The formation of ordered clusters in Ti-7Al and Ti-6Al-4V

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Abstract

Ti-Al alloys can suffer from a chemical decomposition on ageing around 500°C or on air cooling. At long ageing times this results in the formation of $\alpha_2$ (Ti$_3$Al) precipitates. At reduced times or elevated temperatures, diffuse electron or neutron diffraction peaks can be observed, which has been termed ‘short range ordering’ (SRO). Here, we present correlative transmission electron microscopy (TEM) and atom probe tomography (APT) results showing that the reaction proceeds through the formation of ordered Al-rich precipitate clusters. Notably, Al-Al clustering could be observed well before the appearance of distinct precipitates in the TEM. In addition, the V-containing $\alpha$ phase of Ti-6Al-4V formed ordered clusters much faster than in binary Ti-7Al. This implies that the ternary addition of $\beta$-stabilisers exacerbates the problem of $\alpha_2$ precipitate formation in commercial dual phase titanium alloys.

Keywords: Titanium alloys, atom probe tomography (APT), ordering, transmission electron microscopy (TEM)

1. Introduction

Titanium alloys are widely utilised in aero-engine applications for critical rotating parts, with the majority of the commonly used $\alpha+\beta$ alloys possessing an Al concentration between 6 and 8 wt.% [1, 2, 3]. Ti-6Al-4V (wt.%) is an $\alpha+\beta$ alloy that offers a combination of good specific fatigue strength and corrosion resistance, and is therefore commonly used in aerospace applications [2]. The binary $\alpha$-Ti alloy Ti-7Al (12Al at.%) is frequently used [4, 5] as a model alloy to represent the $\alpha$ phase of Ti-6Al-4V. Thus there is an implicit assumption that the $\alpha$ phase is totally depleted in V, which is a $\beta$-stabiliser.

Cold dwell fatigue is a phenomenon where holding periods at load of the order of 2 minutes result in large ($10\times$) reductions in cyclic life. This is of concern to jet engine manufacturers for components such as Ti-6Al-4V fan discs.

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In Al-containing alloys, ordering of the $\alpha$-phase, observed as diffuse spots corresponding to the Ti$_3$Al structure in selected area transmission electron diffraction (SAD) patterns, has been frequently found to co-occur with poor dwell fatigue performance [6, 7]. At long ageing times at low temperatures around 500°C, these diffuse spots can eventually become identifiable single crystal electron diffraction spots that permit the imaging of nanoscale $\alpha_2$ precipitates [8]. The effect of heat treatment times and temperatures on $\alpha_2$ size for Ti-Al alloys with different Al concentrations has been studied since the late 1960s [8, 9, 10, 11, 12], but is still not well understood.

Ordering and spinodal decomposition result in a change in the dislocation behaviour, so the presence of the $\alpha_2$ phase may be suggested based on the observed dislocation network. Short, straight segments of prism $\{11\bar{2}0\}$ dislocations are observed to travel in pairs, as is required to avoid creating stacking faults in the $\alpha_2$ phase [13, 5, 11]. Such changes are observed even where imaging of the $\alpha_2$ phase is impossible, and also in samples that have been subjected to hydrogen-related hot salt stress corrosion cracking [10]. Moreover, planar slip was reported to occur [14] in alloys which were aged at 500°C, with the slip line distribution becoming coarser in alloys with higher oxygen content. Similar results were previously observed by Williams et al. [13, 15] in Ti-10Al wt.% (16Al at.%). It was suggested that the degree of order can influence the the slip nature (planar or wavy), and the slip distribution (coarse or fine). The appearance of the very coarse, planar slip was explained by the fact that dislocations cut the $\alpha_2$ particles.

