Mechanisms of Ti₃Al precipitation in hcp α-Ti

Felicity F. Dear¹, Paraskevas Kontis², Baptiste Gault³, Jan Ilavsky⁴, David Rugg³, David Dye⁴

¹Department of Materials, Royal School of Mines, Imperial College London, Prince Consort Road, London, SW7 2BP, UK
²Max-Planck Institut für Eisenforschung GmbH, Max-Planck-Straße 1, Düsseldorf, Germany
³Argonne National Laboratory, 9700 S. Cass Ave., Bldg. 433A, Argonne, IL 60439, United States
⁴Rolls-Royce plc., Elton Road, Derby, DE24 8BJ, UK

Abstract
Nucleation and growth of Ti₃Al α₂ ordered domains in α Ti–Al–X alloys were characterised using a combination of transmission electron microscopy, atom probe tomography and small angle X-ray scattering. Model alloys based on Ti–7Al (wt.%) and containing O, V and Mo were aged at 550 °C for times up to 120 d and the resulting precipitate dispersions were observed at intermediate points. Precipitates grew to around 30 nm in size, with a volume fraction of 6–10% depending on tertiary solutes. Interstitial O was found to increase the equilibrium volume fraction of α₂, while V and Mo have relatively little influence. Addition of any of the solutes in this study, but most prominently Mo, was found to increase nucleation density and decrease precipitate size and coarsening rate. Growth can be described by the Lifshitz-Slyozov-Wagner model, suggesting a matrix diffusion-controlled growth mechanism (rather than control by interfacial coherency). Solutionising temperature was found to affect nucleation number density with an activation energy of $E_A = 1.5 \pm 0.4 \text{ eV}$, supporting the hypothesis that vacancy concentration affects α₂ nucleation. The observation that all solutes increase nucleation number density is therefore also consistent with a vacancy-controlled nucleation mechanism.

Keywords: Titanium alloys, Phase transformations, Transmission electron microscopy (TEM), Atom probe tomography (APT)

1. Introduction

Predicting the lifetime of safety-critical components in gas turbine engines is crucial to continued improvements in flight safety. Despite a global increase of 90% in passenger journeys and 40% in freight transport by air in the decade to 2018 [1], the accident rate across the same time period dropped by 30% [2]. Sustaining this safety improvement relies on mechanistic understanding of the materials serving in such applications, and this same knowledge can steer the development of more capable alloys.

Titanium alloys form a key materials system for aerospace applications, with α+β alloys such as Ti–64 (Ti–6Al–4V wt.%) widely used in fan and compressor components [3]. Deeper understanding of these alloys’ response to fatigue loading has been an area of intense effort for several years [4,5].

In α+β alloys, the elastic anisotropy and limited slip system availability of the hcp α phase have a significant impact on the polycrystalline material’s overall response to static and cyclic loading regimes [6]. This means that, during high-cycle or dwell fatigue loading, variations in elastic and plastic behaviour from grain to grain can initiate yielding near the boundary of particularly mismatched grains.

The nature of this intragranular plasticity plays a key role in fatigue crack initiation. If easy cross-slip is possible, dislocations are able to travel across an individual grain to intersect its grain boundaries at any location. If dislocations are instead restricted in their ability to cross-slip and travel homogeneously, slip bands are formed and eventually intersect a grain boundary. This results either in slip transmission, where the next grain in its path is well oriented for deformation, or in a dislocation pile-up [7]. A sufficiently large pile-up may impose enough stress to nucleate a fatigue crack [8]. Groups of similarly-oriented grains (macrozones) and slip bands extending across millimetres have been implicated in dwell fatigue [9,4,10], including in the field [11]. Slip band formation and factors promoting the even distribution of slip across the α microstructure are hence of significant interest.

