γ' PHASE INSTABILITIES IN HIGH REFRACTORY CONTENT γ - γ' Ni-BASE SUPERALLOYSStoichko Antonov¹, Dieter Isheim^{2,3}, David N. Seidman^{2,3}, Eugene Sun⁴, Randolph C. Helmink⁴, Sammy Tin¹¹ Illinois Institute of Technology; 10 W. 32nd Street; Chicago, IL 60616, USA² Department of Materials Science and Engineering, Northwestern University; 2220 Campus Drive; Evanston, IL 60208, USA³ Northwestern University Center for Atom Probe Tomography (NUCAPT); 2220 Campus Drive; Evanston, IL 60208, USA⁴ Rolls-Royce Corporation; PO Box 420; Indianapolis, IN 46241, USAKeywords: γ' instability, γ' splitting, phase transformation, γ precipitates, coarsening, Ni-base alloy**Abstract**

Detailed electron microscopy and atom probe tomography (APT) techniques were used to systematically quantify the chemical and morphological instabilities that occur during aging of polycrystalline Ni-base superalloys containing elevated levels of refractory alloying additions. The morphological changes and splitting phenomenon associated with the secondary γ' precipitates were related to the discrete chemical compositions of the secondary and tertiary γ' along with the phase compositions of the γ matrix and the γ precipitates that form within the secondary γ' particles. Compositional phase inhomogeneities led to the precipitation of finely dispersed tertiary γ' particles within the γ matrix and secondary γ particles within the secondary γ' precipitates, which, along with surface grooving of the secondary γ' particles, contributed to the inverse coarsening or splitting of the precipitates during aging.

Introduction

Nickel-based superalloys are the material of choice for use in the "hot section" of modern gas turbine engines for aerospace, marine propulsion and power generation applications [1-9]. The unique microstructure consisting of ordered $L1_2$ intermetallic precipitates, γ' (Ni_3Al), distributed coherently within a disordered FCC Al matrix, γ (Ni), confers strength by providing substantial order and coherency type strengthening by restricting dislocation motion during plastic deformation. The superior high-temperature properties exhibited by modern Ni-base superalloys can largely be attributed to the underlying microstructure. In modern polycrystalline Ni-base superalloys, γ' forming elements (Al, Ti, Nb, and Ta) are utilized to produce an optimized volume fraction of the γ' strengthening phase, while additions of refractory alloying elements such as W, Mo, Cr and Co serve to strengthen the γ matrix phase through solid solution strengthening. Even though modest improvements in the strength of the alloy and the temperature capability can be attained via an increase in the volume fraction of the γ' precipitates, this tends to increase the overall alloy cost, while degrading the processing capabilities and environmental resistance.

As new classes of high refractory content, polycrystalline Ni-base superalloys are being developed, increases in the overall alloying content of Nb, Ta, and Ti additions to γ - γ' Ni-base superalloys can significantly impact the microstructure of the alloy and the levels of these alloying additions need to be carefully optimized. At low alloying concentrations, Nb, Ta, and/or Ti will preferentially partition to the γ' phase and serve to lower the anti-phase boundary energy as well as to strengthen the precipitate's resistance to deformation [10]. However, as the overall concentrations of these elements increase to just below the

solubility limit, residual concentrations of these γ' forming elements may remain in solution within the γ phase and serve as potent solid solution strengtheners [11,12]. This effect may potentially be exploited and used to enhance the strength and the high temperature capability of the alloy, but excessive alloying with Nb, Ta, and Ti can also result in the formation of undesirable intermetallic phases such as δ (Ni_3Nb) and/or η (Ni_6AlNb) within the microstructure when the solubility limits are exceeded [13-17]. One of the primary drawbacks associated with the high refractory content Ni-base superalloys, however, is that in many cases the high refractory alloying content contributes to reducing the overall atomic mobility of the system and makes it difficult to attain a stable microstructure when conventional thermal-mechanical processing techniques are employed.

For binary Ni-Al alloy systems, γ' precipitate coarsening is governed by the minimization of surface energies and is consistent with the Oswald ripening theory. In multiple component γ - γ' Ni alloy systems, however, the γ' precipitate evolution behavior may deviate from classical coarsening. In some instances, inverse coarsening takes place, where smaller precipitates grow at the expense of bigger neighbors due to the elastic fields [18]. Another phenomenon is particle splitting, where the cuboidal precipitates grow to a critical size and split into two or eight smaller particles [19,20]. Calculations have shown that the system energy decreases if the precipitate changes from a cube morphology to an octet [21]. Even though the splitting increases the overall surface energy in the system, various studies claim that the increase in surface energy is compensated by the decrease in elastic strain energy, as the misfit between γ and γ' decreases [19,20,22]. Other studies have reported that the observed morphological instabilities form as a result of re-precipitation of the γ matrix phase at the center of the γ' precipitate during aging [22]. Cha et al. have suggested that the splitting is mediated by interface instability, which causes interface grooving to the center of the precipitate [18].

