σ and η Phase Formation in Advanced Polycrystalline Ni-base Superalloys

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Abstract

In polycrystalline Ni-base superalloys, grain boundary precipitation of secondary phases can be significant due to the effects they pose on the mechanical properties. As new alloying concepts for polycrystalline Ni-base superalloys are being developed to extend their temperature capability, the effect of increasing levels of Nb alloying additions on long term phase stability and the formation of topologically close packed (TCP) phases needs to be studied. Elevated levels of Nb can result in increased matrix supersaturation and promote the precipitation of secondary phases. Long term thermal exposures on two experimental powder processed Ni-base superalloys containing various levels of Nb were completed to assess the stability and precipitation of TCP phases. It was found that additions of Nb promoted the precipitation of η -Ni₆AlNb along the grain boundaries in powder processed, polycrystalline Ni-base superalloys, while reduced Nb levels favored the precipitation of blocky Cr and Mo – rich σ phase precipitates along the grain boundary. Evaluation of the thermodynamic stability of these two phases in both alloys using Thermo-calc showed that while σ phase predictions are fairly accurate, predictions of the η phase are limited.

Keywords- Superalloy, Stability, Secondary Phases, Sigma, Ni₆AlNb, Thermocalc

Introduction

High strength along with considerable fatigue resistance when exposed to corrosive environments at elevated temperatures are the properties that make nickel-based superalloys the material of choice for use in the “hot section” of modern gas turbine engines and power generation applications [1-9]. The unique microstructure consisting of the ordered L1₂ intermetallic precipitates γ' (Ni₃Al) distributed coherently within a disordered FCC A1 matrix γ (Ni), provides substantial order and coherency type strengthening by restricting dislocation motion during plastic deformation. Hence, much of the superior high temperature properties of Ni-base superalloys can be attributed to microstructural strengthening. Additions of refractory alloying elements, such as W, Mo, Cr and Co, in modern polycrystalline Ni-base superalloys, provide strength to the γ matrix phase through solid solution strengthening. Additionally, concentrations of γ' formers Al, Ti, Nb and Ta are utilized to produce an optimized volume fraction of the γ' strengthening phase. Although modest improvements in the properties of the alloy can be attained by increasing the volume fraction of the γ' precipitates, these changes are often accompanied by debits in processing capabilities, environmental resistance and overall alloy cost. Additions of Nb, Ta and Ti at relatively low alloying concentrations will preferentially partition to the γ' phase and serve to increase the anti-phase boundary energy as well as to strengthen the precipitate's resistance to deformation [10]. When present at elevated concentrations, residual levels of γ' forming solutes may remain within the γ phase and subsequently serve as potent solid solution strengtheners [11-14].

As the solubility limit for Ti additions in the matrix is exceeded, the formation of an η precipitate is promoted [15,16]. This phase consists of a hexagonally closed packed $D0_{24}$ crystal structure, with a composition of Ni_3Ti , which recently has been reported to also form as $Ni_3Al_{0.5}Nb_{0.5}$ [15,17-19]. The η phase possesses a lamellar and/or rod like morphology, which is not coherent with the γ matrix, and may negatively impact the mechanical properties of the alloy [20] when excessive precipitation occurs within the microstructure. Formation of Ni_6AlNb along the grain boundaries has also been observed to occur as a discontinuous precipitation reaction and can result in the formation of serrated grain boundaries, which may inhibit grain boundary sliding and greatly enhance creep properties [17,21]. Even though η forms at high temperatures, it can undergo a solid state transformation to γ' at lower temperatures. Historically, the Al/Ti ratio has been carefully controlled in Ni-base superalloys to maintain the phase stability and avoid η precipitation [22]. In addition to the formation of the η phase, excessive alloying concentrations of Nb, Ta and Ti can promote other secondary phases such as the $D0_a$ structured δ (Ni_3Nb), which along with η (Ni_6AlNb), can be detrimental to the forging properties of the alloys if present in excess [23-26]. Alloying additions of Nb, Ta and Ti have also shown to retard MC carbide decomposition into $M_{23}C_6$ as they tend to stabilize primary MC carbides. It has been reported that the order of most to least stable MC carbide is $TaC > NbC > TiC > VC$, where Nb is approximately equivalent to tantalum in stabilizing the MC carbides [27].