The quantification of this ordering and spinodal decomposition phenomenon for air cooled samples or those aged at 625°C has remained very difficult [16, 17]. In principle, the difference between the Ti$_3$Al and hexagonal close packed (HCP) $\alpha$-Ti phases is twofold; (i) $\alpha$-Ti has a solubility for Al of only ~10 at.%, and (ii) in Ti$_3$Al, no Al-Al bonds exist. Therefore, it might be possible for ordering of $\alpha$-Ti to occur without long-scale chemical decomposition (only ii), or that a conventional chemical decomposition must first occur that enables the formation of ordered Ti$_3$Al precipitates. Superlattice spots have been observed [9, 11] in transmission electron microscopy (TEM). Furthermore, Neeraj et al. [18, 19] observed broad diffuse scattering peaks in neutron diffraction in Ti-6Al wt.% (10Al at.%), which have also been observed in Ti-7Al wt.% (12Al at.%) by Fitzner et al. [20]. Both Neeraj [19] and Brandes in Ti-7Al wt.% (12Al at.%) [5] observed diffuse spots in TEM, which could be suppressed by water quenching to provide a fully disordered $\alpha$-Ti structure. More recently, ordering in the $\alpha$ phase of Ti-6Al-4V has been observed by Wu et al. [21] at relatively short ageing times of 35 days at 500°C. In addition, Liew et al. [17] studied Ti-9Al wt.% (15Al at.%) by field ion microscopy (FIM) after 500 hours ageing at 650°C and 750°C, where ordering could be observed in the TEM but compositional variations could not. Therefore, the problem of quantifying this precipitation phenomenon has remained strongly intractable to analysis, by 1998-era atom probe tomography instruments (APT) [22, 23, 24, 25], by TEM and by neutron diffraction.

Recent advances APT enable this question to be revisited, and this is the topic of the present paper. APT is accompanied by conventional TEM using high dynamic range diffraction pattern characterisation. It is found that precipitation appears to occur much faster, and more strongly, in $\alpha$-Ti which is alloyed, very slightly, with V in Ti-6Al-4V than in the pure binary Ti-Al. This is compared to results for Ti-Al-V [21], Ti-Al-
Mo [26] and Ti-Al-Zr [27] alloys, where similar ternary alloying effects are observed.

2. Experimental Description

2.1. Material preparation

An ingot of nominal composition Ti-7Al wt.% (12Al at.%) Al was prepared by vacuum arc melting and hot rolled to 13 × 13 mm square bar at Timet Witton, Birmingham, UK. Commercial purity Ti sponge was used to obtain industrially representative levels of Fe and Si, and an O content of 1800 ppmw. The ingot was first homogenised at 1125°C and then β forged. β phase profile rolling followed by α + β phase profile rolling was performed at 1125°C and 800°C respectively in order to reduce the ingot to the final dimensions. Figure 1 contains images of the ingot preparation.

[Figure 1 about here.]

The rolled bar was then encapsulated in quartz under low pressure Ar and recrystallised at 1125°C for 60 min. An equiaxed microstructure with a homogenous grain size distribution of ~ 30 µm was obtained. Electron backscatter diffraction (EBSD) analyses of the samples were obtained using a Zeiss Auriga scanning electron microscope (SEM). The final microstructure and texture pole figures are provided in Figure 2(a-b). It is evident that a strong {11\overline{2}0} rolling texture was produced.

[Figure 2 about here.]

A plate of Ti-6Al-4V of measured composition 6.49Al, 4.04V, 0.22O, 0.16Fe wt.% (11.0Al, 3.6V, 0.6O, 0.1Fe at.%) manufactured by Timet was supplied by Rolls-Royce plc (heat HUB2428), in a near-equiaxed creep flattened and slow cooled in induction furnace condition. A representative SEM micrograph is shown in Figure 2(c); the material is further characterised in [28].

According to the Ti-Al phase diagram experimentally determined by Namboothiri [29], there is a short-range-ordering (SRO) region at an ageing temperature of ~ 600°C for Ti-Al alloys with concentrations around 6-7 wt.%. The ordering state of Ti-7Al was manipulated by employing different heat-treatment routes to produce five conditions of interest. The heat treatments were as follows: 920°C for 10 min, followed by (i) ice water quenching (IWQ), (ii) air cooling (AC), (iii) AC and then ageing at 625°C for 14 days (625/14), (iv) AC and then ageing at 550°C for 28 days (550/28), and finally (v) AC and then ageing at 550°C for 84 days (550/84). These five conditions were intended to produce progressively greater amounts of ordering. Samples of Ti-6Al-4V were heat treated as follows: 930°C, followed by (i) slow cooling (SC), (ii) SC and then ageing at 625°C for 14 days (625/14), (iii) SC and then ageing at 550°C for 28 days (550/28). The five heat-treatments of Ti-7Al and three heat-treatments of Ti-6Al-4V used in this study are presented in Table 1.
2.2. Transmission electron microscopy

Specimens for TEM were produced by spark eroding thin discs 3mm in diameter, which were then ground to a thickness of $\sim 0.15$mm and thinned to perforation with a Tenupol-5 twin-jet electropolisher using 3% perchloric acid (HClO$_4$), 40% butan-1-ol (C$_4$H$_{10}$O) and 57% methanol (CH$_3$OH) at -40°C with an applied voltage between 20 and 25V. Cooling the electrolyte minimises the amount of adsorbed hydrogen and results in more controlled polishing [30].