Understanding the fundamental effects associated with having an elevated concentration of refractory alloying elements in Ni-based superalloys will contribute to optimization of both chemistry and thermal processes. This knowledge can then be applied to engineer alloys and microstructures with greater temperature capability. In this work, microstructural and compositional changes occurring in a high refractory content Ni-base superalloy were quantified as a function of aging time at 850 °C. Detailed microstructural studies were performed using atom probe tomography (APT) and field emission scanning electron microscope (SEM) at various aging times to quantify and explain the morphological changes occurring within the γ' precipitates. Thermodynamic predictions of phase fractions and chemistries, using ThermoCalc, were compared to the results from the APT

studies. Additionally, the formation and stability of secondary γ' particles forming within the γ' precipitates was documented and studied as a part of this investigation.

Experimental Procedure

An experimental, powder processed Ni-base superalloy, RRHT1, was used in this investigation, Table I. The sample was isothermally forged from a hot isostatically pressed (HIP) billet and solution heat treated at 1170 °C for 1 hour, followed by a controlled cooling rate of 1 °C/s. The samples were subsequently aged at 850 °C for 1, 4, 16, 25 and 50 hours and air quenched. Metallographic samples were prepared using standard grinding and polishing techniques to a final polishing using a solution of 0.06 μm colloidal silica. The samples were etched using a 33% HCL - 33% NO_3 - 33% CH_3COOH - 1% HF γ' etchant for observation under a JEOL JSM 6701-F field emission scanning electron microscope (SEM) in secondary electron (SE) mode with an accelerating voltage of 10 kV. Multiple images of the microstructure were taken at 20,000 x in different regions of each sample in order to obtain a statistically significant representation of the γ' phase and particle size distributions. In addition, higher magnification images, 80,000 x, were taken in order to observe the smaller nano-scale precipitates.

For preparation of specimens for atom probe tomography (APT), thin sheet specimens were prepared by grinding the samples to $\sim 8 \times 14 \times 0.3 \text{ mm}^3$ dimensions for each alloy. Square rods of cross section measuring $\sim 0.34 \times 0.34 \text{ mm}^2$ were cut from the thin sheets using a high speed diamond saw. These thin rods were subsequently electro-polished into needles with an approximate tip diameter of 100 nm. The electro-polishing was done using a two-step sequence: first a coarse polish was performed using a 10% perchloric acid in acetic acid solution at $\sim 25 \text{ V}$, and second, a fine polish was done using a 2% perchloric acid in butoxyethanol solution at $\sim 19 \text{ V}$. APT was conducted using a local electrode tomograph with a picosecond ultraviolet (wavelength of 355 nm) laser energy of 25 pJ per pulse, a pulse repetition rate of 500 kHz, a microtip temperature of 34 K and an evaporation rate of 4%. All of the APT data was analyzed using

IVAS 3.6.8 software from Cameca. Average phase compositions were obtained by creating a proxigram concentration profile [23] with respect to each interface, while the phase instabilities were determined by creating a cylindrical region of interest measuring $15 \times 15 \times 200 \text{ nm}^3$ through the phase.

Table I. Composition of RRHT1 (at.%)

Alloy	Ni	Cr	Al	Mo	Co	Nb	Ta	W
RRHT1	Bal.	5-16	7.94	0-3	18.37	5.54	0-3	0-2

Results

Micrographs in Figure 1 show the representative microstructure of the RRHT1 alloy following thermal exposures at 850 °C for different times. Starting from the as-solutioned condition, up to aging for 16 hours, the γ' precipitates exhibit normal coarsening behavior as the γ' precipitates evolve from being initially, near cubical to possessing an irregular-shaped morphology. Upon aging at 850 °C for 25 hours, the γ' precipitates have split into noticeably smaller, cubical precipitates. Average particle size distributions for the various precipitate populations are reported in Table II. After 50 hours at 850 °C, the precipitates do not appear to have coarsened significantly when compared to the 25 hours exposure.

At higher magnifications, Figure 2, it is possible to observe the finer features of the microstructure at different aging times. After 1 hour at 850 °C, the γ - γ' microstructure of the as solutioned sample, forms tertiary γ' precipitates and very fine secondary γ particles inside the larger γ' precipitates. As the sample is aged further, to 4 hours, both, tertiary γ' and secondary γ precipitates, coarsen noticeably. At 16 hours, the tertiary γ' precipitates have re-dissolved and are not present, but the secondary γ precipitates have coarsened even further. Once the coarsened γ' particles have split, after 25 hours in Figure 1, the secondary γ particles appear to have dissolved back into the matrix phase. The average sizes of the secondary γ particles were measured and listed in Table II.

Figure 1. Effects of aging time on the microstructure and the precipitate stability of alloy RRHT1 during aging at 850 °C.

Figure 2. Effect of aging time on the evolution and stability of the γ and tertiary γ' precipitates.

Table II. Average secondary γ and tertiary γ' precipitate size as a function of aging time at 850 °C

Condition	As Solutioned Average Size [nm]	1 Hour Average Size [nm]	4 Hour Average Size [nm]	16 Hour Average Size [nm]	25 Hour Average Size [nm]	50 Hour Average Size [nm]
Secondary γ' precipitates	214 +/- 60	235 +/- 72	241 +/- 75	257 +/- 84	182 +/- 57	207 +/- 81
Secondary γ precipitates	N/A	8.9 +/- 4.5	14.7 +/- 3.0	19.5 +/- 6.8	N/A	N/A
Tertiary γ' precipitates	N/A	18 +/- 4	44 +/- 18	N/A	N/A	N/A

The precipitates coarsen from ~ 9 nm, 1 hour at 850 °C, to ~ 15 nm, 4 hours at 850 °C, to finally ~ 20 nm, 16 hours at 850 °C.