During long term temperature exposure, the formation of topologically closed packed (TCP) phases is of significant concern, as these secondary phases could have undesired effects on the alloys' properties. TCP phases such as σ are intermetallic compounds, possessing high hardness and brittleness. Sigma (σ), which has previously been characterized to belong to the D_{4h}^{14} space group, with a composition range of AB_7 to A_7B , where A and B commonly are Cr and Mo and/or Ni and Co, respectively [28-30]. For superalloys, the formula is usually given as $(Ni,Co)_x(Cr,Mo)_y$, where x and y can add up to 7 [31]. Work on U720 and U720Li has shown that the composition for σ in these two alloys is $(Cr_{0.5}, Mo_{0.1}), (Ni_{0.2}, Co_{0.2})$ [32]. σ phase precipitates can exhibit different morphologies, ranging from platelets and needlelike σ inside the grain, which can be detrimental to properties, to globular precipitation and σ films along grain boundaries, which have been shown to not be as damaging [31, 33, 34]. As globular precipitation occurs, due to its composition, σ absorbs Cr atoms from the matrix, which in turn reduces the amount of Cr solute in solid solution of the γ phase, and reduces the corrosion resistance of the alloy.

In recent years, Thermo-Calc or Pandat by CompuTherm and various other thermodynamic database models have been demonstrated to be effective in predicting the multicomponent thermodynamic stability of complex phases in commercial and experimental alloys with compositions that fall within the range of alloys over which substantial experimental data exists. As a result, these computational tools have been effectively used to accelerate the design and optimization of a variety of new metallic alloy systems. However, challenges in the ability of these models to accurately predict microstructural stability arise as experimental alloy compositions become more complex and include more alloying additions. Due to the limited amount of experimental thermodynamic information pertaining to the partitioning of Nb in γ - γ' alloy system, the precision of the thermodynamic database models is lacking. An improved fundamental understanding of how the different elemental alloy additions in combination with each other effect on the microstructure and the properties of this novel class of Ni-base superalloys is needed in order to design and successfully implement Ni-base superalloys with improved properties. The present report aims to investigate the effect of Nb and Al additions on the stability of carbides and secondary phases along the grain boundaries and provide a comparison with thermodynamic predictions.

Methods and Materials

The compositions of RRHT2 and RRHT4 alloys used in this study are presented in Table 1. The actual compositions of the alloys are not disclosed but the levels of Cr, Mo, Ta and W are nominally identical for both alloys and fall within the ranges specified in Table 1. The actual, measured concentrations of Al, Co and Nb in the RRHT alloys are reported in Table 1 and were systematically varied to elucidate the effects of these elements on the microstructure. The samples were received in the as-forged condition from a hot isostatically pressed (HIP) billet and were solution heat treated at 1170°C for 1h, followed by controlled cooling at 1°C/s. The samples were subsequently aged at 850°C for 4h in a MTI KSL-1500X chamber furnace and slow cooled inside the furnace. In order to get a better indication of the starting microstructure of each alloy, metallographic samples were prepared via grinding and polishing down 0.06 μm colloidal silica and etched using a 33% HCL - 33% NO_3 - 33% CH_3COOH - 1% HF γ' etchant for observation in secondary electron (SE) mode, under a JEOL JSM 6701-F field emission scanning electron microscope (FESEM), with an accelerating voltage of 10kV and current of 10 μA . Ten distinct images of the microstructure were taken at 20,000 $\times$ in different regions of each sample in order to obtain a good representation of the γ' phase distribution. The software ImageJ was used to determine the area fraction and ferret size of the γ' precipitates in each alloy, as well as the standard deviation across the 10 regions. In addition grain size was characterized using an Oxford Instrument Nordlys-HKL electron back-scatter diffractometer (EBSD) attached to a JEOL JSM 5900-LV scanning electron microscope (SEM). A minimum of four 800x600 μm^2 regions were mapped, with a step size of 1.8 μm .

Samples for atom probe tomography (APT) were prepared by cutting rods with a square cross section measuring $\sim 0.34 \times 0.34$ mm using a high speed saw. These thin rods were subsequently electro-polished into needles with an approximate apex diameter of 100 nm using a two-step sequence: first a coarse polish was performed using a solution of 10% perchloric acid in acetic acid at $\sim 25\text{V}$ DC, and second, a fine polish was done using solution of 2% perchloric acid in butoxyethanol at $\sim 19\text{V}$ DC. APT was conducted using a Cameca LEAP 4000X Si 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 base temperature of -239°C (34 K) and an evaporation rates of up to 5%. Two APT tips were obtained for each alloy and all of the APT data was analyzed using IVAS 3.6.12 software from Cameca. Average phase compositions were obtained by creating a proxigram with respect to each γ -secondary γ' interface and averaging over the plateau regions at least 10 nm away from the γ - γ' interface and 50 nm into each phase, respectively.