Samples from primary $\alpha$ grains in the Ti-6Al-4V alloy were produced by in-situ lift out in a dual beam focused ion beam/scanning electron microscope (FIB/SEM) [31, 32].

Transmission electron microscopy was performed using a (i) JEOL 2000FX 200kV TEM equipped with an Oxford Instruments ultra-thin window energy dispersive X-ray spectrometer (EDS), (ii) JEOL 2100F 200kV TEM/STEM equipped with EDS (XMax, Oxford Instruments) and EELS (Gatan, Quantum GIF with 0.8 eV energy resolution) and an (iii) FEI Titan 80-300 keV monochromated and dual Cs-corrected TEM/STEM.

2.3. Atom probe tomography

APT samples were prepared by the FIB lift-out method using a FEI Helios NanoLab 600 DualBeam system equipped with an Omniprobe™. A detailed description of the lift-out and tip sharpening procedure can be found in references [33, 34, 35, 36]. Atom probe experiments were performed in the voltage-pulsing mode using a CAMECA LEAP 3000X HR and a LEAP 4000X Si. The stage temperature and the voltage pulse fraction were set to 55K and 15%, respectively. After data collection, the atom maps from the runs were reconstructed utilising IVAS™ data analysis software [37].

3. Results and discussion

3.1. TEM investigation

The APT investigations were complemented by dark field TEM imaging based on electron diffraction experiments carried out to identify and visualise any precipitates or ordered structures present.

Prior experimental work on Ti-Al alloys showed that ordering could develop in alloys that had been aged or have been used in service at relatively low temperatures of around 500°C [18, 6]. A variety of methods have been used to investigate this phenomenon. Some contention has arisen around the $\alpha/(\alpha + \alpha_2)$ phase boundary due to the fact that the ordered regions are indirectly visible only using high resolution techniques after prolonged heat treatments [18, 6, 17]. The majority of publications on SRO have been based on TEM studies, particularly the analysis of SAD patterns. It was previously reported that Ti$_3$Al precipitates could be easily identified, as these produce superlattice reflections in SAD patterns [39]. Superlattice reflections occur symmetrically between the reflections from the disordered matrix along certain directions. This phenomenon is due to the fact that the lattice parameter of $\alpha_2$ is approximately twice...
that of $\alpha$. However, many studies [10, 11, 12, 17, 18] have shown the superlattice reflections in diffraction patterns of $\alpha$ and near-$\alpha$ titanium alloys after ageing, but very often it has not been possible to image ordered regions in dark field TEM. This has been explained by suggesting that the ordered regions were too small to be resolved. Although more work needs to be done to obtain conclusive evidence of the ordered structure, it seems to be reasonable to attribute the extra electron diffraction spots to the formation of ordered structures in the Ti-Al system.

[Figure 4 about here.]

In the IWQ and AC samples, only fundamental reflections from the matrix are evident in the SAD patterns, Figure 3(a-b). In contrast, the extra diffraction spots seen in Figures 3(c-d) arise from the ordered phase. After heat treatment for 84 days at 550°C, the superlattice reflections were strong enough to allow imaging in dark field of the ordered regions, Figure 4. From the samples which were aged for shorter times, it was not possible to obtain dark field images of precipitates.

The intensity of superlattice reflections depends on the sample thickness, holder tilt, and time of exposure. As a result, various zone axes and long exposure times were used to study ordering through the analysis of the diffraction patterns. Table 1 qualitatively compares the intensity of the visible superlattice reflections for different heat treatment conditions. The charge-coupled devices (CCD) commonly used in modern TEM cameras can be damaged by prolonged exposures, and so a JEOL 2100F TEM/STEM electron microscope was used, equipped with a camera and photographic film, allowing long exposure times. In the Ti-7Al (IWQ and AC) samples, even after a long exposure times, only reflections from the matrix were visible on the negatives. Reflections described as very, very weak were only seen on the negative when overexposed. In Ti-7Al samples 550/28 and 625/14, although the superlattice spots were clearly dimly visible, it was not possible to image precipitates of the $\alpha_2$ phase in dark field mode, even with prolonged exposure times.