Aluminium is commonly included at around 6 wt.% in α+β alloys, stabilising the α phase and providing solid solution strengthening. Phase segregation produces an α composition closer to 7 wt.% (11.8 at.%) meaning that, at temperatures of 500–700 °C, crystallographic ordering of Al can occur and lead to precipitation of the α₂ phase (Ti₃Al, DO₁₉ structure) [12]. The position of the α/α₂ phase boundary has been the subject of several studies [13][14], with successive iterations of the Ti–Al phase diagram shifting it towards lower Al content. A region of SRO between truly disordered α and the α+α₂ field has also been proposed [15]. Recent diagrams place the boundary at around 10 at.% in calculated diagrams and 12 at.% in Schuster and Palm’s diagram drawing together numerous experimental observations [16][17][18].

Even in the early stages of α₂ formation, where some form of ordering exists prior to precipitates being observable in TEM, there is a significant impact on slip behaviour. Cross-slip is hindered, such that first dislocations passing across a grain disrupt the local ordering, leaving a trail of disrupted structure that offers an easier route for subsequent dislocations. This results in slip band formation and the associated deleterious micromechanical effects, with notable implications for tensile
and fatigue response [5]. The earliest stages of ordered domain formation have been shown to restrict primary creep in α-Ti [19, 20]. Dislocation pinning by α2 precipitates has also been observed [21]. In macroscopic plastic deformation, α2 causes initial strain hardening followed by localised strain softening [20, 22], due to initial resistance to slip by the ordered domains being overtaken by the establishment of slip bands as easy paths for slip.

Studies on the formation mechanism of α2 are challenging due to the nanometre length scales and small compositional variations between matrix and precipitate that are involved, especially during the early stages of phase separation. Long-term ageing at temperatures around 500-600 °C typically produces precipitates 5–10 nm in size. Morphology is spheroidal, with elongation along the shared c-axis occurring as growth proceeds [23] and the precipitates undergo coarsening. The earliest stages of phase separation remain less well understood. Possible mechanisms include homogeneous nucleation or spinodal decomposition, and a spinodal decomposition triggered by recrystallisation, and a spinodal decomposition initiated by a reduction in the solubility of Al in Ti with increasing O content [27]. The presence of β stabilisers in α+β alloys is also thought to influence α2 formation [30].

This work investigates the factors controlling α2 formation in an isothermal ageing study of a model alloy series based on Ti–7Al (wt.%), with additions of O, V and Mo. Microstructures were observed in TEM, and local compositions were measured in atom probe tomography. Precipitate dispersion parameters such as number density were analysed using small angle X-ray scattering. Insights are then drawn regarding the role of vacancies in nucleation, a hypothesis which is then tested, allowing the role of solutes in enhancing α2 precipitation to be understood.

2. Experimental methodology

Alloys listed in Table 1 were melted from Ti sponge (Toho, Japan), TiO powder and pure Al, V and Mo pellet in an Arc cast200 27 kW low pressure argon arc melter and cast to produce 23×23×55 mm ingots. The alloys were then rolled and recrystallised in the α phase followed by ice water quenching, Table 1 10 mm cubes were then encapsulated under an Ar atmosphere in quartz and aged at 550 °C for up to 120 d to evolve the α2 precipitate dispersion, and furnace cooled.

Microstructures were initially observed in backscatter electron imaging on a Zeiss Sigma 300 FEG-SEM operated at 8 kV. SEM specimens were prepared by electropolishing with a 3% perchloric acid solution at −35 °C and 20 kV. Bulk compositions were confirmed using ICP-OES and combustion analysis provided by TIMET UK Ltd, Table 1.

Formation of α2 was observed with conventional TEM methods, with specimens prepared by jet electropolishing with a 3% perchloric acid solution at −35 °C and 20 V to perforation. Using a JEOL 2100F TEM operated at 200 kV, selected area electron diffraction patterns were collected for each sample along (011) directions. Dark field images of the α2 precipitates were then made using the [2 1 0] reflections. This provided qualitative observation of precipitate and dispersion characteristics, and allowed measurement of precipitate aspect ratios by measuring several wholly contained, clearly visible precipitates in images for each sample.

