Compositional variations for small-scale gamma prime (\(\gamma'\)) precipitates formed at different cooling rates in an advanced Ni-based superalloy

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Abstract—Size-dependent compositional variations under different cooling regimes have been investigated for ordered L1 2-structured gamma prime (\(\gamma'\)) precipitates in the commercial powder metallurgy Ni-based superalloy RR1000. Using scanning transmission electron microscope imaging combined with absorption-corrected energy-dispersive X-ray spectroscopy, we have discovered large differences in the Al, Ti and Co compositions for \(\gamma'\) precipitates in the commercial powder metallurgy Ni-based superalloy RR1000. Using scanning transmission electron microscope imaging combined with complementary information from electron diffraction, we have discovered large differences in the Al, Ti and Co compositions for \(\gamma'\) precipitates in the commercial powder metallurgy Ni-based superalloy RR1000. Using scanning transmission electron microscope imaging combined with complementary information from electron diffraction, we have discovered large differences in the Al, Ti and Co compositions for \(\gamma'\) precipitates in the commercial powder metallurgy Ni-based superalloy RR1000. Using scanning transmission electron microscope imaging combined with complementary information from electron diffraction, we have discovered large differences in the Al, Ti and Co compositions for \(\gamma'\) precipitates in the commercial powder metallurgy Ni-based superalloy RR1000. Using scanning transmission electron microscope imaging combined with complementary information from electron diffraction, we have discovered large differences in the Al, Ti and Co compositions for \(\gamma'\) precipitates in the commercial powder metallurgy Ni-based superalloy RR1000.

Keywords: Ni-based superalloys; Cooling rate; Energy-dispersive X-ray spectroscopy; Scanning transmission electron microscopy

1. Introduction

Polycrystalline nickel-based superalloys for turbine disc applications typically employ complex alloy chemistry in order to produce the required properties. Excellent fatigue performance and damage tolerance, and good creep resistance at operating temperatures close to 1023 K [1–3] originate principally from the presence of a high volume fraction (close to 50%) of gamma-prime (\(\gamma'\)) precipitates coherently embedded within the gamma (\(\gamma\)) matrix [4,5]. The precipitate size distribution (PSD) for \(\gamma'\) phase can be varied in a controlled manner by applying different heat treatments, allowing the mechanical properties of the material to be optimised for certain applications [6]. Changes in the PSD and/or phase chemistry have a direct impact on material performance, so controlling the mechanical properties requires an accurate understanding of precipitate phase chemistry and its evolution during cooling.

Primary \(\gamma'\) precipitates are intergranular and only form when the superalloy is heated above the \(\gamma\)-solvus temperature. Supersolvus annealing above the \(\gamma\)-solvus dissolves the primary \(\gamma'\) and subsequent solution cooling, at rates of around 10 K min \(^{-1}\) or less, causes the formation of intragranular \(\gamma\) precipitates during the early stage of cooling, commonly termed secondary \(\gamma\). Further cooling results in the growth of secondary \(\gamma'\) precipitates until the low elemental diffusivities of the \(\gamma\) stabilizing elements make it difficult for these elements to reach the comparatively coarse (hundreds of nanometres) secondary \(\gamma\). This results in supersaturation of these elements within the \(\gamma\) matrix and consequently drives the nucleation of additional intragranular \(\gamma\). In the remaining cooling range these new precipitates only grow to sizes in the range of tens of nanometres, and are often termed tertiary \(\gamma'\) [5,7].

In contrast, fast solution cooling results in higher nucleation rates and limits the time available for diffusion to occur. This produces microstructures with smaller \(\gamma'\) precipitates and a narrower size distribution. As summarised in Fig. 1, the \(\gamma'\) stabilizing elements have different interdiffusion rates in the matrix and in the \(\gamma\) precipitates [8–12]. Considering the complexity of \(\gamma\) formation, which occurs over a wide range of temperatures under different cooling regimes, the phase chemistry of \(\gamma\) has the potential to be highly size dependent, as demonstrated using three-dimensional atom probe microscopy [13] and in our recent work [14]. What is not yet well understood are details of the diffusion kinetics and how different cooling rates affect the local phase chemistry within different sizes of \(\gamma'\) precipitate.

