POLYCRYSTALLINE $\gamma(\text{Ni})/\gamma'(\text{Ni}_3\text{Al})\text{-}\delta(\text{Ni}_3\text{Nb})$ EUTECTIC Ni-BASE SUPERALLOYS: CHEMISTRY, SOLIDIFICATION AND MICROSTRUCTURE

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Abstract

A novel type of $\gamma/\gamma'\text{-}\delta$ eutectic polycrystalline Ni-base superalloy has been recently demonstrated to possess promising mechanical properties at 700–800 °C, yet much of our knowledge regarding this eutectic alloy system is still qualitative in nature. A matrix of alloys spanning a broad range of alloy compositions were examined to improve our understanding of various alloying effects on the solidification behavior and as-cast microstructure of multi-component $\gamma/\gamma'\text{-}\delta$ eutectic alloys. While the volume fraction of constituent phases was observed to be closely related with the Nb concentration, it could also be effectively modified by additions of other elements. Solidus and liquidus temperatures of these $\gamma/\gamma'\text{-}\delta$ alloys were also found to vary with different solute concentrations, with a general decrease in solidus temperature as solute content increases. Interestingly, Cr, Mo and W were found to induce similar changes on the solidification and microstructure of this eutectic system. Extensive comparison between these experimental results and Computherm Pandat predictions was carried out, which confirmed the reliability of Pandat in predicting the qualitative trends for this eutectic system. Although satisfactory agreement was found between the measured and calculated solidus temperatures, additional phase equilibria information of multi-component $\gamma/\gamma'\text{-}\delta$ alloys is required to improve the predictive capability on other properties.

Introduction

As an extraordinary class of metallic materials, Ni-base superalloys have been successfully implemented into advanced turbine engines for aerospace and land-based power generation applications [1-6]. Most polycrystalline Ni-base superalloys possess microstructures consisting of ordered intermetallic precipitates $\gamma'(\text{L1}_2)$ and/or $\gamma''(\text{D0}_{22})$ distributed coherently within a disordered $\gamma(\text{FCC})$ matrix [1-5]. The remarkable high temperature mechanical properties associated with Ni-base superalloys largely rely on this two-phase microstructure, which provides substantial order and coherency strengthening that hinders the movement of dislocations during deformation. Modern polycrystalline Ni-base superalloys often contain intermediate levels of Al, Ti and Nb to yield an optimized volume fraction of strengthening phase (γ'/γ''), as well as controlled concentrations of refractory elements (W, Mo) to deliver further solid solution strengthening to the γ matrix and the precipitates [3, 5, 6].

Over the years, many new polycrystalline Ni-base superalloys and their variants have been developed and optimized to meet the challenge of higher thermal efficiency and lower CO_2 emission requirements associated with advanced gas turbine engines. Much of these efforts have been dedicated towards optimizing the $\gamma/\gamma'(\gamma'')$ microstructure by enhancing the strength, microstructural stability and temperature capability of both the matrix and

precipitates via iterative compositional variations [6-8]. Despite these substantial efforts, only modest improvements in physical and mechanical properties have been achieved in these conventional polycrystalline Ni-base superalloys. More often than not, these improvements in properties have been attained at the expense of manufacturing difficulty, lower environmental resistance and higher cost. Existing $\gamma/\gamma'(\gamma'')$ polycrystalline Ni-base superalloys also appear to be approaching their limits and new alloying concepts need to be considered to accommodate the design requirements associated with future generations of ultra-efficient turbine engines.

Starting in the 1970's, Pratt and Whitney proposed directionally solidified $\gamma(\text{Ni})/\gamma'(\text{Ni}_3\text{Al})\text{-}\delta(\text{Ni}_3\text{Nb})$ eutectic alloys as candidate materials for turbine blade applications [9]. Processed under a combination of high thermal gradient and low withdraw rate, these alloys formed a characteristic *in situ* composite microstructure comprised of aligned δ lamellae embedded within a γ/γ' matrix [10, 11]. Although these eutectic alloys were shown to possess superior longitudinal tensile strength and creep resistance when compared to state-of-the-art Ni-base superalloys available at that time [12-14], many intrinsic deficiencies associated with the large degree of anisotropy of these directionally solidified lamellar structures, such as the low interfacial strength [15], mismatch in thermal expansion coefficients [16] and limited oxidation resistance [17], had rendered these alloys unsuitable for the intended applications. However, this eutectic alloy system has many inherently attractive properties, such high volume fraction of reinforcing phases ($\gamma'+\delta$), excellent long-term thermal stability and remarkable resistance to macro- and micro-segregation induced defects due to the narrow melting range [10, 11, 18-22]. If these unique attributes can be properly harnessed, a novel type of $\gamma/\gamma'\text{-}\delta$ eutectic polycrystalline alloys with a balanced set of properties can be potentially designed for high performance structural applications where the temperatures are limited to below 800°C.