Subsequently, additional samples were cut and aged at 800°C in MTI KSL-1100X chamber furnace for extended periods of time: 100, 300, 500 and 1000 hours. Metallographic samples were prepared using standard grinding and polishing techniques to a final polish using a solution of 0.06 μm colloidal silica and observed under a Phenom ProX scanning electron microscope (SEM) in backscatter mode with an accelerating voltage of 10 kV. Images of the microstructure were taken at 10,000 $\times$ in different regions of each sample in order to obtain a good representation of the precipitate distribution inside the grains, as well as at the grain boundaries. In order to better observe the particle morphology, the samples were electrochemically etched with a solution of 90% H_2O and 10% phosphoric acid for 6 seconds at 500 mA and 5V. Images were subsequently taken with a JEOL JSM-6701F field emission scanning electron microscope in back-scattered mode with an accelerating voltage of 15kV.

To identify the secondary phases that formed during the long term thermal exposure in the alloys, thin foils for transmission electron microscopy (TEM) observation were prepared by twin-jet thinning in a solution of 7% Perchloric acid and 93% ethanol at -25°C and 40V. A JEOL JEM 2000 transmission electron microscope equipped with an Oxford Instruments EDS system operated at 200kV was used for observation and selected area diffraction (SAD).

Table 1. Composition of the RRHT alloys (at.%).

Alloy	Ni	Cr	Al	Mo	Co	Nb	Ta	W	C	Hf
RRHT2	Bal.	5-16	7.95	0-3	12.67	5.59	0-3	0-2	0.025-0.06	0
RRHT4	Bal.	5-16	9.46	0-3	11.91	4.70	0-3	0-2	0.025-0.06	0-0.5

Results

The micrographs in Fig. 1 show the general microstructure of each of the two alloys after aging at 850°C for 4 hours. Besides the scattered MC carbides, the grain boundaries appear to be free of any other phase. In order to better compare the two alloys, the average grain and γ' particle size were measured and provided in Table 2. The average grain size of both alloys is comparable at 27.7 μm and 23.4 μm for RRHT2 and RRHT4, respectively. The γ' volume fraction of RRHT4 was measured to be ~5% higher when compared to RRHT2 following aging at 850°C [14]. In addition, the average γ' size in RRHT4 is noticeably larger than in RRHT2 at 358 and 261 nm, respectively.

Fig. 1. SEM images of the starting microstructures of RRHT2 and RRHT4.

Table 2. Microstructural Characterization of the RRHT alloys after aging at 850°C.

Alloy	Average secondary γ' size (nm)	Average Grain Size (μm)
RRHT2	261 +/- 21	27.7 +/- 1.2
RRHT4	358 +/- 20	23.4 +/- 0.8

Atom probe needles were analyzed for each of the alloys with dataset sizes of 66 and 65 million atoms for RRHT2 and RRHT4, respectively. Fig. 2 shows the 3D tomography of the γ' precipitates for each of the RRHT alloys where the interfaces were observed. Note that only Cr atoms, in blue, and Al atoms, in red, are displayed as these partition strongly to the γ and γ' phases, respectively, and provide a better visual representation of phases when the APT data is reconstructed. Only results from the secondary γ' precipitates were used as they are closer to the thermodynamic equilibrium. In addition, data from regions associated with narrow γ channels between two γ' precipitates and those originating close to a tertiary γ' was not used as local concentration gradients resulting from these transient microstructural features are considered to be non-equilibrium. The results were averaged among the interfaces of each needle for each alloy and the results are provided in Table 3. These results are

different from the phase compositions in Table 3 of Ref [14], as selection criteria for the origination of the data is different in order to reflect near equilibrium phase compositions, whereas in Ref [14], an averaged phase chemistry was reported in order to model the strengthening behavior.

Consistent with the higher overall concentration of Nb present in the bulk alloy, approximately ~8 at.% Nb was found in the γ' phase of RRHT2, while ~6 at.% Nb was present in the γ' phase of RRHT4. Interestingly, modest levels of Nb were also found to remain in solution within the γ phase with ~2.3 at.% in RRHT2, but only ~1.5 at.% in the γ matrix of RRHT4. Compared to the levels of the other γ' forming elements such as Ta, Nb was found to exhibit a much higher degree of solubility within the γ phase. In both alloys, both Ta and Al additions were found to strongly segregate to the γ' phase at ~1.5 at.% for Ta in both alloys and ~13 at.% and 15 at.% for Al in RRHT2 and RRHT4, respectively. Consequently, the partition coefficient, $k=C_{\gamma}/C_{\gamma'}$, for Nb was found to be 0.30 for RRHT2 and 0.23 for RRHT4. Alloying additions of Mo and Cr, on the other hand, were found to partition preferentially to the γ phase, with RRHT4 containing ~30 at.% Cr and 3 at.% Mo compared to ~27 at.% Cr and ~3 at.% Mo in RRHT2. The concentration of W and Co were found substantially higher in the γ phase; however, modest amounts were also found in the γ' phase.

Fig. 2. APT 3D reconstructions of (a) RRHT2 and (b) RRHT4.

Table 3. Phase composition of the RRHT alloys from APT (at.%).