Three-dimensional atom probe microscopy was the first technique used that was able to quantify the phase chemistry of \(\gamma'\) precipitates [13]. Energy-dispersive X-ray (EDX) spectroscopy within a scanning transmission electron microscope (STEM) provides an alternative approach to measuring the phase chemistry within thin samples, as well as providing complementary information from electron diffraction.
Traditional electropolished transmission electron microscope (TEM) thin film samples facilitate accurate EDX compositional measurements for precipitates with diameters approaching the foil thickness (\( \sim \) 100 nm). However, for smaller sizes of precipitate, it is difficult to distinguish the composition of the precipitate from that of the surrounding matrix. To overcome this problem, an alternative technique for TEM sample preparation was demonstrated by Mukherji et al. \([18]\), who employed an electrochemical method to extract individual \( \gamma' \) precipitates by dissolving the surrounding matrix. More recently, we have demonstrated the use of this technique coupled with absorption-corrected EDX spectroscopy to semi-quantitatively analyse precipitate compositions \([14]\). In this paper, we have applied this same approach to study the size-dependent compositional variations of \( \gamma' \) precipitates formed by employing different cooling regimes. Our results reveal new insights into the role of diffusion kinetics for determining precipitation mechanisms in the commercial powder metallurgy (PM) Ni-based superalloy RR1000.

2. Experimental

2.1. Materials and heat treatment

The commercial PM Ni-based superalloy RR1000 studied in the present work has the nominal composition shown in Table 1 and is used for disc applications in aero engines. This polycrystalline Ni-based superalloy was manufactured via the powder metallurgical route followed by subsequent forging, and typically has trinodal \( \gamma' \) PSD \([14]\). In this work, blanks of size 10 \( \times \) 10 \( \times \) 10 mm\(^3\) were first heat treated for 2 h at a supersolvus temperature (20 K above the \( \gamma' \)-solvus) in order to homogenise the microstructure and chemistry of the material. These blanks were then subjected to a super-\( \gamma' \)-solvus heat treatment at 1453 K followed by cooling to room temperature using a range of controlled cooling rates, both slow (1 and 10 Kmin\(^{-1}\)) and fast (100 and 360 Kmin\(^{-1}\)), to produce different PSDs with which to study size-dependent precipitation behaviour. In order to control and monitor the heat treatment, equivalent size samples were fabricated and a thermocouple fitted into the centre of the block in order to allow continuous monitoring of the cooling rate.

2.2. Analysis methodology of large \( \gamma' \) precipitates

Samples were mechanically polished using standard metallography and finished with a final polish using colloidal silica solution for 30 min in order to obtain the required surface quality. To reveal the different microstructures, specimens were etched using a two-part etchant to dissolve the \( \gamma' \) phase but retain the matrix \([19]\). High-resolution scanning electron microscope (SEM) imaging was...
2.3. Analysis methodology of fine γ' precipitates

The thin foil samples described above were suitable for EDX spectroscopy compositional measurements when precipitate diameters were greater than the foil thickness. However, for smaller precipitates we employed the approach of Mukherji et al. [18], whereby an electrochemical method dissolves the surrounding γ matrix in order to extract individual γ' precipitates. Once extracted, the precipitates are prepared for S/TEM imaging by being drop cast from solution onto holey carbon TEM support grids.