Measurement of compositional features of the precipitates at sub-nanometre resolution was achieved using atom probe tomography (APT). Specimens were prepared by conventional Ga+ FIB lift-out methods using a FEI Helios 600 [51]. In addition here, specific grain orientations were targeted using EBSD mapping prior to FIB work. Titanium and Ti-based alloys are prone to forming hydrides during specimen preparation for TEM and APT, an artefact that can be avoided by performing the final thinning or sharpening of specimens at cryogenic temperatures [32]. Here, we used the infrastructure described in Refs. [33, 34] for cryogenic preparation, yet upon comparing with specimens obtained on the same FIB at room temperature, no significant differences in the H uptake were noticed. The low solubility of H in α-Ti and the targeted preparation far from any interfaces likely explains these observations. This produced specimens with the APT analysis direction oriented within a few degrees of the (210) axis zone. APT samples were then run on a Cameca LEAP 5000 XS operated in voltage mode at 50 K, with a pulse frequency of 200–250 kHz, pulse fraction of 20% and detection rate of 0.20–0.40%. The data collected were then analysed using Cameca’s IVAS analysis suite for reconstruction and MATLAB scripts for further analysis.

Quantification of dispersion statistics and precipitate evolution was achieved using small angle X-ray scattering (SAXS). Specimens were prepared by electrode discharge machining of a 3 mm diameter cylinder, from which discs of 300 μm thickness were cut with a precision saw. The discs were then ground to the appropriate thickness (~100 μm) by hand using SiC grit papers up to a 4000 grit finish, followed by polishing with a neu-

| Alloy (nominal composition) | Measured composition/wt.% | $T_{\text{init}}$ | $T_{\text{RX}}$ | $t_{\text{RX}}$ |
|-----------------------------|--------------------------|------------------|----------------|--------------|
| Ti–7Al                      | 6.58 <0.01               | 0.01             | 0.05           | 0.02         | 900 980 850 |
| −0.25O                      | 7.14 <0.01               | 0.01             | 0.24           | 0.05         | 900 980 850 |
| −1.1V                       | 7.04 1.21                | <0.01            | 0.07           | 0.04         | 900 850 850 |
| −1.1V–0.25O                 | 7.04 1.17                | <0.01            | 0.26           | 0.08         | 900 850 850 |
| −0.8Mo                      | 7.17 <0.01               | 0.30             | 0.18           | 0.08         | 850 850 18  |
| −0.8Mo–0.25O                | 7.16 <0.01               | 0.90             | 0.30           | 0.01         | 850 850 18  |

Table 1: Compositions of the Ti–7Al model alloy series measured by ICP-OES and LECO combustion analysis by TIMET (Witton, UK). Hydrogen contents in each alloy were measured to be 0.01 wt.% or less. Alloys in this study are referred to by their nominal compositions. Rolling ($T_{\text{init}}$) and recrystallisation ($T_{\text{RX}}$) temperatures for these steps were chosen according to the β transus for each alloy, identified by iterative heat treatments and metallography. Recrystallisation times ($t_{\text{RX}}$) were chosen to account for the varying recrystallisation kinetics in each system.
3. Results

3.1. Microstructural characterisation

Equiaxed α microstructures were produced, Fig. 1, with grain sizes of 10–50 µm depending on alloy composition. Alloys containing no β stabilisers showed a larger grain size due to the limited opportunity to restrict grain size during processing of alloys with almost no α+β phase field. The Mo-containing alloys contained a small fraction of β due to the very low solubility for Mo in α; it was later demonstrated in APT results that the α phase contained a small amount of Mo, as intended.

3.2. Transmission electron microscopy

Selected area electron diffraction patterns taken for $B = \langle 0 \bar{1} 1 \rangle$, Fig. 2, show the development of superlattice reflections as the ordered $\alpha_2$ phase forms and grows. After a short hold of 2 hours at 550°C, a small amount of intensity was observable at superlattice spot locations. Upon further ageing for 10 days or more, superlattice reflections became distinct spots and increased in intensity as ageing progressed.

Dark field images provide a qualitative view of trends in precipitate morphology, size and number density during ageing, Fig. 3. Imaging was attempted for the 2 hour aged specimens, but no image contrast was evident. The base alloy Ti–7Al–0.05O showed formation of nanoscale precipitates after 10 days, which coarsened over time whilst growing in size and increasing in aspect ratio.