Element	RRHT2		RRHT4	
	γ' (at%)	γ (at%)	γ' (at%)	γ (at%)
Ni	68.2 +/- 0.2	47.1 +/- 0.5	66.5 +/- 0.8	42.6 +/- 0.3
Cr	1.36 +/- 0.09	27.4 +/- 0.6	1.7 +/- 0.1	30.5 +/- 0.2
Al	13.0 +/- 0.2	1.12 +/- 0.07	15.1 +/- 0.4	2.15 +/- 0.04
Mo	0.45 +/- 0.03	2.6 +/- 0.1	1.0 +/- 0.3	3.23 +/- 0.06
Co	6.8 +/- 0.1	17.6 +/- 0.4	7.2 +/- 0.4	18.3 +/- 0.2
Nb	8.2 +/- 0.4	2.3 +/- 0.2	6.3 +/- 0.8	1.50 +/- 0.02
Ta	1.4 +/- 0.1	0.20 +/- 0.03	1.4 +/- 0.2	0.12 +/- 0.00
W	0.49 +/- 0.03	1.35 +/- 0.08	0.64 +/- 0.05	1.21 +/- 0.01
Hf			0.06 +/- 0.05	0.01 +/- 0.00

Fig. 3 shows the microstructure of each alloy after exposure at 800°C for 100 and 1000 hours. The grain boundaries of RRHT2 after the 100 hour exposure appear free of secondary phases, while blocky σ phase has formed along the boundaries in

RRHT4. After 1000 hours, all of the alloys have formed a secondary phase along the grain boundaries. Precipitate morphologies in RRHT2 exhibit a characteristic needle like shape typical of η phase precipitates, while the grain boundaries of RRHT4 are populated with blocky σ precipitates forming a nearly continuous film.

Fig. 3. SEM images of the grain boundary phases forming during long term exposure at 800°C for RRHT2 and RRHT4.

In order to better determine the structure and composition of the secondary phases in the alloys, TEM work was done on the 1000 hour samples and the corresponding images and selected-area diffraction (SAD) patterns for RRHT2 in the zone axis parallel to $[010]_{\eta}$, $[021]_{\eta}$, and $[\bar{1}10]_{\eta}$ for the Ni_6AlNb were obtained. SEM and a TEM image, along with a select SAD pattern are provided in Figure 4 for the η phase. The needle phase can clearly be seen in Fig 4a, following a light electrochemical etch and can be identified as Ni_6AlNb with a hexagonal $\eta\text{-Ni}_3\text{Ti D0}_{24}$ crystal structure from Fig. 4c and d. The composition of the needle phase, as determined by TEM-EDX, is provided in Table 4, and shows that it has 71.6 at.% Ni, 8.8 at.% Nb and 7.4 at.% Al, which can be approximated as Ni_6AlNb . Note that the reported deviations are the deviations between up to three particles and show that the compositional difference between particles is minimal.

Fig. 4. Images of RRHT2 showing a) Ni₆AlNb needles after γ etching (BSE), b) Ni₆AlNb needles and MC carbides (BSE), c) Ni₆AlNb needle (TEM), and d) SAD pattern for Ni₆AlNb needle in the $[\bar{1}10]_{\eta}$ axis.

Table 4. Composition of the secondary phases in RRHT2 from TEM-EDS (at.%).

Phase	Chemical Composition (at.%)							Space Group
	Ni	Cr	Al	Mo	Co	Nb	Ta	
Ni ₆ AlNb	71.6+/-1.6	2.9+/-0.2	7.4+/-0.2	0.8+/-0.5	7.3+/-1.1	8.8+/-0.6	1.2+/-1.7	P6 ₃ /mmc

Fig. 5c and d show the TEM and a corresponding SAD pattern for RRHT4, after being exposed to 800°C for 1000 hours, SAD patterns for the σ phase in RRHT4, in the zone axis parallel to $[120]_{\sigma}$, $[110]_{\sigma}$, and $[122]_{\sigma}$ were obtained. Fig. 5c and d show the TEM image and a corresponding SAD pattern for this alloy.. The blocky σ phase can clearly be seen surrounded by γ' phase in Fig 5a, following a light electrochemical etch and can be identified with a tetragonal CrNi D8_h crystal structure from Fig. 5c and d. The compositions of the blocky σ phase, provided in Table 5, is 17.6 at.% Ni, 46.1 at.% Cr, 12.4 at.% Mo, and 20.7 at.% Co, which can be approximated as (Cr,Mo)₆(Ni,Co)₄.

Fig. 5. Images of RRHT4 showing a) σ after a γ etch (BSE), b) σ (BSE), c) σ (TEM), d) SAD pattern for σ along the $[120]_{\sigma}$ axis.

Table 5. Composition of the secondary phases in RRHT4 from TEM-EDS (at.%).