Watanabe et al. [15,21] have shown that, for Ni3Al thin films, the difference in absorption of the AlKα X-rays (1.48 keV) compared to NiKα X-rays (7.47 keV) can lead to EDX compositional measurements that vary by ~12% for thicknesses in the range of 80 nm. To compensate for these errors in thin foil samples, they introduce an absorption correction factor (ACF), which is given as [15,21]:

\[
ACF = \frac{\frac{\mu}{\rho} A \text{sp}}{\frac{\mu}{\rho} \text{i} \text{sp}} \left( 1 - e^{-\frac{\mu}{\rho} \text{sp} t \cosec} \right) \left( 1 - e^{-\frac{\mu}{\rho} \text{i} \text{sp} t \cosec} \right)
\]  

(1)

where \(\mu/\rho\) is the mass-absorption coefficient of species A in the specimen, \(\rho\) is the density of the specimen, \(t\) is the specimen thickness and \(\beta\) is the detector take-off angle. \(t \cosec\) in the exponentials of Eq. (1) can be considered as the equivalent X-ray penetration depth with specimen tilt as the gradually attenuated X-rays travel through a specimen. In order to apply the ACF to samples consisting of isolated spherical particles, we have previously shown that this equation can be modified such that the particle radius \(R\), as the equivalent X-ray penetration depth, is substituted for \(t \cosec\) [14], with the new ACF given by:

\[
ACF = \left( \frac{\mu}{\rho} A \text{sp} \right) \left( 1 - e^{-\frac{\mu}{\rho} \text{sp} R} \right) \left( 1 - e^{-\frac{\mu}{\rho} \text{i} \text{sp} R} \right)
\]

(2)

Conveniently, the similarity of these equations means that it is possible to apply the standard ACF implemented in commercial software packages to isolate spherical particles by simply calculating the input value for thickness as \(R/\cosec\). In this work we employed an Oxford Instruments X-MaxN 80T SDD for EDX spectroscopy with a take-off angle of 20° fitted into an FEI Tecnai F30 S/TEM. EDX spectroscopy measurements with counts of greater than 250,000 were performed using a STEM probe with a convergence semi-angle of 12.5 mrad and a spot size of around 1 nm, so that even for the smallest precipitates, with diameters of less than 20 nm, the interaction volume includes tens of thousands of atoms and the measured compositions can be approximated as homogeneous at this length scale.

3. Results

3.1. Precipitate size distributions for different cooling rates

Fig. 2 compares the SEM images revealed by surface etching of typical microstructures for the PM Ni-based superalloy RR1000 cooled at different rates. The PSDs and precipitate volume fractions vary dramatically for different cooling rates, as shown from the size analysis in Fig. 3. The total volume of γ' precipitates decreases with increasing cooling rate, although the fraction of precipitates with sizes less than 300 nm increases significantly. Slow cooling rates (1 and 10 K min\(^{-1}\)) are found to show a multi-modal precipitate size distribution, whilst the fast
precipitates have lower Al contents: 12.5 and 12.0 at.% Al for cooling rates of 1 and 10 Kmin\(^{-1}\), respectively. Ti has the opposite size-dependent variation for both the slower cooling rates, increasing from \(\sim 7.5\) at.% in 20 nm tertiary \(\gamma'\) to \(\sim 9.6\) at.% Ti in 250 nm secondary \(\gamma'\). Ta is also slightly depleted in the fine-scale (<80 nm) tertiary \(\gamma'\) produced by a cooling rate of 1 Kmin\(^{-1}\), but is approximately constant at \(\sim 1.9\) at.% Ta for larger precipitates and for all sizes of precipitate formed at a cooling rate of 10 Kmin\(^{-1}\). The Co content is virtually constant at approximately 7.3 at.% for all sizes of precipitate formed at a cooling rate of 1 Kmin\(^{-1}\), but decreases from 10.5 at.% in \(\sim 250\) nm secondary \(\gamma'\) to 7.6 at.% in \(\sim 25\) nm tertiary \(\gamma'\) generated at a cooling rate of 10 Kmin\(^{-1}\). The contents of both Cr and Mo increase slightly in the smallest precipitates for both the 1 and 10 K min\(^{-1}\) cooling rates, although the variability in both elements is larger in the 10 K min\(^{-1}\) data set. In contrast, the compositional data for the fast cooling rates of 100 and 360 K min\(^{-1}\) (Fig. 4c and d) shows much smaller compositional variations, even for the 100 K min\(^{-1}\) cooling rate, which has a significant size distribution.

