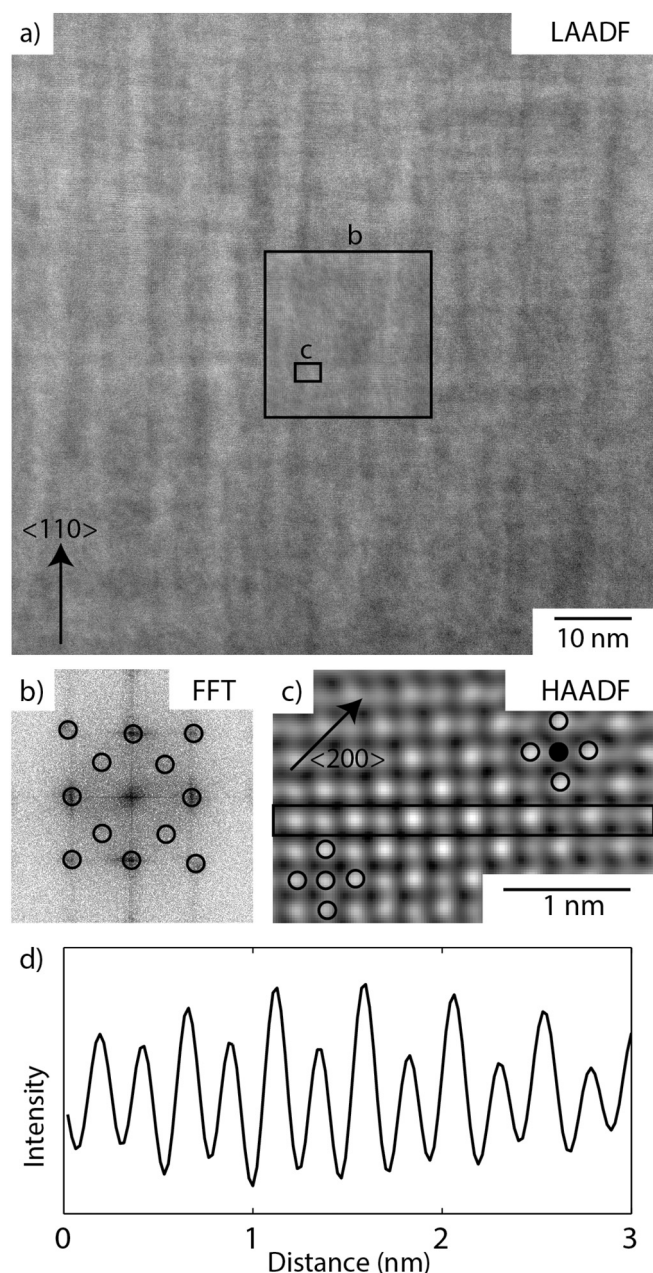


Fig. 9. a) LAADF image of the regions studied, showing the bright contrast strained channels, b) reduced fast Fourier frequency map from region b including the frequencies selected (within circles) to produce subfigure c, c) Fourier filtered HAADF image from region c and d) intensity profile of the atomic columns within the box shown in part c.

5. Conclusions

The phase and microstructural evolution of Ti-15Mo wt% during heat treatment at 300 °C has been characterised through transmission electron microscopy using both *in situ* and *ex situ* techniques.

In all cases, the samples were taken from an 8 mm bar, which had been quenched from the β phase field. The microstructure of this bar has previously been characterised in detail [11], and consisted of retained β grains within which extremely fine athermal ω precipitates were observed.

A bulk, 400 μ m thick, disc was isothermally heat treated *ex situ* at 300 °C for 1 h. Following this exposure, no discernable change in the microstructure had occurred but the diffraction spots corresponding to the ω phase had sharpened. This is thought to be consistent with the

structural and chemical alterations associated with the transition of athermal ω to isothermal ω .

Pre-thinned foils, produced by twin jet electropolishing, were also thermally exposed at 300 °C, both *in situ* and *ex situ* of the electron microscope. In both samples, new additional reflections were observed in the selected area diffraction patterns, which were consistent with a B2 structured phase. In addition, regular arrays of square cross section features separated by thin channels became apparent in the electron images. The alignment of the diffraction patterns suggested that the two phases had a cube-cube orientation relationship. Compositional analysis using EDX and EELS indicated that the B2 phase was enriched in Mo, whilst the surrounding channels were enriched in Ti. Low and High Angle Annular Dark Field imaging supported the compositional analysis and indicated that the channels also contained an elevated level of strain. Analysis of high resolution images of the atom columns showed that the lattice parameter of the B2 phase was smaller than that of the β phase, rationalising the observed strain in the channels.

Whilst this is believed to be the first observation of the B2 phase in a Ti-Mo binary alloy, its formation is also thought to be a thin foil effect, as this phase was not observed in the bulk sample. The exact mechanism enabling the formation of the B2 phase in the thin foils is unknown, but is hypothesised to be due to hydrogen up-take, reduced constraint, or a combination of the two.

Acknowledgements

The authors would like to thank the EPSRC/Rolls-Royce Strategic Partnership for funding under EP/M005607/1 and EP/H022309.

Data Availability

The raw and processed data required to reproduce these findings are available to download from the following location: <https://doi.org/10.17863/CAM.20978>.

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