Phase	Chemical Composition (at.%)								Space Group
	Ni	Cr	Al	Mo	Co	Nb	Ta	W	
σ	17.6+/-0.5	46.1+/-2.6	0.22+/-0.0	12.4+/-1.8	20.70+/-0.0	0.68+/-0.0	0.0+/-0.0	2.4+/-0.3	P42/mnm

Thermodynamic database models such as Thermo-calc, allow for the prediction of equilibrium phases that may form in the alloy system. Figure 6 shows the predicted phase fraction plots as a function of temperature for both alloys obtained using Thermo-calc with the TCNI8 database. It is interesting to note that for the two alloys the formation of δ , or $\text{Ni}_3\text{Ta DO}_a$, phase and σ phase is predicted. However, the predicted volume fraction of the $\text{Ni}_3\text{Ta DO}_a$ and σ tend to vary between the two alloys, where $\text{Ni}_3\text{Ta DO}_a$ is predicted to be the dominant phase in RRHT2 with 13 %, compared to 6.5 % σ , while RRHT4 has 8.1% and 6.5% σ and $\text{Ni}_3\text{Ta DO}_a$, respectively. The γ' phase is also predicted to have a much lower volume fraction that the actual, which can be attributed to the predicted formation of the $\text{Ni}_3\text{Ta DO}_a$ phase. In addition, the equilibrium phase composition of the secondary phases of each alloy can be determined at 800°C, and are provided in Table 6. For RRHT2, the predicted Ni_3Ta phase has a composition of 67 at.% Ni and 22 at.% Nb, while the σ in RRHT4 has 68 at.% Cr, 15 at.% Ni, 9 at.% Mo and 22 at.% Co, which is found to be in very good agreement with the experimental results in Table 5. Phase compositions for the γ and γ' phases were also obtained at 850°C. The Nb concentration in the γ' phase is elevated for the higher Nb content alloy, RRHT2, at approximately 10 at.%, while RRHT4, having a lower overall Nb content, was calculated to have ~7 at.% Nb in the γ' phase. The Nb content in the γ phase was predicted to be relatively limited with RRHT2 having a concentration of 1.7 at.% and RRHT4 having 1.3 at.%. The Cr and Mo content in the γ phase of both alloys was predicted to be fairly constant at ~ 27 at.% and ~3 at.%, respectively.

Fig. 6. Thermo-calc phase predictions for a) RRHT2 and b) RRHT4.

Table 6. Composition of the secondary phases from Thermo-calc (at.%).

Alloy	Phase	Ni	Cr	Al	Mo	Co	Nb	Ta	W
RRHT2	Ni ₃ Ta (800°C)	67.32	1.05	0.25	0.47	6.65	22.22	1.64	0.39
	γ (850°C)	44.49	25.49	3.58	2.59	20.31	1.76	0.37	1.32
	γ' (850°C)	66.10	1.51	13.24	0.11	3.91	9.62	1.74	0.12
	σ (800°C)	14.83	52.11	0.01	8.90	22.81	0.28	0.00	0.94
RRHT4	γ (850°C)	43.86	26.51	4.03	2.66	19.77	1.45	0.21	1.36
	γ' (850°C)	68.77	1.96	14.86	0.19	4.57	7.34	1.76	0.18

Discussion

Two high Nb content γ - γ' Ni-base superalloys were investigated in order to better understand the microstructural stability and evolution of the secondary phases that nucleate along the grain boundaries of a powder processed, polycrystalline Ni-base superalloy during thermal exposure at 800°C for up to 1000 hours. Even though these two alloys have very similar nominal compositions, Table 1, substituting Al for Nb in RRHT 4 has led to distinctly different phases forming on the grain boundaries. Upon aging RRHT2 at 850°C for 4 hours, the γ phase was found to contain a moderately high level of the γ' forming element Nb at around 2.3 at.%. Meanwhile, the γ phase of RRHT4 contains only about 1.5 at.% Nb, Table 3, which is likely due to the fact that the bulk alloy composition of RRHT2 has a higher Nb content, Table 1. Since Nb partitions less strongly to the γ' precipitates when compared to Ta, higher degrees of Nb alloying will lead to higher levels of Nb solute remaining in the γ matrix [14]. Interestingly Cr and Mo, which are present at nominally identical levels in both alloys, were found to partition differently and exhibited a modestly higher concentration in the γ phase of RRHT4, ~30 at.% and ~3 at.%, respectively, when compared to the matrix composition of RRHT2, ~27 at.% and ~3 at.%, respectively. This difference can likely be attributed to