Multiple atom probe needles and large datasets were collected and analyzed during the course of this investigation, Figure 3. For the as-solutioned sample and the samples aged for 4 and 50 hours at 850 °C, a total of 320, 450, and 130 million atoms, respectively, were collected. For visualization purposes, all atoms have been hidden, except for Cr and Al, as these elements strongly partition to the γ and the γ' phases, respectively. APT results from the as-solutioned sample reveal very fine tertiary γ' particles, which form during the cooling process, while the 50 hour aged sample contains very small secondary γ precipitates in one of the bigger secondary γ' precipitates. One of the primary benefits of APT is that it is able to provide quantitative compositional information and resolve nano-scale features that are too fine to be resolved in the SEM images. The average composition of the γ matrix and γ' precipitates for the three conditions was measured by assessing

the constituent atoms comprising each phase. To avoid interface biasing effects, results for each respective phase were measured 50 nm away from the interface and into the phase. The results were averaged among the interfaces of each needle for each condition and are listed in Table III. A higher degree of elemental segregation was noted in the sample that was aged at 850 °C for both, 4 and 50 hours. Comparison of the results between the as-solutioned and 4 hour aged samples reveals that the γ' forming elements, Al, Nb, and Ta, all have approximately halved their concentrations in the γ phase during the aging treatment. Consequently, the partition coefficient, $k=c_{\gamma}/c_{\gamma'}$ for these three elements have also reduced from 0.25, 0.46, and 0.19 to 0.14, 0.26, and 0.11, respectively. Interestingly, after aging for 50 hours, the partition coefficients for these elements have remained nominally unchanged at 0.11, 0.24 and 0.11, respectively. The partition coefficient for Mo and W remained the same throughout the heat treatment at ~ 5 and ~ 2.5 , respectively. Elements that usually preferentially partition to the γ matrix, Cr and Co, have

Table III. γ and γ' phase compositions of RRHT1 (at.%) as a function of aging time at 850 °C

Element	Solutioned			Aged 850 °C 4 hours			Aged 850 °C 50 hours		
	γ matrix [at.%]	Secondary γ' [at.%]	Partition Coefficient	γ matrix [at.%]	Secondary γ' [at.%]	Partition Coefficient	γ matrix [at.%]	Secondary γ' [at.%]	Partition Coefficient
Ni	42.6	61.8	0.69	38.8	63.3	0.61	39.4	63.9	0.62
Cr	24.4	2.6	9.23	28.5	1.6	17.69	28.4	1.6	17.35
Al	3.4	13.4	0.25	1.7	12.1	0.14	1.4	13.1	0.11
Mo	3.0	0.6	4.82	2.9	0.7	4.18	2.6	0.5	5.06
Co	21.4	11.6	1.85	24.2	10.6	2.29	24.4	10.4	2.35
Nb	3.5	7.6	0.46	2.1	8.3	0.26	2.0	8.1	0.24
Ta	0.35	1.83	0.19	0.16	1.48	0.11	0.19	1.70	0.11
W	1.19	0.48	2.49	1.17	0.58	2.03	1.30	0.52	2.50

Figure 3. APT needles from RRHT1 with the following heat treatments: for a) the as-solutioned, b) aged 4 hours, and c) 50 hours at 850 °C. Displayed are a fraction of the Al and Cr atoms with 6.0 at.% Al isoconcentration surfaces, superposed to highlight the precipitates.

increased concentrations in the γ phase, while becoming more lean in the γ' phase after the aging treatment. The partition coefficient of Cr almost doubles from 9.2 to 17.6 from the as-solutioned to the 4 hour aged condition, while Co has a more modest increase from 1.9 to 2.3. Similarly, the partition coefficients for Cr and Co remained the same in the sample aged for 50 hours at 17.4 and 2.4, respectively.

Table IV. γ and γ' phase compositions of RRHT1 aged at 850 °C for 4 hours obtained via APT (at.%)

Element	Secondary γ precipitates [at.%]	Tertiary γ' [at.%]
Ni	32.5	63.8
Cr	35.1	1.6
Al	1.1	11.3
Mo	2.0	0.7
Co	27.0	10.4
Nb	1.2	8.2
Ta	0.19	1.34
W	0.54	0.62

In order to better assess the stability of each phase, 1-dimensional line concentration profiles were extracted from the γ matrix channel and from inside the secondary γ' particles, Figure 4. The degree of chemical heterogeneity of the as-solutioned sample appears to be much more pronounced in the γ matrix than in the secondary γ' precipitates. In the 50 hour aged sample the elemental concentrations seem to be much more homogeneous, which suggests that the sample has approached its equilibrium phase composition.