The addition of oxygen to the alloy system causes an increase in precipitate number density, and produces smaller precipitates. The effect of oxygen on volume fraction of the $\alpha_2$ phase is unclear from qualitative micrographs; it should be recalled that these are projections of contrast through the foil thickness. TEM images do not show evidence of a significant effect of vanadium on the precipitate dispersion. The addition of molybdenum considerably restricts precipitate sizes, and precipitate aspect ratio does not increase as significantly over the duration of the study. However, these micrographs only provide a qualitative impression of the alloying trends; for a quantitative comparison we turn next to atom probe tomography and SANS.

3.3. Atom probe tomography

Atom probe tomography results provided a quantitative analysis of local compositional features. Of specific interest were the compositions of phases present, segregation of solutes between these phases, compositional features of the $\alpha/\alpha_2$ inter-

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**Figure 1:** Backscatter micrographs of alloy microstructures, showing the equiaxed α microstructure as intended. In the Mo-containing alloys, the very limited solubility of Mo in α led to the formation of small, micron-scale β domains at grain boundary triple points, which also contributed to grain size refinement during processing.

**Figure 2:** Selected area electron diffraction patterns obtained for Ti–7Al–0.05O (wt.%) in the quenched (disordered) state, and in selected subsequent ageing states. Diffuse superlattice reflections are faintly visible after 2 hours ageing at 550°C (AC condition), which intensify as phase separation progresses after 10 days. Continued growth of $\alpha_2$ is evident in the intensification of superlattice reflections at longer times.
Figure 3: Dark field transmission electron micrographs recorded for specimens of each alloy at different ageing times, using a two-beam condition with the [2110] reflection for $B = [0111]_a$. The base alloy Ti–7Al–0.05O (wt.%) shows formation of spheroidal precipitates that increase in size and aspect ratio as ageing progresses. Additional solutes modify the way in which precipitate size, aspect ratio, spacing and number density evolve over time.
face, and the crystallographic site partitioning of V and Mo on the α2 DO19 lattice. Measurements were performed for Ti–7Al–0.05O in the quenched condition as a reference dataset, for this alloy at 49 days ageing, and for this alloy and Ti–7Al–0.05O, Ti–7Al–1.1V–0.25O and Ti–7Al–0.8Mo–0.25O in the 120-day aged condition to observe α2 precipitates. Data reconstruction was informed by TEM observations of precipitate morphology and by crystallographic information about the material. Since specimens were prepared from a known crystallographic orientation, partial indexing of desorption maps was possible and confirmed that the pole approximately parallel to the analysis direction was ⟨110⟩. Here, proximity histograms were produced to analyse the nature and extent of phase segregation for each solute, Fig. 5. The α2 phase was identified according to its Al enrichment to around 25 at.%.

Elements seen to promote α2 formation in dark field TEM observations were expected to show segregation to this phase. For both O and V, segregation to the α matrix was instead observed. Previously we have shown [29] that O enhances α2 formation whilst segregating to the α phase, owing the curvature of the phase boundary in the Ti–Al–O ternary. Mo showed no segregation between the phases despite its significant effect on the α2 precipitate dispersions.

For each specimen, proximity histograms were used to choose values for a set of Al concentration isosurfaces at 6.5% to select α and 10.5% to select α2 without including the interfacial region. This approach was used to obtain phase compositions, Table 2 which showed the expected Ti3Al stoichiometry in the α2 phase. These phase compositions were used to provide contrast values for SAXS analysis, allowing deconvolution of the volume fraction and compositional contributions to peak size in SAXS data.

3.4. Small angle X-ray scattering

SAXS curves for each alloy in the ageing study, Fig. 6 showed evolution of a high-Q peak over time, along with a low-Q peak that showed no systematic variation with the ageing
process. These are ascribed to α2 precipitation and to the presence of grain boundaries as large scatterers respectively. The α2 peak is distinctly visible for larger precipitates, but for very fine dispersions as in the Mo-containing materials it is less easily discerned. For all alloys, a slight difference in curve shape at high \( Q \) between quenched and air-cooled states is seen.