the modestly higher γ' volume fraction in RRHT4, thereby resulting in the γ phase being comparatively more highly saturated with Cr and Mo solute atoms. Referring to the isothermal section of the Ni-Cr-Nb ternary system at 800°C, Figure 7a, the levels of Nb and Cr measured in RRHT2 and RRHT4 in the γ phase place them both in the two phase field of γ (Ni) + Ni_3Ta . This suggests that the matrix of the two alloys is supersaturated and exceeds the solubility limits for these elements. However, since the degree of solute supersaturation in RRHT2 is higher as it is located further into the two phase field, this would appear to suggest that the Ni_3Ta or Ni_3Nb phase is more likely to form when compared to RRHT4 which is just slightly past the solubility limit into the two phase region. Similarly, in Figure 7b, the Ni-Cr-Mo ternary system at 800°C reveals that the higher levels of Cr and Mo push the γ composition of RRHT4 closer to the matrix solubility limits and to the γ (Ni) + σ two phase field, whereas RRHT2 is located far enough away from the solubility line such that the σ phase is not thermodynamically stable. Although using these ternary systems to assess the phase stability of these multicomponent alloys may not be entirely accurate, they are consistent with the experimental observations in this study. However, it should be noted that changes in the levels of alloying of other elements, such as W and Co, may modify the solubility limits for the σ and η phases and the preferential formation of one phase over the other could change accordingly.

Fig. 7. Thermocalc (TCNI8) calculated partial isothermal sections of a) the Ni-Cr-Nb ternary and b) the Ni-Cr-Mo ternary at 800°C.

As Nb and Cr are major formers of η and σ , respectively [17, 28, 31], the concentration of these solutes in the γ matrix likely serve as the primary driving force for the precipitation of secondary phases. Interestingly, Nb has a very limited solubility in the σ phase, while Cr has limited solubility in the η phase [15, 29], Tables 4 and 5. When significant concentrations of these solute atoms are both present in the γ matrix, competitive processes may serve to retard or prevent the nucleation and growth of these phases. For nucleation and growth of the η phase, diffusive processes must form a Nb-rich nucleus and transport Nb atoms to the interface while simultaneously transporting Cr away from the interface. Precipitation and growth of σ phase requires clustering of Cr solute atoms and diffusion of Nb atoms away from the σ/γ interface. Based on the results in this study, it appears that the ratio of Cr to Nb atoms in the γ matrix can serve as a good indicator of the phase stability and determine the likelihood of η or σ forming. Computing this ratio from the composition of the γ phase for the two alloys, Table 7, RRHT2 has twice as many Nb atoms, for each Cr atom available, which would suggest that the η phase has a higher probability of forming in RRHT2, while σ has a higher likelihood of forming in RRHT4 since the ratio of Cr to Nb atoms is noticeably higher. Thermo-calc phase fraction plots for the two alloys are shown in Figure 6. Although the thermodynamic calculations predict that both η and σ phases form in the two alloys, the respective fraction of the phases are different and serve as a good indicator of their relative stability. The predicted fraction of η for RRHT2 is twice as high as the η fraction in RRHT4, 13.5% vs. 6.5%, but the fraction of σ remains fairly similar with 6.5% in RRHT2 and 8.5% RRHT4. Considering the phase compositions for the phases at 850°C, calculated from Thermo-calc in Table 6, the γ phase composition in RRHT2 has a much lower Nb content, ~1.7 at.%, when compared to the 2.3 at.% measured from the APT data. In RRHT4, both the calculated and measured concentration of Nb in the γ phase are similar at about 1.4 at.%. In addition, Thermo-calc predictions of the Cr content in the γ phase of both alloys is similar at around 27 at.%, and consequently, the calculated ratio of Cr to Nb in RRHT2 and RRHT4 are 14.5 and 18.3, respectively, in Table 7.

Table 7. Cr to Nb ratio from the γ phase compositions.

	RRHT 2 APT	RRHT 4 APT	RRHT 2 TC	RRHT 4 TC
Cr/Nb	11.9	20.3	14.5	18.3

It would appear that a much better approximation for assessing the phase stability would be to use the APT data for the γ phase as the starting composition in the Thermo-calc phase stability predictions, Figure 8. This way, the actual Cr to Nb ratio can be used to evaluate the stability of the η and σ phases. Looking at the phase fraction plot for RRHT2 in Figure 8, at 800°C, the phase fractions of η and σ are 8.1% and 7%, in the γ matrix, respectively, which suggests that the η phase is slightly more stable than the σ phase. For RRHT4, however the σ phase has a fraction of 18.5% as compared to only 4% for the η phase. Due to the higher degree of Nb saturation in the γ phase in RRHT2, the driving force for η phase is much higher; meanwhile the limited solubility of Nb in the σ phase prevents the phase from forming. In RRHT4, as the Nb saturation in the γ phase is lower, Table 3, σ phase is more readily formed, as less Nb solute needs to be transported away from the interface. As the σ phase forms, it scavenges γ forming elements from the surrounding matrix and rejects γ' forming elements thereby resulting in the formation of a γ' film around the σ particles, Figure 5a.