3.3. Equilibrium calculations

In order to gain a deeper understanding of the experimentally measured compositional variations, equilibrium thermodynamic calculations were performed using Pandat software [22] with data from the Ni-based superalloy database [23] for a temperature range between 873 and 1323 K. The \(\gamma\)-solvus (1323 K) can be considered as the upper temperature limit for \(\gamma\) nucleation. The lower temperature limit for \(\gamma'\) precipitation and growth can be estimated by considering the elemental diffusivity of the \(\gamma'\) stabilizers, Al and Ti, in the \(\gamma\) matrix phase (Fig. 1a), together with the minimum precipitate size observed experimentally. The smallest \(\gamma'\) precipitates observed in this work were \(\sim 10\) nm in terms of square root particle area. Considering the slowest cooling rate of 1 K min\(^{-1}\) and a broad range of possible starting temperatures (803–933 K), the corresponding diffusion distance for Al can be calculated as shown in Fig. 5. This data shows that, for \(\gamma\) nucleation temperatures below 873 K, it is not possible for Al and Ti to diffuse more than 10 nm in the \(\gamma\) matrix phase during continued cooling to room temperature. Therefore, all observed precipitates are expected to have nucleated above 873 K, and this can be considered as the low-temperature limit for equilibrium thermodynamic calculations.

As shown in Fig. 6, for most elements these calculations predict a thermodynamically stable composition that is largely independent of temperature in the range 873–1323 K, with mean values of 12.3 ± 0.3 at.% Al, 8.7 ± 0.1 at.% Ti, 1.5 ± 0.1 at.% Ta, 0.3 ± 0.1 at.% Hf, 2.5 ± 0.2 at.% Cr and 0.6 ± 0.1 at.% Mo. Co is the exception, showing a marked decrease with decreasing temperature, from 11 at.% Cr at 1323 K to 6.0 at.% Cr at 873 K.

In a binary Ni–Al alloy the \(\gamma\) phase has the composition Ni\(_3\)Al, with the ordered L\(_1\)\(_2\) structure, in which the face-centred sublattice (\(x\)) is occupied by Ni atoms and the corner sublattice (\(\beta\)) is occupied by Al atoms. For the more complex case of the PM Ni-based superalloy RR1000, the chemistry of the \(\gamma\) phase is generally given as (Ni, Co, Cr, Mo\(_3\)) (Al, Ti, Ta, Hf). The elements Ni, Co, Cr and Mo are generally assumed to substitute into the \(x\)-sublattice, while Al, Ti, Ta and Hf occupy the \(\beta\)-sublattice, as predicted by first principle calculations [24–29]. We note that

3.2. Composition-size relationships for small-scale \(\gamma'\) precipitates

Previously, we have demonstrated the measurement of size-dependent \(\gamma'\) compositional variations for the as-received alloy RR1000 [14]. In this work we follow the same analytical approach for calculating size-dependent elemental compositions as a function of cooling rate for the small-scale \(\gamma'\) precipitates (less than 300 nm). Our experimental measurements of the different size/cooling dependant compositional behaviours are shown in Fig. 4, together with dark-field TEM images showing the microstructure of the precipitates within electron transparent thin films.

For the two slower cooling rates (1 and 10 Kmin\(^{-1}\)), the Al content of \(\gamma'\) is found to be increased in the smallest \(\gamma'\) precipitates whilst the Ti and Co concentrations are decreased. The smallest \(\gamma'\) precipitates are likely to be generated at the slowest cooling rate and have the highest Al content (16.7 at.% Al in 20 nm tertiary \(\gamma'\) for a cooling rate of 1 Kmin\(^{-1}\), compared to 15.0 at.% Al in 20 nm tertiary \(\gamma'\) for a cooling rate of 10 Kmin\(^{-1}\)). The 240 nm secondary \(\gamma'\) precipitates (16.7 at.% Al in 20 nm tertiary \(\gamma'\)).