The raw data were fitted using two scatterer populations for precipitates, based on TEM images showing that precipitate aspect ratio increases with time. This shape is described by a structure factor effect occurring in some of the samples (appearing as a dip in measured intensity at the low-\( Q \) shoulder of the α2 peak). This effect is strengthened or subdued according to the extent to which each dispersion can be considered dilute.

Contrast values were calculated using the Irena analysis package [37], using composition data from APT. The α and α2 compositions for each sample were used to calculate the average atomic weight of each phase. This was then used to estimate the density of the phase, assuming no difference in unit cell volume compared to pure Ti, and these phase compositions and densities were then used to calculate scattering length density contrast. After calculating this for the different samples, values between 1.7–2.7 × 10^{20} \text{ cm}^{-4} were obtained but showed no systematic variation with alloy composition, so an average value of 2.2 × 10^{20} \text{ cm}^{-4} was taken for fitting of all SAXS datasets in this study.

In the fitting process, \( A \) is an input parameter along with phase contrasts calculated in the Irena analysis suite using APT data. Model outputs include \( r_e \) and volume fraction of α2 phase, \( f \). These can be used to calculate precipitate number density, \( n = f/V \), and if, in the absence of any specific model or description, a simple cubic array of precipitates in the matrix is assumed, the average spacing may be calculated as \( s_{\text{eff}} = n^{-1/3} \). The low-\( Q \) peak associated with grain boundaries was modelled as a cylindrical disc of appropriate diameter and thickness, and fitted using an arbitrary contrast that was not deconvolved from volume fraction for this microstructural component.

Direct comparison of \( f \) between alloys is possible but, due to the variation in precipitate aspect ratio with both alloy and ageing time, the model output parameter \( r_e \) is not an appropriate metric for comparing precipitate sizes across the study. A directly comparable quantity is the average volume of a precipitate, \( V = \frac{4}{3} \pi r_e^3 \). For easy cross-reference with TEM images and APT reconstructions, the diameter of a sphere having equal volume to the modelled spheroid can be calculated as \( d_{\text{equiv}} = 2r_e = 2r_eA^{1/3} \). This equivalent sphere diameter provides a directly comparable metric of precipitate size at different ageing times, and allows easy comparison with TEM and APT data.

Fitting results for α2 volume fraction, size and spacing showed similar trends with time for each alloy composition, but clear differences were apparent between different alloys, Fig. 7. Volume fraction \( f \) showed the expected rapid initial increase followed by plateauing towards the equilibrium volume fraction for each system. An equilibrium volume fraction was reached for the base alloy and variants containing additions of O, V or both. A higher fraction of α2 was observed in Ti–7Al–0.25O compared to Ti–7Al. The addition of V alone caused no significant difference in volume fraction, and the addition of O to the V-containing alloys did not influence the fraction of α2. The Mo-containing alloys did not appear to reach an equilibrium state, with volume fraction still apparently increasing after 120 days at 550 °C. The final measured volume fractions for these alloys after 120 days were slightly higher than for the base alloy. As with the V-containing alloys, no significant difference in volume fraction was seen between the Mo alloys with different O levels.

Precipitate size and spacing were reduced compared to the Ti–7Al base alloy upon adding any of the three solutes investigated. Mo had the most significant effect, producing very fine dispersions of small, closely-spaced precipitates. As with volume fraction, precipitate size and spacing showed no significant influence from oxygen content in the V- and Mo-containing materials. In each system, number density was found to vary as expected for precipitate coarsening behaviour, with an initial rapid increase corresponding to nucleation and early growth of precipitates. This was followed by a more gradual decrease as the microstructure underwent coarsening, with larger precipitates growing at the expense of smaller ones.

Comparing IWQ and AC datasets (i.e. quenched/disordered and SRO/early nucleation stage), a difference in curve shape is consistently seen across the different alloys. This takes the form of an increased intensity across a broad \( Q \) range from around 0.01 to 0.05 Å^{-1}. Modelling of the AC datasets was attempted using a low aspect ratio spheroid, but produced unphysical modelling results.