Interestingly, it has been reported in a variety of commercial Ni-base superalloy systems that decomposition of $M_{23}C_6$ carbides may lead to the precipitation of blocky σ phase along the grain boundaries, as the two phases have the same crystal structures without the carbon atoms [28, 31, 34]. $M_{23}C_6$ carbides are usually formed from MC carbides decomposing and releasing C atoms, which react with the Cr atoms in the γ matrix and form $M_{23}C_6$ precipitates surrounded by the γ' film [35]. It has been found that, as Ni atoms diffuse more effortlessly through the γ' film towards the $M_{23}C_6$ particles, it can combine with

Ti to form η phase at the interface between the $M_{23}C_6$ and MC carbides [36, 37]. As shown in Figure 6, MC decomposition into $M_{23}C_6$ for both alloys is predicted to occur around 650°C and so $M_{23}C_6$ is not expected to be present at 800°C, which is consistent with the experimental observations. This is likely due to the fact that the NbC carbides are more thermodynamically stable and as a consequence, there are few C atoms in solution, which otherwise, along with Cr, would form the $M_{23}C_6$ [27].

Fig. 8. Thermo-calc phase predictions for a) RRHT2 and b) RRHT4 from APT data for the γ phase.

From Figures 6 and 7, the Ni_3Ta phase with a crystal structure of DO_a is predicted with a composition of Ni_3Nb , Table 6, which is actually the δ phase in Ni-base superalloys [23, 25]. When compared to the TEM results, which predict the η - Ni_6AlNb with a DO_{24} crystal structure, it can be concluded that Thermo-calc has difficulty predicting this phase, and so the predicted stability of this phase may not be entirely correct. Pickering et. al. have performed detailed studies of the precipitation in 718Plus and have found the presence of small δ strips in Nb rich regions of the η - Ni_6AlNb , but not in significant amounts [17]. This could also be the case for RRHT2 and so trace amounts of δ - Ni_3Nb could exist in the η needles, but the amount of δ , when compared to η , would be very minor and no δ phase was detected with the TEM. On the other hand, as shown by the predicted composition of the σ phase, Table 6, and by its comparison to the experimental compositions in Table 5, the agreement is very good and the phase can be approximated as $(Cr_{0.5}, Mo_{0.1})(Ni_{0.2}, Co_{0.2})$, which is exactly the same as the reported σ phase composition in U720 and U720Li alloys [28, 32].

Conclusions

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

1. Elevated concentrations of Nb result in a higher level of Nb solute saturation in the matrix and contributes to the formation of the Nb-rich η phase along the grain boundaries.

2. Higher concentrations of Mo and Cr in the γ matrix, due to higher γ' volume fractions, result in the preferred formation of blocky σ phase along the grain boundaries, surrounded by a γ' film formed from the rejected γ' forming solutes.
3. In alloys, with compositions close to the solubility limits of Nb, Cr and Mo, a Nb/Cr ratio based on the γ phase composition can be used in order to predict the relative stability of η and σ phases, with ratios closer to 10 forming Ni_6AlNb , while ratios around 20 preferably forming σ .
4. Thermocalc predictions of the σ phase formation and composition are relatively accurate, but the predictions are limited when it comes to the Ni_6AlNb η phase.