![Graph](image1.png)

**Fig. 3.** Quantification of \(\gamma'\) precipitate size (square root of the measured visible area) as a function of cooling rate for the PM Ni-based superalloy RR1000 (measured using a large number of SEM microstructure images). (a) The different precipitate size distributions for each cooling rate considering only the size range 20–300 nm (measurements include data for >1000 precipitates at each cooling rate). (b) The volume fraction of \(\gamma'\) considering all sizes of precipitate. Cooling rates (100 and 360 Kmin\(^{-1}\)) exhibit narrower or unimodal precipitate distributions.
in this work precipitates in the size range of interest have Hf contents below experimentally detectable levels, hence Hf is not considered in further discussions. The ratio \( \frac{C_{(Ni,Co,Cr,Mo)}}{C_{(Al,Ti,Ta)}} \) can be used to estimate the stoichiometry of the precipitate phase chemistry for different sizes of precipitate formed at different cooling rates. As shown in Fig. 7, for all cooling rates, the large (>240 nm) precipitates show mean ratios of 3.41 ± 0.08 (3σ), but this decreases for smaller precipitates, with a mean ratio of 2.85 ± 0.30 (3σ) for precipitates of less than 70 nm. Our thermodynamic calculations predict an almost constant
value of 3.4 for the equilibrium $C_{(Ni, Co, Cr, Mo)}/C_{(Al, Ti, Ta)}$ ratio at all temperatures between 873 and 1323 K. The experimentally measured values for the $C_{(Ni, Co, Cr, Mo)}/C_{(Al, Ti, Ta)}$ ratio are close to this equilibrium prediction for the larger particles in this study but decrease quickly for smaller precipitates, with these smaller precipitates having non-stoichiometric compositions significantly away from equilibrium.

Fig. 8 compares mean compositions at different cooling rates for three elements in different size ranges: Al, Ti and Co content was compared for particles of size (a) 0–70 nm, (b) 70–140 nm and (c) 140–300 nm. Note that, for fast cooling rates, the $\gamma'$ precipitates only have a limited size range, and consequently it is only possible to show compositions for certain sizes of precipitate (only 70–140 nm at 100 K min$^{-1}$ and only 0–70 nm for 360 K min$^{-1}$). We note that, for the smallest precipitates, the size range observed in the TEM measurements (as illustrated in Fig. 4) is slightly different to that determined from the SEM images (Fig. 2). In particular, at 100 K min$^{-1}$, TEM analysis shows fewer very small precipitates than the SEM measurements (Fig. 3a). However, as the size analysis of the extracted precipitates (Fig. 4) agrees with the unimodal distribution observable by dark-field TEM, this PSD difference is likely to be the result of an artefact in the SEM analysis where chemical inhomogeneity results in unwanted pitting of the matrix being identified as small-scale precipitates.

4. Discussion

The fast-cooled microstructures show small size distributions and negligible compositional variations, consistent with all precipitates being formed over a small temperature range with a limited time for diffusion. In contrast, clear size-dependent compositional variations are observed at slow cooling rates. Secondary $\gamma'$ generated at all cooling rates display compositions that are closer to thermodynamic predictions than tertiary $\gamma'$. For example, at our slowest cooling rate of 1 K min$^{-1}$, 240 nm secondary $\gamma'$ precipitates have effectively near-field compositions, displaying mean values of 12.5 at.% Al and 8.9 at.% Ti, compared to the equilibrium means of 12.3 ± 0.3 at.% Al and 8.7 ± 0.1 at.% Ti, respectively (Fig. 4a). Tertiary $\gamma'$ are farther away from the near-field compositions predicted by equilibrium thermodynamics, having compositions of 16.7 at.% Al and 8.3 at.% Ti for a 1 K min$^{-1}$ cooling rate. This implies that our experimentally observed compositional variations are unlikely to be caused by differences in the thermodynamically stable composition at different temperatures.