### Table 2: Bulk and phase compositions measured in APT

| Material      | Ageing state | Composition / at.% |
|---------------|--------------|---------------------|
|               |              | Ti  | Al  | O   | V   | Mo  | N   |
| Ti–7Al        | IWQ          | 83.8| 15.2| 0.5 | 0.4 |
|               | 49 d         | 82.9| 16.4| 0.3 | 0.1 |
|               |              | α   | 84.1| 15.2| 0.3 | 0.1 |
|               |              | β   | 73.7| 25.9| 0.2 | 0.1 |
|               | 120 d        | 82.9| 16.2| 0.5 | 0.1 |
|               |              | α   | 83.3| 15.6| 0.6 | 0.1 |
|               |              | β   | 73.9| 25.6| 0.2 | 0.1 |
| −0.25O        | 120 d        | 81.5| 17.2| 0.9 | 0.1 |
|               |              | α   | 83.5| 15.1| 1.0 | 0.1 |
|               |              | β   | 72.2| 26.4| 0.4 | 0.2 |
| −1.1V–0.25O   | 120 d        | 82.1| 16.0| 0.8 | 0.9 |
|               |              | α   | 83.5| 14.5| 0.9 | 0.2 |
|               |              | β   | 72.2| 26.5| 0.4 | 0.6 |
| −0.8Mo–0.25O  | 120 d        | 83.4| 15.2| 0.9 | 0.3 |
|               |              | α   | 84.9| 13.6| 0.9 | 0.3 |
|               |              | β   | 75.6| 23.4| 0.6 | 0.2 |

Sample characteristics and values between 1.7–2.7 × 10^{20} \text{ cm}^{-4} were obtained but showed no systematic variation with alloy composition, so an average value of 2.2 × 10^{20} \text{ cm}^{-4} was taken for fitting of all SAXS datasets in this study.

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|               |              | β   | 75.6| 23.4| 0.6 | 0.2 |
3.5. APT crystallography

Attempts were made to analyse the APT data for crystallographic information, specifically regarding site partitioning of substitutional solutes V and Mo on the $\alpha_2$ lattice. Spatial distribution maps (SDMs) were calculated for individual precipitates that had been identified as being located directly on a $\{2\bar{T}\bar{T}\bar{0}\}$ pole, for Ti–Ti, Ti–Al and Ti–V species pairs, Fig. 8. However, due to the significant differences in evaporation field between Ti and Al under the measurement conditions applicable to these alloys, artefacts were seen in the interplanar spacing both in atom maps and in SDMs. This artefact has been described by Vurpillot et al. [39]. By comparison, in Ni–Al $\gamma/\gamma'$ alloys, the evaporation field difference is smaller so that site partitioning is more easily accessible through on-zone APT [40]. The low solubility of V and Mo in the $\alpha$ and $\alpha_2$ phases also made this analysis challenging due to limited V or Mo atoms available for measurement and SDM analysis.

4. Discussion

The use of TEM, APT and SAXS in combination has allowed the analysis of volume fraction, size and spacing of $\alpha_2$ in this set of model alloys. Comparisons between the various alloying elements may be made.

4.1. Volume fractions

First, considering volume fraction, the increase from 6% to 10% due to increased oxygen content supports the small shift in the position of the $\alpha/\alpha_2$ boundary upon adding oxygen that has been previously suggested [27, 25, 23]. Based on the results of this study, vanadium does not appear to significantly alter the volume fraction of $\alpha_2$ produced after 120 days ageing at 550 °C. Molybdenum causes a slight increase from 6% to 8%, but due to retardation of phase separation kinetics by this solute, the Mo-containing systems did not reach equilibrium volume fractions during the 120 days of this study.

4.2. Size and spacing

Regarding the size and spacing of precipitates, these were largest at all times for the base alloy Ti–7Al–0.05O. Additions of any of the three solutes investigated causing refinement of the $\alpha_2$ dispersion. Molybdenum had the most significant effect on this, followed by oxygen, while vanadium had a fairly minimal effect on the size and spacing of precipitates. The varying degrees of refinement are reflected in the extent to which each sample’s scattering curve shows structure factor effects. Considering also the number density at short and long times for the different alloys, all solutes are seen to increase $n$ during the early stages of phase separation. This suggests that adding any of these solutes causes increased nucleation density. Molybdenum produces an order of magnitude increase in early number density compared to the other alloys in the study. It is suggested that the resulting reduction in interparticle distances then causes smaller precipitate sizes due to soft impingement.