[Table 1 about here.]

High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) imaging was carried out to try to visualise any compositional changes due to Ti$_3$Al ordering in Ti-7Al and Ti-6Al-4V (wt.%), in all conditions. No obvious contrast differences were observed on length scales from 1-500nm that could be attributed to Ti$_3$Al ordering. EDX, carried out on a JEOL 2100F TEM/STEM operating at 200kV and fitted with an Oxford Instruments XMax detector, confirmed that 6-7 wt.% Al was present in the Ti samples, but it was not possible to detect any local compositional variations.

According to Blackburn [10], $\alpha_2$ particles observed in Ti-8Al wt.% (13Al at.%) are spherical in shape initially and maintain this geometry up to around 50nm, finally elongating to form ellipsoids with the major axis lying along the [0001] direction. Blackburn observed rapid growth of the $\alpha_2$ phase once it was formed, however, the growth rate decreased at long ageing times. Similar results were later obtained by Namboodhiri et al. [11] in alloys containing 8.5 and 16.5 wt.% Al (13.8 and 23.8Al at.%). They...
observed a change in morphology from an irregular shape to an elliptical one with a diameter of 10nm. Our own observations are consistent with these results. In the Ti-7Al alloy aged for 84 days at 550°C, dark-field microscopy using a superlattice reflection revealed features 20 × 150nm in size with an elliptical morphology. These can be clearly seen in Figure 4.

Electron diffraction experiments were also carried out on the Ti-6Al-4V samples. The α phase in Ti-6Al-4V was found, using EDX in the SEM, to have the approximate composition of Ti-7.6Al-2.3V wt.% (12.8Al-2.0V at.%) , with the remaining vanadium mostly rejected to the β, as seen using EDX in the SEM. Diffraction patterns taken from the α phase of the SC sample contained additional spots to the fundamental reflections, Figure 5a. These additional weak reflections in the recorded SAD patterns imply that ordered domains are present. Figure 5(b-c) presents electron diffraction patterns taken from Ti-6Al-4V samples which were aged for 14 days at 625°C and for 28 days at 550°C, respectively. Clearly visible superlattice reflections suggest that such ordered domains have an α2 hexagonal D019 crystal structure.

The results of the SAD pattern observations in the present specimens of Ti-6Al-4V aged at temperatures between 550 and 625°C, suggest that the ordering in this alloy is faster than in the binary Ti-7Al alloys under similar conditions. Thus, while it is confirmed that ordering occurs in Ti-Al alloys with Al concentrations of around 6 wt.% (10 at.%), then moreover it appears that V additions to α Ti, even at quite small concentrations, result in faster α2 formation.

The Ti-6Al-4V sample aged at 550°C for 28 days was also examined by HRTEM in the JEOL 2100F, Figure 6. Spatial variations in the overall intensity of the atomic columns in high resolution imaging could be observed. When fast Fourier transforms (FFT) were taken of different subregions of the image, then in some of these regions (2 and 4), faint evidence of an α2 spot could be observed. Line profile analyses between the {011} and {000} spots are shown in Figure 7, and also indicate the presence of a peak corresponding to the α2 in subregions 2 and 4.

A dark field image taken using the superlattice spot from this sample in a image aberration-corrected Titan TEM is shown in Figure 8, which also shows spatial variations in intensity. Therefore, there is strong evidence for local variations in the extent of ordering, on the scale of 15-300nm.

The TEM studies in Ti-6Al-4V of Wu et al. [21] found weak superlattice maxima in doubly exposed diffraction patterns taken from a sample slowly cooled from 930°C. However, it was not possible to obtain dark field images of precipitates from these reflections as they were very weak. Furthermore, in samples aged for 35d at 500°C,
the development of $\alpha_2$ precipitates within the $\alpha$ phase was observed. It was reported that these precipitates possessed a composition of Ti$_3$Al with a diameter between 5 and 10 nm. Wu et al. [21] also presented APT studies illustrating Al-rich clusters corresponding to the Ti$_3$Al phase observed in the electron diffraction patterns. In the centre of the precipitates, the Al concentration was reported to be 20 at.% and the V concentration was approximately 2 at.%. The latter figure was much greater than the expected value, and it was speculated that slower diffusion of V contributes to this; the fact that diffusion would have to take place through an ordered $\alpha_2$ structure would further decrease the rate of diffusion. However, no experimental work was reported to confirm this hypothesis.