An alternative possible cause of non-equilibrium elemental distributions in fine-scale particles is the Gibbs–Thomson effect [30], where a particle's composition in the
presence of a curved interface under tension is altered so as to lower the free energy of the system. The free energy resulting from interfacial tension, $\Delta G_I$, is given as [31]:

$$\Delta G_I = 2\Gamma/r$$  \hspace{1cm} (3)

where $\Gamma$ is the interfacial tension and $r$ is the precipitate radius. However, in Ni-based superalloys the interfacial tension is exceptionally low ($\Gamma = 0.01 \text{ J m}^{-2}$), compared to typical values of $1 \text{ J m}^{-2}$ in Al-Cu alloys [32]. For the smallest precipitates considered here, $r = 5 \text{ nm}$, an interfacial energy, $\Delta G_{I/3}$, of $4 \times 10^5 \text{ J m}^{-1}$ is calculated when using Eq. (3). Experimentally, we observe an increase of 4.3 at.% Al in the slow-cooled samples, from 12.4 at.% Al in the 250 nm secondary precipitates to 16.7 at.% Al in the 20 nm tertiary ones (Fig. 4a).

Our thermodynamic calculations predict that for RR1000 this approximately equates to a chemical free energy increase of between $4 \times 10^6$ and $8 \times 10^6 \text{ J mol}^{-1}$ at $2000 \text{ K}$. Thus the interfacial free energy is only able to account for $\sim 0.5\%$ of the observed increase in Al content for the 10 nm diameter precipitates and therefore the Gibb–Thomson effect is not believed to be responsible for the Al enrichment we observe experimentally for the fine-scale tertiary Al precipitates formed on slow cooling.

Having determined that neither the interfacial energy nor the chemical free energy of Ni-based superalloys could produce the changes in Al content we observe experimentally in the fine-scale tertiary Al at slow cooling rates, it is necessary to next consider the influence of diffusion kinetics. The smallest precipitates (sizes less than 70 nm) are likely to have formed last and at the lowest temperature. These show clear cooling rate dependent compositional variations (Fig. 8a), while precipitates larger than 140 nm (Fig. 8c) were generated at high temperatures and show fairly flat mean compositions for all cooling rates. The temperature for fine-scale Al formation and growth decreases with decreasing cooling rate, so we can predict that diffusion effects will have the largest influence on the fine-scale precipitates and the slowest cooling rates. In fact, this is what we observe experimentally, with larger precipitates and fast cooling rates showing equilibrium compositions while small-scale precipitates at slow cooling rates have enhanced Al contents and reduced Ti and Co contents. Compositional variations are smaller for fast compared to slow cooling rates: comparing Fig. 8a and b shows that the increase in Al content for precipitates of 0–70 nm compared to 140–250 nm is 7.3 at.% at 1 K min$^{-1}$ but 5.3 at.% at 10 K min$^{-1}$. With regular intrasublattice diffusion limited growth, tertiary precipitates will have been generated from a supersaturated matrix in which Al forms are not confined to the $\gamma$-sublattice. Gopal and Srinivasan [34] have recently demonstrated that this mechanism provides a good fit to experimental data measured by diffusion couples [35] for the binary Ni$_3$Al system and validates the argument of antisite-assisted diffusion by Mishin [36]. A similar diffusion mechanism is particularly important at low temperature and will enhance the diffusivity of Al in the $\gamma$ precipitates. For example, Ti and Ta are only confined to the $\beta$-sublattice, while $\gamma$ forms Cr, Co and Mo are confined to the $\alpha$-sublattice. All these elements diffuse slowly, especially at low temperatures, as there is a high activation barrier for diffusion via vacancy–atom exchange. Aluminium's anomalously fast diffusion behaviour at low temperatures has recently been explained by intrasublattice vacancy-mediated diffusion, i.e. vacancy-mediated antisite-bridging diffusion [9,10,33]. This allows aluminium to diffuse preferentially within the $\beta$-sublattice via the $\gamma$-sublattice due to the lower energy barrier compared to the direct vacancy–atom exchange diffusion. This unusual diffusion mechanism is particularly important at low temperature and will enhance the diffusivity of Al in the $\gamma$ precipitates.