In addition to the γ and γ' phase composition in the sample aged for 4 hours, APT data was obtained for the secondary γ particles inside the secondary γ' precipitates, Figure 5, and tertiary γ' precipitates that were also observed. Compositional data for these two transient phases, present in the sample, are compiled in Table IV. Comparing the composition of the γ matrix, Table II, to that of the secondary γ precipitates, a few differences can be noted. The concentrations of the γ' forming elements Al and Nb are significantly leaner in the secondary γ precipitates, 1.6 at.% and 2.1 at.% compared to 1.1 at.% and 1.2 at.%, respectively. Interestingly, major differences were also noted in the Cr, Co, and Ni concentrations, where the nano-scale γ precipitates have higher concentrations of Cr and Co, but are lean in Ni. Cr, and Co are elevated by ~6 at.% and ~3 at.%, respectively, when compared to the matrix, while there is ~6 at.% less Ni in the γ particles contained within the γ' precipitates. Looking at the compositions of the secondary and tertiary γ' particles, it can be noted that in the tertiary γ' particles the Al and Ta concentrations are modestly lower than in the secondary γ' precipitates.

Using data from Tables III and IV, plots of $C_i^n - C_i^\gamma$ vs $C_i^{\gamma'} - C_i^\gamma$ where $i = \text{Ni, Cr, Al, Mo, Co, Nb, Ta, and W}$ were made to calculate the overall γ' fraction present in the alloy and presented in Figure 6. C_i^n , C_i^γ and $C_i^{\gamma'}$ correspond to the concentration of element i contained in the bulk, γ and γ' phases. The slope of the best fit line of the dataset corresponds to the molar volume fraction of γ' in the alloy. The values obtained were 0.41 for the as-solutioned, 0.49 for the sample aged for 4 hours and 0.48 for the sample aged for 50 hours at 850 °C. These values are a bit elevated when compared to those obtained from the SEM images, but this can be explained by the fact that such data only takes into account the two phases and foregoes phases such as carbides, which are also present in small fractions. Since the microstructure is comprised primarily of γ - γ' , the volume fractions are in the correct range and the effect from other phases is negligible.

Figure 4. 1D concentration profiles for a) as-solutioned γ phase, b) 50 hour aged γ phase, c) as-solutioned γ' phase, and d) 50 hour aged γ' phase.

Figure 5. APT reconstruction of RRHT1 with 288 million atoms, showing the γ precipitates within the γ' precipitates along with an inset SEM image showing the four phases. Displayed are a fraction of the Al and Cr atoms with 6.0 at. % Al isoconcentration surfaces superposed to highlight the precipitates.

Figure 6. Plots of the normalized compositional distribution in the γ - γ' phases for a) as-solutioned, b) aged 4 hours, and c) 50 hours at 850 °C.

To understand the influence of the lattice misfit on the precipitate instability, APT phase composition data was used in order to estimate the lattice parameters of each phase, using Vegard's relation, Equation (1), with published Vegard coefficients [24],

$$\begin{aligned} a_{\gamma} &= a_0^{\gamma} + \sum_i \Gamma_i^{\gamma} x_i^{\gamma} \\ a_{\gamma'} &= a_0^{\gamma'} + \sum_i \Gamma_i^{\gamma'} x_i^{\gamma'} \end{aligned} \quad (1)$$

Where a_{γ} and $a_{\gamma'}$ are the calculated lattice parameters for γ and γ' , respectively. a_0^{γ} and $a_0^{\gamma'}$ are the lattice parameters for pure Ni and Ni_3Al [25], Γ_i^{γ} and $\Gamma_i^{\gamma'}$ are the Vegard coefficients for element i , and x_i^{γ} and $x_i^{\gamma'}$ are the concentrations of element i for γ and γ' , respectively. Lattice misfit, δ , was calculated using Equation (2),

$$\delta = 2 \frac{a_{\gamma'} - a_{\gamma}}{a_{\gamma'} + a_{\gamma}} \quad (2)$$

Calculations of the lattice parameters and mismatch for RRHT1 were carried out on both the as-solutioned and 4 hour aged samples, Table V. In addition, lattice mismatch calculations for as-solutioned RR1000 samples and RR1000 samples aged for 16 hours at 760 °C were also calculated based on published APT data by Collins et al. [27], respectively. It is important to note that, both of these alloys exhibit positive misfits, meaning that the γ' lattice parameter is larger than the γ lattice. The mismatch in RRHT1 was found to increase from 0.22% in the as-solutioned state, to 0.54% in the 4 hour aged condition, while the mismatch in RR1000 remains relatively constant ~0.3% both before and after aging.

Table V. Calculated lattice parameters and mismatch of RRHT1 and RR1000

Alloy	RRHT1 As-Solutioned	RRHT1 Aged 4h at 850 °C	RR1000 As-Solutioned	RR1000 Aged 16h at 760 °C
γ Lattice [nm]	0.3608	0.3598	0.3593	0.3592
γ' Lattice [nm]	0.3616	0.3618	0.3603	0.3603
Mismatch δ	0.22%	0.54%	0.29%	0.31%

Thermocalc simulations with the TCNI8 database were used to generate a phase fraction vs. temperature plot, Figure 7, and determine the γ' solvus temperature and the equilibrium phase compositions of the γ and γ' phases at 850 °C, Table VI. Comparison of the APT measured phase compositions of the constituent phases for the 50 hour aged condition, from Table III, reveals reasonable agreement with the Thermocalc predictions at 850 °C.