In summary, electron diffraction shows that ordered $\alpha_2$ hexagonal D0$_19$ forms more rapidly in Ti-6Al-4V than in Ti-7Al. Thus, V in the $\alpha$ phase increases the precipitation kinetics. Dark field imaging of Ti-7Al shows aligned $\alpha_2$ precipitates of elliptical morphology, 20 $\times$ 150 nm in size. This is in agreement with Blackburn and Namboodhiri et al. [10, 11]. For Ti-6Al-4V 550/28, FFT analysis of HRTEM micrographs combined with dark field imaging from an aberration corrected Titan TEM provide strong evidence for local variation in the extent of ordering through the microstructure.

### 3.2. APT studies

Even though many cluster identification algorithms have been developed, identifying the early formation of such features and determining their composition from APT reconstructed volumes may be non-trivial, particularly for alloys containing increasing amounts of solute [25]. A description of SRO can be attempted in terms of the nearest neighbour (NN) distributions. One technique commonly used to investigate this problem within an APT reconstruction is applying a $k$th-order nearest neighbour ($k$NN) analysis, which is particularly useful when looking for subtle clustering effects in alloys containing a significant amount of solute [22, 23, 24]. Other approaches are also available [38]. For very dilute alloys, the average 1NN distance between solutes in a cluster compared to solutes in the matrix will be significant, and therefore sufficient to isolate any clusters. However, for the present alloy, the 1NN distance between Al atoms in a cluster will be very similar to that in the matrix. (i.e. there is always another Al atom very close by). Only if we look at higher order nearest neighbours, such as 10NN, 20NN, 50NN and 100NN do we start to see clear deviations from a random distribution. On the other hand, it should be recalled that if $k$ is small it is more sensitive to very small fluctuations, for example clusters that may only consist of 5 solute atoms. However small $k$ analyses may be subject to significant random fluctuations. Larger $k$ values are more resistant to random fluctuations, but they also reduce the sensitivity (i.e. the size of clusters that can be identified) [24]. In the present case the bulk concentration of Al requires the use of a large $k$. The above discussion justifies the variety of different $k$NN chosen to highlight the distribution of distances separating each Al atom and its $k$th nearest neighbour Al atoms, Figure 9. In each case, a randomised data set is used as a comparator, (R).

[Table 2 about here.]

[Figure 9 about here.]
Analysing the 10NN distribution of the Ti-6Al-4V 550/28 sample, Figure 9, it can be seen that the experimental data and corresponding random distribution closely coincide. The broadening of the peaks for 50NN, 70NN and 100NN in comparison to their respective random distributions indicates a non-random distribution of Al atoms in the experimental data. The relatively greater counts at lower separations indicate a significant number of Al atoms distributed closer together than would be randomly expected, indicative of solute clustering [24]. In Figure 10(a-b), the data (D) and randomised (R) distributions are visualised, with blue points marking Al atoms that have Al neighbours within 1.12 nm. Visually, nearest-neighbour ordered regions on the order of 5 nm in size can be observed quite clearly in the data, which are barely present in the randomised data. The features appearing in the complementary random distribution are indicative of trajectory aberrations in the experiment leading to high density regions at the top of the reconstruction. However, since these regions are incorporated in both the experimental and randomised 50NN distributions they will not affect the statistical comparison between the two distributions.

These isolated Al-rich clusters were demarcated using a 20 at.% Al isosurface, and an Al concentration profile averaged across five similar clusters was generated. This suggests that these clusters have an Al content in excess of 20 at.%, Figure 10(c). This whole analysis was repeated on a duplicate sample of 550/28 Ti-6Al-4V, with the same results obtained. The 550/28 and 625/14 Ti-7Al samples were also examined, and no such clusters were found. In the Ti-6Al-4V 625/14 sample, some very tentative evidence for clustering could be observed in the 50NN distribution, but not at a level that was distinguishable from the randomised distribution.

In Ti-7Al the composition profiles showed only very marginal statistical fluctuations for the 50NN, 70NN and 100NN distributions in comparison to the randomised datasets. Although the TEM images show superlattice reflections, there was no evidence of Ti3Al precipitates from the APT experiments. The overall compositions of Ti-7Al needles examined using the LEAP 3000X HR after different heat treatments are shown in Table 2. It is significant that the Al concentration in a sample which was aged for 84 days at 550°C dropped to 4 wt.%. It is suggested that in this sample, the missing Al content was located in α2 precipitates in regions not contained within the atom probe analysis volume. From the TEM image, Figure 4, it can be clearly seen that the spacing between individual ordered regions is very large compared to the very small analysis volumes of APT samples. Thus it is possible that APT needles were lifted out between α2 precipitates.