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References

- [1] T.M. Pollock, S. Tin, *J Propul Power* 22 (2006) 361-74.
- [2] D. Furrer, H. Fecht, *J Miner Met Mater Soc* 51 (1999) 14-7.
- [3] C.T. Sims, N.S. Stoloff, W.C. Hagel. *Superalloys II*. New York: Wiley; 1987.
- [4] R.F. Decker, C. T. Sims, *The Metallurgy of Nickel-base Superalloys*. New York: Paul D. Merica Research Laboratory; 1972.
- [5] R.R. Unocic, G.B. Viswanathan, P.M. Sarosi, S. Karthikeyan, J. Li, M.J. Mills, *Mater Sci Eng A* 483 (2008) 25-32.
- [6] R.R. Unocic, L. Kovarik, C. Shen, P.M. Sarosi, Y. Wang, J. Li, et al, *Superalloys*, TMS, Warrendale, PA, 2008, 377-385.
- [7] D. Locq, P. Caron, S. Raujol, F. Pettinari-Sturmel, A. Coujou, N. Clément, *Superalloys*, TMS, Warrendale, PA, 2004, 179-187.
- [8] R.C. Reed, *The Superalloys: Fundamentals and Applications*. New York: Cambridge University Press; 2006.
- [9] M.J. Donachie, S.J. Donachie, *Superalloys: A Technical Guide*. 2nd ed. Materials Park, OH: ASM International; 2002.
- [10] T.M. Pollock, R.D. Field, Chapter 63 Dislocations and high-temperature plastic deformation of superalloy single crystals. *Dislocat. Solids* 2002;11:547-618.
- [11] R.W. Kozar, A. Suzuki, W.W. Milligan, J.J. Schirra, M.F. Savage, T.M. Pollock, *Metall Mater Trans A* 40 (2009) 1588-603.
- [12] Y. Mishima, S. Ochiai, N. Hamao, M. Yodogawa, T. Suzuki, *T Jpn I Met* 27 (1986) 648-55.
- [13] Y. Mishima, S. Ochiai, M. Yodogawa, M. Suzuki, *T Jpn I Met* 27 (1986) 41-50.
- [14] S. Antonov, M. Detroids, D. Isheim, D.N. Seidman, R.C. Helmink, R.L. Goetz, E. Sum, S.Tin. *Mater. Design*. 86 (2015) 649-655.
- [15] G.K. Bouse, *Superalloys Conference Proceedings*, 1996, pp. 163-172.
- [16] N.G. Jones, K.A. Christofidou. P.M. Mignanelli, J.P. Minshull, M.C. Hardy, H.J. Stone. *Mater. Sci. Technol*. 30 (2014) 1853-1861.
- [17] E.J. Pickering, H. Mathur, A. Bhowmik, O.M.D.M. Messé, J.S. Barnard, M.C. Hardy, et al, *Acta Mater* 60 (2012) 2757-69.
- [18] F. Long, Y.S. Yoo, C.Y. Jo, S.M. Seo, Y.S. Song, T. Jin, Z. Q. Hu, *Mater. Sci. Eng. A* 527 (2009) 361-369.
- [19] X. Xie, G. Wang, J. Dong, C. Xu, W.D. Cao, R. Kennedy, *Superalloys 718, 625, 706 and Derivatives*, TMS, Warrendale, PA, 2005, 179-91.
- [20] M. Detroids, R.C. Helmink, S. Tin, *Metall Mater Trans A* 45 (2014) 5332-43.
- [21] R.J. Mitchell, H. Y. Li, Z.W. Huang, *J. Mater. Process. Technol.* 209 (2009) 1011-1017.
- [22] J.P. Shingledecker, G.M. Pharr. *Metall. Mater. Trans. A* 43A (2012) 1902-1910.

- [23] S. Antonov, M. Detrois, R.C. Helmink, S. Tin, *J Alloys Compd.* 626 (2015) 76-86.
- [24] P.M. Mignanelli, N.G. Jones, K.M. Perkins, M.C. Hardy, H.J. Stone, *Mater Sci Eng A* 621 (2015) 265-71.
- [25] M. Detrois, S. Antonov, R.C. Helmink, S. Tin, *JOM* 66 (2014) 2478-85.
- [26] M. Detrois, R.C. Helmink, S. Tin, *Mater. Sci. Eng. A* 586 (2014) 236-244.
- [27] C.T. Sims, *Niobium-Proceedings of the International Symposium*, ed. H. Stuart. (TMS, Warrendale, PA, 1981), pp. 1169-1220.
- [28] R.C. Reed, M.P. Jackson, Y.S. Na. *Metall. Mater. Trans. A* 30A (1999) 521-533.
- [29] C.T. Sims. *J. Met.* 18 (1966) 1119-1130.
- [30] *Smithells Metal Reference Book*, 7th. Ed., E.A. Brandes, G.B. Brooks, eds., Butterworth-Heinemann, Oxford, UK (1992) 57.
- [31] R.J. Mitchell, C.M.F. Rae, S. Tin. *Mater. Sci. Tech.* 21-1 (2005) 125-132.
- [32] M.P. Jackson. Ph.D. Thesis, The University of Cambridge, 1998.
- [33] G.F. Vander Voort, H.M. James *Metals Handbook*, K. Mills, J.R. Davis, J.D. Destefani, D.A. Dieterich, G.M. Crankovic, J.H. Frissell, and D.M. Jenkins, eds., ASM, Metals Park, OH, 1985, vol. 9, pp. 305-13.
- [34] H. Kitaguchi. Chapter 2 Microstructural-Property Relationship on Advanced Ni-Based Superalloys. *Metallurgy – Advances in Materials and Processes*.ed. Y. Parghi 2012; 19-42.
- [35] W.H. Jiang, X.D. Yao, H.R. Guan, Z.Q. Hu. *Metall. Mater. Trans. A* 30A (1999) 513-520.
- [36] X.Z. Qin, J.T. Guo, C. Yuan, C.L. Chen, H.Q. Ye. *Mater. Trans. A* 38A (2007) 3014-3022.
- [37] X.Z. Qin, J.T. Guo, C. Yuan, C.L. Chen, J.S. Hou, H.Q. Ye. *Mater. Sci. Eng. A*, 485 (2008) 74-79.