Figure 7. Phase fractions for RRHT1 calculated with Thermocalc (TCNI8).

Table VI. γ and γ' phase compositions of RRHT1 as predicted by Thermocalc (TCNI8) at 850 °C (at.%)

Element	850 °C (TCNI8)		998 °C (TCNI8)	
	γ matrix [at.%]	Secondary γ' [at.%]	γ matrix [at.%]	Secondary γ' [at.%]
Ni	38.7	66.2	50.2	65.1
Cr	24.1	1.6	14.6	2.1
Al	4.0	13.6	8.0	14.4
Mo	2.3	0.16	1.4	0.20
Co	26.9	7.0	18.5	7.4
Nb	2.2	9.7	5.3	8.9
Ta	0.49	1.68	0.99	1.6
W	1.3	0.12	0.77	0.14

Discussion

High refractory content γ - γ' Ni-base superalloys were investigated in order to better understand the morphological and compositional changes that occur within the microstructure of a powder processed, polycrystalline Ni-base superalloy during aging at 850 °C. Starting from the as-solutioned condition, both compositional and morphological changes occurring during aging at 850 °C were systematically quantified at various time intervals. Following solutioning, the transient γ' precipitates that formed during cooling from the solution temperature evolved to reach a near equilibrium state after 50 hours of aging at 850 °C. During this process, the γ' precipitates evolve from exhibiting an irregular-shaped morphology in the as-solutioned state to a more cubical morphology in the near equilibrium state through the formation of transient phases, surface grooves, and finally, particle splitting. Figures 1 and 2. Figure 8 shows the morphological evolution of the size for all of the precipitates and particle distribution of the secondary γ' precipitates as a function of aging time. From the as-solutioned condition up to 16 hours of aging, the secondary γ' precipitates coarsen as the distribution is shifted to the right, however, after 25 hours, the secondary γ' distribution shifts to the left as the precipitate size becomes smaller. Note that the error bars on the plot show the actual standard deviation in the precipitate size and for all conditions, the deviation in secondary γ' precipitates is about 150 nm.

Compositional changes that occur during the aging process were elucidated using the APT data. Quantitative phase composition data extracted from the APT results reveal that the as-solutioned microstructure is supersaturated and phase concentrations fluctuate and are inhomogeneous throughout both the γ and γ' phases, Figure 4. These fluctuations and heterogeneities can largely be attributed to the high refractory content in RRHT1 leading to sluggish diffusion of the constituent alloying elements that become trapped in the γ' precipitates as they nucleate and coarsen during the cooling from the solution temperature. During aging of the as-solutioned structure, compositional redistribution,

nucleation, and growth of the constituent γ - γ' phases all occur in order to alleviate solute supersaturation and approach equilibrium. Since the large majority of the secondary γ' precipitates form during cooling from the solution temperature, the magnitude of undercooling may vary as a function of the cooling rate as the γ' precipitates nucleate and grow during continuous cooling. Moreover, as the equilibrium volume fraction and composition of the γ' precipitates vary as a function of temperature, the γ' precipitates that are present in the as-solutioned condition are chemically heterogeneous and the γ matrix is supersaturated with γ' forming elements, as the volume fraction of γ' precipitates is far from equilibrium. Ideally, aging temperatures and times should be selected to alleviate the excess solute supersaturation in the constituent phases, normalize the chemical heterogeneity, and stabilize the microstructure. However, as the overall refractory content of Ni-base superalloys increases, the limited atomic mobility of the refractory alloying elements requires higher aging temperatures or longer times in order to normalize and stabilize the microstructure. The APT results from the as-solutioned RRHT1 sample reveal that these secondary γ' particles that formed during cooling from the solutioning temperature tend to be rich in Cr and Co. During aging, the solubility, and hence the concentration of these elements in the γ' precipitates decreases and contributes to the formation of secondary γ precipitates that reside within the γ' phase, Figure 2. In a similar fashion, the formation of tertiary γ' serves to alleviate the supersaturation of Al, Nb, and Ta atoms from the γ matrix.

Comparing the phase compositions of the nano-scale tertiary γ' and secondary γ , Table IV, with those of the primary phases, Table III, reveals distinct differences between the various precipitate size populations. It should be noted that the two populations of nano-scale precipitates are not thermodynamically stable at 850 °C and are transient, metastable phases that form to alleviate supersaturation and eventually return back into solution as the volume fraction of the secondary γ' precipitates approaches equilibrium. Even though the tertiary γ' particles can be resolved in the SEM after 1 hour of aging, APT studies reveal the presence,

Figure 8. Effects of aging time on a) the precipitate size and b) the secondary γ' particle size distribution in RRHT1 as a function of aging time at 850 °C.

or nucleation of smaller nano-scale precipitates or clusters immediately following the solutioning step, Figure 3a. As the sample is aged for 4 hours at 850 °C, these nano-scale precipitates, or clusters, form tertiary γ' precipitates that continue to coarsen and alleviate the level of solute supersaturation within the γ matrix channels. Eventually, as the secondary γ' precipitates coarsen, the meta-stable tertiary γ' precipitates dissolve into the matrix and are completely gone after 16 hours of aging at 850 °C. In comparison, the secondary γ' precipitates that form inside the secondary γ' particles after 1 hour of aging, coarsen throughout the 16 hours of aging and appear to return back into solution only after splitting of the secondary γ' precipitates occurs. However, in select instances, APT analysis showed that secondary γ' particles were observed to persist in some of the larger γ' precipitates even after 50 hours of aging, Figure 3c. This would appear to suggest that the kinetics associated with these secondary γ' particles are more sluggish and that these γ' particles are more thermodynamically stable than the tertiary γ' and dissolve only after the secondary γ' have split.