In the V- and Mo-containing alloys, there is little difference in volume fraction, size and spacing of $\alpha_2$ precipitates between the low- and high-oxygen variants in each case. This indicates that the $\alpha/\alpha_2$ boundary in the corresponding ternary equilibrium phase diagrams shifts more significantly with O content than with V or Mo content.
4.3. Coarsening and LSW modelling

In order to compare the precipitate growth rate and coarsening between alloys, the Lifshitz–Slyozov–Wagner (LSW) model was applied for the precipitate effective radius, \( r_{\text{eff}} = d_{\text{eq}}/2 \) (for direct comparison between samples with different precipitate aspect ratios). This model describes the evolution of precipitate size with time according to

\[
r^3(t) - r_0^3 = \frac{8\Gamma D C V_m^2}{9RT} t = Kt,
\]

where \( \Gamma \) is the precipitate/matrix interfacial energy, \( D = D_0 \exp(-Q/RT) \) is the diffusion coefficient of the rate-limiting species through the matrix, \( C \) is the equilibrium concentration of the rate-limiting species in the matrix, \( V_m \) is the molar volume of the precipitate phase, \( R \) is the ideal gas constant and \( T \) is the absolute temperature at which phase separation has been observed [41,42]. The gradients of linear fits hence provide a growth rate constant, \( K \), that can be compared between alloys.

A nonzero value of \( r_0 \) would indicate an incubation period between the introduction of isothermal ageing conditions and the onset of precipitation. In this study, \( r_0 = 0 \) was set for LSW fitting as no incubation period is expected nor evident in the data. Fits with \( K \) values of 0.9 or above were obtained for each alloy, Fig. 9 and these good fits for a \( \frac{1}{3} \) power law indicate a diffusion-limited growth process, rather than an interface-controlled mechanism [43]. The \( K \) values obtained for these alloys, Table 3, are reasonable when compared to those reported...
Table 3: Lifshitz–Slyozov–Wagner modelling was successfully applied to the SAXS data, Fig. 9, with goodness of fit \( R^2 \) of 0.91 or better. This model provides rate constants \( K \) and an estimate of the growth rate of precipitates in each alloy in terms of volume per unit time. The peak precipitate number density during the coarsening process, as analysed in SAXS, is shown for comparison.

To establish whether a link exists between vacancy concentration and \( \alpha_2 \) nucleation density, a single alloy composition was used, Ti–7Al–0.05O, while the thermal history of the samples prior to \( \alpha_2 \) ageing was varied. Vacancy concentration in metals is known to have an empirically Arrhenius-type dependence on temperature. Aiming to control the vacancy concentration in samples prior to ageing, pieces of the alloy in the IWQ starting condition were annealed at 750 °C and 950 °C to generate two different vacancy concentrations while remaining within the \( \alpha \) phase field and staying above \( \alpha_2 \) formation temperatures. The samples were then ice-water quenched, cleaned to remove any oxide, and encapsulated under argon in a quartz ampoule before ageing at 550 °C for 23 days. The resulting \( \alpha_2 \) dispersions were then characterised using dark field TEM imaging and SAXS measurements Fig. 10. The SAXS data were fitted using a spheroidal precipitate shape with an aspect ratio of 2.0 and a contrast value of 2.2 \( \times 10^{-20} \) cm\(^{-4} \), following the same methodology as for the main SAXS dataset.

In order to establish whether these results are consistent with a vacancy-controlled nucleation mechanism, the number densities in each sample were compared to predicted vacancy concentration behaviour. The vacancy concentration at a temperature \( T \) is empirically given by

\[
N = N_0 e^{-E_T/k_B T},
\]

where \( N_0 \) is a constant prefactor and \( E_T \) is the vacancy formation energy. For two different temperatures, \( T_1 \) and \( T_2 \),

\[
\frac{N_1}{N_2} = \frac{\exp(-E_T/k_B T_1)}{\exp(-E_T/k_B T_2)},
\]

such that

\[
E_T = k_B \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \ln \left( \frac{N_1}{N_2} \right). \tag{3}
\]

If it is assumed that \( n \propto N_0 \) independent of temperature, then the \( \alpha_2 \) number densities \( n \) may be used to estimate the vacancy formation energy in Ti–7Al–0.05O.