For this intrasublattice diffusion mechanism, slowing the cooling rate further supports the importance of diffusion. The simultaneous depletion of Ti and Ta for the small precipitates formed at slow cooling rates (1 and 10 K min$^{-1}$) can also be explained by the relatively lower diffusivity of these elements at lower temperature. Mishin [36] used first-principle calculations to demonstrate that, in $\gamma$, Al-rich off-stoichiometry is characterised by high Al antisite concentrations, while Ni-rich off-stoichiometry has dramatically fewer Al antisites. This supports the conclusion that our experimentally measured decrease in the $C_{\text{Ni,Co,Mo}}/C_{\text{Al,Ti,Ta}}$ ratio for slower cooling rates (Fig. 7) is produced by increased concentrations of Al antisites. This again demonstrates that the enhancement of Al in the fine-scale tertiary precipitates results from the surviving antisites within the $\beta$-sublattice and the importance of the antisite diffusion mechanism at low temperatures.

It is worth noting that, for the fast cooling rates, all precipitates are likely to have been nucleated at relatively high temperatures, similar to the temperatures at which the secondary Al precipitates were generated within the slow-cooled samples. In comparison to those of the tertiary formation, i.e. faster cooling rates result in fine-scale precipitates being formed at higher temperatures compared to those of the same size precipitates generated at 1 or 10 K min$^{-1}$. Consequently, at 360 K min$^{-1}$, precipitates of 30–50 nm grow by the same diffusion mechanism as observed for 240 nm secondary precipitates formed at cooling rates of 1 K min$^{-1}$, i.e. growth occurs via intrasublattice vacancy–atom exchange, and these precipitates do not
show anomalous compositions. This implies a transition for aluminium from intrasublattice diffusion at high temperature to antisite at low temperature.

5. Conclusions

In conclusion, absorption-corrected EDX spectroscopy has been performed in an S/TEM on a large number of extracted $\gamma'$ precipitates in order to study the size-dependent compositional variations present for the PM Ni-based superalloy RR1000 at different solution cooling rates. Our results provide new experimental data to support the importance of considering differences in diffusion kinetics for different alloying elements when predicting the precipitation and phase chemistry. In summary:

1. The secondary $\gamma'$ precipitates (140–300 nm) are found to have near-field equilibrium compositions, whilst the fine-scale tertiary $\gamma'$ precipitates have far-field compositions.

2. Aluminium is observed to be enriched in the fine-scale tertiary $\gamma'$ for slow-cooled alloys and exhibits different compositional variation behaviour from the other $\gamma'$ stabilizers (Ti and Ta are depleted in these same precipitates).

3. A slow cooling rate of 1 K min$^{-1}$ led to greater Al enrichment compared to the same sizes of tertiary $\gamma'$ precipitates formed with a cooling rate of 10 K min$^{-1}$. This suggests abnormal diffusion kinetics in aluminium, which can be explained by the importance of the antisite diffusion mechanism at low temperature.

The experimentally observed differences in the Al enrichment observed for different cooling rates suggests a transition of Al diffusion kinetics from intrasublattice at high temperature to antisite at low temperature. Our results provide new experimental evidence validating Al antisite-bridged diffusion at low temperatures and provide valuable structural data towards improving the accuracy of predicting the precipitate phase chemistry and microstructural evolution in Ni-based superalloys.

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