Interestingly, compositional changes in the secondary γ' were not detected to vary substantially as a function of aging time, whereas the average composition of the γ phase matrix did vary notably, Table III. This can be attributed directly to the increase of the volume fraction of γ' precipitates, which increases from 0.41 in the as-solutioned sample to 0.49 for the 4 hour aged sample, Figure 6. During aging, growth of the secondary γ' precipitates accommodates any excess γ' solute that exists in the γ matrix and the dissolution of the tertiary γ' . Table II reveals that the majority of the chemical heterogeneity present in the as-solutioned structure has been reduced after 4 hours of aging. However, morphological instabilities still persist and the presence of the tertiary γ' and secondary γ' particles shows that phase segregation persists within the microstructure. Referring to the experimentally measured compositions for the secondary γ' inside the secondary γ' , Table IV, the Cr and Co levels remain elevated at 35 at.% and 27 at.% when compared to 29 at.% and 24 at.%, measured in the γ phase channels. This observation is consistent with reports that Cr has a much lower solubility limit in the γ' than Co, and suggests that as the secondary γ' precipitates reach a certain size, segregation of these elements from the γ' precipitates into the γ channels becomes more difficult due to the expanding diffusion distances and small clusters of γ phase are formed [28-30]. These clusters or precipitates of γ coarsen during aging as more γ solute is rejected from the γ' phase. Interestingly, these precipitates are shown to exhibit a relatively low concentration of Nb, 1.2 at.% compared to 2.2 at.% in the γ matrix, but higher Ta 0.19 at.% compared to 0.15 at.%.

The experimental observations would appear to suggest that the interfacial energy increase caused by the nucleation and coarsening of these transient nano-scale tertiary γ' and secondary γ' phases is offset by the reduction of the solute supersaturation energy of each primary phase. Although both the composition and fraction of the secondary γ' precipitates remain relatively unchanged from aging of 4 hours up to 50 hours at 850 °C, Table III and Figure 6, continuous morphological changes in the precipitate shape are occurring during aging. This implies that once the supersaturation, in the γ' precipitates, is alleviated by the formation of the transient phases, the system continues to evolve in a purely morphological manner as precipitates reduce their average precipitate size and transition from cubical to irregular and back to cubical morphologies, Table II. Since the γ phase of

the as-solutioned sample is supersaturated with γ' forming elements, while the γ' phase is enriched with γ solid solution strengtheners, the magnitude of the initial lattice mismatch between the two phases is relatively low, Table V. However, as the volume fraction of γ' precipitates increases and the degree of solute supersaturation is reduced, redistribution of the solute atoms among the constituent phases results in a significant increase in the magnitude of the lattice misfit.

In RRHT1, the lattice misfit induced grooving of the precipitate surfaces becomes noticeable during aging up to 16 hours, which drives the splitting and the eventual formation and coarsening of fine secondary γ' particles that can serve to feed solute and propagate these grooves and accelerate the splitting reaction [18, 29, 31]. This grooving is driven by the elastic strain energy which has been shown to cause splitting along the most elastically compliant $\langle 001 \rangle$ direction and cause various precipitate morphology changes, such as cube to octet transformation, as in this case [20, 29 32]. After the sample has been aged for 25 hours at 850 °C, the grooves have fully extended and split the γ' precipitates into eight smaller, more cubical particles. Upon the completion of the eight-fold splitting, the average secondary γ' size (~180 nm) is approximately two-thirds of the size before splitting (~260 nm), as shown in Table II and Figure 8, a result of the particle volume density being inversely proportional to d^3 . The splitting or refinement of the γ' precipitates also coincides with the dissolution of the secondary γ' particles. Upon another 25 hours of aging at 850 °C, the γ' precipitates have not evolved further. Meanwhile, lattice mismatch calculations from APT data for RR1000, Table V, show that the lattice mismatch remains almost unchanged throughout the aging process and the precipitates are not subject to surface grooving and eventual splitting.

Aging of the samples for a total of 50 hours at 850 °C normalizes the compositional variations as more time enables diffusive processes to occur and serve to minimize the magnitude of the fluctuations and bring the phases closer to equilibrium. Comparison of the Thermocalc equilibrium phase compositions, Table VI, with the constituent γ and γ' phases of the samples aged for 50 hours at 850 °C, Table III, reveals good agreement. Interestingly, the tertiary γ' precipitates were found to possess chemical compositions close to that of the secondary γ' , except that they tended to be leaner in the γ' forming elements, Al and Ta. This is to be expected as they formed during aging within the γ channels in a γ' solute lean environment as Ta and Al preferentially partition to the γ' phase. The levels of Nb in the tertiary γ' precipitates, however, were found to be similar/higher than that in the secondary γ' precipitates. This can be attributed to the characteristically higher degree of Nb solubility in the γ phase that allows Nb solute atoms to reside in the γ phase more readily than many of the other γ' forming elements [17]. Compared to the nano-scale secondary γ' precipitates, the tertiary γ' coarsen and dissolve back into solution much more rapidly during aging at 850 °C. This is likely due to the atomic bond strengths and kinetics of lattice diffusion being faster in the FCC γ phase when compared to the ordered, intermetallic $L1_2$ γ' phase.