For the samples quenched from 750 °C and 950 °C, number densities of 2.2 \( \times 10^{21} \) m\(^{-3} \) and 3.5 \( \times 10^{22} \) m\(^{-3} \) were obtained from SAXS data fitting respectively, Table 4. Using Eqn. 3 this gives an estimate of \( E_T = 1.5 \pm 0.4 \) eV. Previous experimental studies for vacancy formation in \( \alpha \)-Ti are relatively scarce, but comparison may be made with the findings of Hashimoto et al. [45] who measured a value of 1.27 ± 0.05 eV using positron annihilation. First-principles calculations for \( E_T \) in \( \alpha \)-Ti have found values of 1.87 eV [46] and 1.97 eV [47]. The value obtained in the present work is consistent with these earlier studies, lending support to a vacancy-mediated nucleation mechanism for \( \alpha_2 \) in \( \alpha \)-Ti Al–X alloys, as a second-order effect of tertiary solute additions.

4.4. Effect of quenching temperature on \( \alpha_2 \) formation

A second heat treatment study was conducted in order to establish a clearer mechanistic connection between the tertiary solutes (O, V, Mo) and differences in \( \alpha_2 \) formation. Upon adding any of the three solutes, refinement of the \( \alpha_2 \) dispersion was observed, to a greater or lesser extent depending on the solutes included. Noting the homogeneous distribution of \( \alpha_2 \) precipitates across \( \alpha \) grains in these alloys, it was suggested that the nucleation points must correspond to a homogeneously distributed lattice defect. A plausible candidate is the vacancy concentration in each alloy. It was proposed that, upon adding any solute, the resulting increased entropy of the alloy causes an increase in vacancy concentration, and that this is the common underlying mechanism controlling nucleation density.

In this study, the precipitation and coarsening of \( \alpha_2 \) Ti3Al in a Ti-Al alloy was studied, using TEM to identify the existence of the precipitates and their morphology. APT to characterise...
their composition and SAXS to quantify their number density, size and fraction. The aspect ratio of 2.0 were used.

| $T_{\text{sol}}/°C$ | $f_{\alpha_2}$ | $d_{\text{eq}}$/nm | $n/10^{21}$ m$^{-3}$ |
|------------------|--------------|------------------|-----------------|
| 750              | 0.012        | 21.8             | 2.21            |
| 950              | 0.058        | 14.7             | 34.9            |

Table 4: SAXS fitting results for specimens solutionised at and quenched from different solutionising temperatures. $T_{\text{sol}}$ prior to ageing for 23 days at 550°C in order to compare the effects of different vacancy concentrations on volume fraction $f_{\alpha_2}$, precipitate size as equivalent sphere diameter $d_{\text{eq}}$ and precipitate number density $n$. For both materials, a contrast value of 2.2 $\times$ 10$^{30}$ cm$^{-3}$ and an aspect ratio of 2.0 were used.

The following conclusions are drawn.

- Interstitial O increases the volume fraction of $\alpha_2$ formed at equilibrium, which is in the region of 8–10 vol%, while V and Mo have a relatively small effect. The precipitates grow in size to up to 30 nm after 120 d at 550 °C (Ti-7Al-0.05O), with interparticle spacing of a similar magnitude;
- Addition of O, V or Mo increases the nucleation density of $\alpha_2$, and leads to a finer precipitate dispersion;
- Growth of $\alpha_2$ can be described using an LSW model, indicating diffusion control (rather than interface coherency control);

- A secondary study comparing $\alpha_2$ formation between samples differing only by quenching temperature showed a difference in nucleation number density. This gave an activation energy consistent with a vacancy nucleation mechanism, $E_1 = 1.5 \pm 0.4$ eV;
- This leads to the inference that the effect of solute O, V and Mo is, broadly speaking, to increase the nucleation number density and thereby slow coarsening due to an earlier onset of soft impingement.

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