In summary, a nearest neighbour analysis clearly illustrates Al clusters in Ti-6Al-4V 550/28. Based on the extensive TEM study presented, these clusters correspond to ordered α2 precipitates. There is tentative evidence of similar clustering in Ti-6Al-4V 625/14, and no evidence of clustering in the Ti-7Al alloys. Thus there is agreement between APT and TEM, that V in the α phase increases the precipitation rate of α2.

3.3. Discussion

Many aluminium-containing titanium alloys are used at elevated temperatures up to 500°C, for example in aero engine compressors. In such components, dwell fatigue
can be of concern and is associated with the localisation of deformation due to the formation of \((\alpha)\)-type dislocation ribbons in \(\alpha\)-Ti that shows evidence of so-called short range ordering (SRO). In fact, almost all commercial titanium alloys contain \(\alpha\) phase with Al contents high enough to place them within the \(\alpha + \alpha_2\) phase region originally identified by Namboodhiri et al. [11]. However, a clear, universal definition of what is meant by SRO has been lacking. Clearly, long range ordering is observed, as corresponding diffraction peaks in electron diffraction. The large breadth and low intensity of these diffraction peaks equally clearly indicate that ordering is incomplete. The APT analysis performed here suggests that such precipitates are clusters with an Al content in excess of 20 at.%. 

It is also interesting that the appearance of electron diffraction peaks was much clearer, and occurred after less ageing, in Ti-6Al-4V than in the Ti-Al binary alloy, even for quite similar \(\alpha\) phase Al contents. This suggests that in the ternary alloy, the \(\sim 2\) at.% V present in the \(\alpha\) plays an important role in promoting cluster formation. This indicates that V perhaps lowers the energy of formation for the \(\alpha_2\) phase and/or raises the diffusivity of Al in \(\alpha\)-Ti, e.g. by promoting vacancy formation. This is consistent with the hypothesis presented by Ramachandra [40]. 

Liew et al. [17, 12] have previously suggested that the formation of Al-rich clusters proceeds via a spinodal decomposition mechanism. In a spinodal, the compositional waves first form and then increases in amplitude until the stoichiometric phase compositions are formed. This is distinct from the case of, e.g. Ni\(_3\)Al, where only fully stoichiometric, ordered precipitates are observed [41]. The present work supports this hypothesis.

4. Conclusions

The formation of \(\alpha_2\)-Ti\(_3\)Al related structures in Al-containing \(\alpha\) Ti has been investigated during low temperature ageing from the disordered state. The following conclusions can be drawn:

1. TEM studies on Ti-7Al showed no evidence of chemical ordering in the IWQ and AC samples. Ordering, observed through the diffuse superlattice reflections in the selected area diffraction patterns, was found in samples which were annealed between at 550°C and 625°C for times up to 84 days.

2. After heat treatment of Ti-7Al for 84 days at 550°C, the superlattice reflections were strong enough to allow imaging of the ordered regions using TEM. At shorter ageing times it was not possible to obtain dark field images of precipitates. The same experiment was repeated on Ti-6Al-4V (slow cooled, 550/28,625/14), and in \(\alpha\) grains of the sample aged for 28 days at 550°C, ordered and disordered regions were observed to co-exist.

3. A \(k = 50\) nearest neighbour analysis of APT data from Ti-6Al-4V in the 550/28 condition showed that distinct Al rich regions could be observed, with an Al concentration greater than 20 at.%. Such clusters could not be observed in the Ti-7Al samples or in Ti-6Al-4V aged for lower times.

4. In the light of the present work and earlier investigations on Ti\(_3\)Al precipitation in Ti-Al alloys [40, 26, 42, 4, 43, 21, 27, 41] it is evident that ordering can occur in titanium
alloys containing more than 6 wt.% Al along with Zr, Si, Mo, or V after shorter ageing times than in the binary Ti-Al alloys.

Finally, APT was shown to be an excellent complementary method to electron diffraction studies and imaging by TEM for the study of ordering in Ti alloys.

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Table 2: Overall composition of the Ti-7Al needles examined, in wt. and at.%. Trace levels of H, N and C were also present.

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