To summarize, the morphological and compositional changes of a high refractory content Ni-base superalloy were assessed as a function of aging time at 850 °C. Due to the comparatively higher concentration of slow diffusing refractory alloying additions, aging of super-solvus treated microstructures resulted in the formation of both, dispersions of nano-scale γ' precipitates

contained within the γ channels, and nano-scale γ precipitates contained within the secondary γ' precipitates. Prolonged aging times are required to stabilize the microstructure and the transient morphological instabilities observed during aging appear to be driven by a combination of compositional heterogeneities and lattice misfit. From this study, it is apparent that optimization and control of the extent of microstructural strengthening requires a fundamental understanding of the mechanisms responsible for their characteristic behavior. This will enable the development of manufacturing processes that are capable of fully utilizing the intrinsic physical and mechanical properties of advanced superalloy compositions.

Conclusions

Based on the results and observations presented in this study, the following conclusions can be reported:

1. High refractory content Ni-based superalloys undergo both compositional and morphological changes during aging at 850 °C. Even after near equilibrium γ' volume fractions and phase compositions are attained during aging, morphological instabilities result in phase separation in the form of finely dispersed particles in both the γ and γ' phases.
2. Combined with the lattice misfit driven surface instabilities, grooving and growth of nodes caused by coalescence of nano-scale γ precipitates serve to drive precipitate splitting and inverse coarsening of the precipitates during aging.
3. Thermodynamic database models, such as Thermo-Calc with TCNI8, predicted equilibrium phase compositions close to those obtained from APT. However, some differences in the partitioning characteristics were noted.

Acknowledgements

Financial support for this work was provided by Rolls-Royce Corporation. Additionally, the local-electrode atom-probe tomograph at the Northwestern University Center for Atom-Probe Tomography (NUCAPT) was acquired and upgraded with equipment grants from the MRI program of the National Science Foundation (grant number DMR-0420532) and the DURIP program of the Office of Naval Research (grant numbers N00014-0400798, N00014-0610539, N00014-0910781). NUCAPT is a Research Facility at the Materials Research Center of Northwestern University, supported by the National Science Foundation's MRSEC program (grant number DMR-1121262). Additional instrumentation at NUCAPT was supported by the Initiative for Sustainability and Energy at Northwestern (ISEN).

References

- [1] T.M. Pollock and S. Tin, "Nickel-based superalloys for advanced turbine engines: chemistry, microstructure and properties," *Journal of Propulsion Power*, 22 (2006), 361-74.
- [2] D. Furrer and H. Fecht, "Ni-based superalloys for turbine discs," *Journal of the Minerals, Metals & Materials Society*, 51 (1999), 14-7.
- [3] C.T. Sims, N.S. Stoloff, and W.C. Hagel, *Superalloys II*

(New York, NY: Wiley, 1987).

- [4] R.F. Decker and C.T. Sims, *The Metallurgy of Nickel-base Superalloys* (New York, NY: Paul D. Merica Research Laboratory, 1972).
- [5] R.R. Unocic, G.B. Viswanathan, P.M. Sarosi, S. Karthikeyan, J. Li, and M.J. Mills, "Mechanisms of creep deformation in polycrystalline Ni-base disk superalloys," *Materials Science and Engineering: A*, 483 (2008), 25-32.
- [6] R.R. Unocic, L. Kovarik, C. Shen, P.M. Sarosi, Y. Wang, J. Li, S. Ghost, and M.J. Mills, "Deformation mechanisms in Ni-base disk superalloys at higher temperatures," *Superalloys 2008*, 377-385.
- [7] D. Locq, P. Caron, S. Raujol, F. Pettinari-Sturmel, A. Coujou, and N. Clément, "On the role of tertiary γ' precipitates in the creep behavior at 700°C of a PM disk superalloy," *Superalloys 2004*, 179-187.
- [8] R.C. Reed, *The Superalloys: Fundamentals and Applications* (New York, NY: Cambridge University Press, 2006).
- [9] M.J. Donachie and S.J. Donachie, *Superalloys: A Technical Guide. 2nd ed.* (Materials Park, OH: ASM International, 2002).
- [10] T.M. Pollock and R.D. Field, "Chapter 63 Dislocations and high-temperature plastic deformation of superalloy single crystals," *Dislocations in Solids*, 11 (2002), 547-618.
- [11] R.W. Kozar, A. Suzuki, W.W. Milligan, J.J. Schirra, M.F. Savage, and T.M. Pollock, "Strengthening Mechanisms in Polycrystalline Multimodal Nickel-Base Superalloys," *Metallurgical and Materials Transactions A*, 40 (2009), 1588-603.
- [12] H. A. Roth, C.L. Davis, and R.C. Thompson, "Modeling Solid Solution Strengthening in Nickel Alloys," *Metallurgical and Materials Transactions A*, 28 (1996), 1329-35.
- [13] P.M. Mignanelli, N.G. Jones, K.M. Perkins, M.C. Hardy, and H.J. Stone, "Microstructural evolution of a delta containing nickel-base superalloy during heat treatment and isothermal forging," *Materials Science and Engineering A*, 621 (2015), 265-71.
- [14] M. Detroy, R.C. Helmink, and S. Tin, "Microstructural Stability and Hot Deformation of γ - γ' - δ Ni-Base Superalloys," *Metallurgical and Materials Transactions A*, 45 (2014), 5332-43.
- [15] S. Antonov, M. Detroy, R.C. Helmink, and S. Tin, "Precipitate phase stability and compositional dependence on alloying additions in γ - γ' - δ - η Ni-base superalloys," *Journal of Alloys and Compounds*, 626 (2015), 76-86.

- [16] M. Detroy, S. Antonov, R.C. Helmink, and S. Tin, "Precipitate Phase Stability in γ - γ' - δ - η Ni-Base Superalloys," *Journal of the Minerals, Metals & Materials Society*, 66 (2014), 2478-85.
- [17] S. Antonov, M. Detroy, D. Isheim, D. Seidman, R. Helmink, R. Goetz, E. Sun, and S. Tin, "Comparison of thermodynamic database models and APT data for strength modeling in high Nb content γ - γ' Ni-base superalloys," *Materials and Design*, 86 (2015), 649-655.
- [18] P. Cha, D. Yeon, and S. Chung, "Phase-field study for the splitting mechanism of coherent misfitting precipitates in anisotropic elastic media," *Scripta Materialia*, 52 (2005), 1241-1245
- [19] M. Doi and T. Miyazaki, "The Effects of Elastic Interaction Energy on the shape of γ' -Precipitates in Ni-Based Alloys," *Superalloys 1984*, 543-552.
- [20] M. Doi, T. Miyazaki, and T. Wakatsuki, "The Effects of Elastic Strain Energy on the Morphology of γ' Precipitates in Nickel-Based Alloys," *Materials Science and Engineering*, 67 (1984), 247-253.
- [21] M. Doi, T. Miyazaki, and T. Wakatsuki, "The effects of Elastic Interaction Energy on the γ' Precipitate Morphology of Continuously Cooled Nickel-Base Alloys," *Materials Science and Engineering*, 74 (1985), 139-145.
- [22] T. Miyazaki, H. Imamura, and T. Kozakai, "The Formation of " γ' Precipitate doublets" in Ni-Al alloys and their Energetic Stability," *Material Science and Engineering*, 54 (1982), 9-15.
- [23] O.C. Hellman, J.A. Vandenbroucke, J. Rüsing, D. Isheim, and D.N. Seidman, "Analysis of Three-dimensional Atom-probe Data by the Proximity Histogram," *Microscopy and Microanalysis*, 6 (2000), 437-444.
- [24] Y. Mishima, S. Ochiai, and T. Suzuki, "Lattice parameters of Ni (γ), Ni₃Al (γ') and Ni₃Ga (γ') solid solutions with additions of transition and B-subgroup elements," *Acta Metallurgica*, 33 (6) (1985), 1161-1169.
- [25] T.M. Pollock and A.S. Argon, "Creep resistance of CMSX-3 nickel base superalloy single crystals," *Acta Metallurgica et Materialia*, 40 (1) (1992), 1-30.
- [26] A.M. Wusatowska-Sarnek, G. Ghosh, G.B. Olson, M.J. Blackburn, and M. Aindow, "Characterization of the microstructure and phase equilibria calculations for the powder metallurgy superalloy IN100," *Journal of Materials Research*, 18 (2003), 2653-63.
- [27] D.M. Collins, L. Yan, E.A. Marquis, L.D. Connor, J.J. Ciardiello, A.D. Evans, and H.J. Stone, "Lattice misfit during ageing of a polycrystalline nickel-base superalloy," *Acta Materialia*, 61 (2013), 7791-7804.
- [28] M. Doi, D. Miki, T. Moritani, and T. Kozakai, "Gamma/Gamma-Prime microstructure formed by phase separation of gamma-prime precipitates in a Ni-Al-Ti alloy," *Superalloys 2004*, 109-114.
- [29] A. Baldan, "Review: Progress in Oswald ripening theories and their applications to the γ' -precipitates in nickel-base superalloys," *Journal of Materials Science*, 37 (2002), 2379-2405
- [30] F. Vogel, N. Wanderka, Z. Balogh, M. Ibrahim, P. Stender, G. Schmitz, and J. Banhart, "Mapping the evolution of hierarchical microstructures in a Ni-based superalloy," *Nature Communications*, (2013), 1-7.
- [31] R.J. Mitchell, M.C. Hardy, M. Preuss, and S. Tin, "Development of γ' morphology in P/M rotor disc alloys during heat treatment," *Superalloys 2004*, 361-370.
- [32] A. Khachaturyan, S. Semenovskaya, and J. Morris Jr, "Theoretical analysis of strain-induced shape changes in cubic precipitates during coarsening," *Acta Metallurgica*, 36 (1988), 1563-1572.