Apart from a limited number of published studies on directionally solidified quaternary and quinary $\gamma/\gamma'\text{-}\delta$ alloys, however, much of our knowledge about the $\gamma/\gamma'\text{-}\delta$ eutectic alloy system remains qualitative in nature [23-25]. A fundamental understanding of how various alloy additions influence the solidification characteristics and microstructure of multi-component eutectic alloys is critical to the development of high performance polycrystalline $\gamma/\gamma'\text{-}\delta$ eutectic alloys with optimized properties. The present study is aimed at providing a general understanding of the effect of Cr, Ta, Nb, Mo and W on the solidification behavior and microstructural characteristics of the multi-component $\gamma/\gamma'\text{-}\delta$ eutectic system. A critical comparison between experimental results and thermodynamic calculations generated with a commercially available thermodynamic software package, Pandat (Computherm LLC.) was performed.

Table I. Compositions of experimental γ/γ' - δ eutectic alloys. (at. %)

Alloy	Ni	Cr	Co	Al	Ti	W	Mo	Ta	Nb
0Cr	Bal.	0.0	-	5.5	-	-	-	-	13.5
2Cr	Bal.	2.0	-	5.5	-	-	-	-	13.5
4Cr	Bal.	4.0	-	5.5	-	-	-	-	13.5
6Cr	Bal.	6.0	-	5.5	-	-	-	-	13.5
8Cr	Bal.	8.0	-	5.5	-	-	-	-	13.5
10Cr	Bal.	10.0	-	5.5	-	-	-	-	13.5
X1Ta	Bal.	2.0	2.0	5.0	0.5	0.5	1.0	1.0	12.7
X3Ta	Bal.	2.0	2.0	5.0	0.5	0.5	1.0	3.0	10.7
X5Ta	Bal.	2.0	2.0	5.0	0.5	0.5	1.0	5.0	8.7
X2Mo	Bal.	2.0	2.0	5.0	0.5	0.5	2.0	1.0	12.7
X3Mo	Bal.	2.0	2.0	5.0	0.5	0.5	3.0	1.0	12.7
X1.5W	Bal.	2.0	2.0	5.0	0.5	1.5	1.0	1.0	12.7
X2.5W	Bal.	2.0	2.0	5.0	0.5	2.5	1.0	1.0	12.7
899	Bal.	6.9	-	5.7	-	-	-	1.0	11.5
900	Bal.	6.9	-	6.3	0.3	-	-	1.0	10.8
TaNb	Bal.	2.0	2.0	5.0	0.5	0.5	1.0	6.0	6.0
E1	Bal.	-	-	6.2	-	-	-	-	15.7
E2	Bal.	1.1	-	6.3	-	-	-	-	15.5
E3	Bal.	3.3	-	6.2	-	-	-	-	15.1
E4	Bal.	5.1	-	6.1	-	-	-	-	14.8
E5	Bal.	7.0	-	5.9	-	-	-	-	14.5
E6	Bal.	6.0	-	7.2	-	-	-	-	14.3
E7	Bal.	1.0	-	6.3	-	-	-	-	15.6
E8	Bal.	5.0	6.0	7.2	-	-	-	-	14.3
E9	Bal.	10.0	3.0	7.2	-	-	-	-	14.3
E10	Bal.	5.0	3.0	7.2	-	-	-	-	14.3
E11	Bal.	8.5	-	7.0	0.2	-	-	-	14.3
E12	Bal.	6.0	-	4.6	-	-	-	-	15.3
E13	Bal.	6.0	-	5.6	-	-	-	-	15.1
E14	Bal.	6.0	-	6.6	-	-	-	-	14.5
E15	Bal.	6.0	-	7.5	-	-	-	-	14.2

Experimental Materials and Procedures

A matrix of γ/γ' - δ alloys with different combinations of constituent elements was designed to enhance our understanding of this multi-component eutectic system, Table I. Cr, XTa, XMo and XW alloy series were prepared to systematically investigate the effects of these individual alloying additions on the solidification behavior and as-cast microstructure of pseudo-eutectic γ/γ' - δ alloys. For the Cr, XMo and XW alloys, the concentration of solute additions was gradually increased by substituting directly for Ni. In the XTa alloys, levels of Ta were raised to substitute for Nb, maintaining a constant (Ta+Nb) content. All substitutions were made on an equiatomic basis. This set of alloys was designed to study the influence of the Ta/Nb ratio on this alloy system. Other alloys were prepared to provide additional information of this γ/γ' - δ system at lower and higher Nb levels.

Pure Ni (99.95%), Cr (99.5%), Co (99.9%), Al (99.9%), Ti (99.9%), W (99.9%), Mo (99.8%), Ta (99.9%) and Nb (99.98%) were melted in a MRF ABJ-900 arc melter under an argon atmosphere. The melting chamber was purged under vacuum to a pressure level of 10^{-3} mbar and then backfilled with high purity argon (99.998 %) to ensure alloy cleanliness. This procedure was repeated three times before melting. Each of the arc melted ingots

was melted and remelted up to six times to ensure uniform mixing of the elemental additions. The solidified button ingots were observed to have approximately the same dimensions (~3cm in diameter and ~1cm in height) and weight (~60 grams). Mass loss during arc melting was determined to be less than 0.1 % for all the alloys. Nominally constant solidification conditions (solidification rate $\approx 20^\circ\text{C/s}$, thermal gradient $\approx 300^\circ\text{C/cm}$) [26] were ensured by exercising identical melting procedures.

To better characterize the dendritic microstructure, all button ingots were sectioned perpendicularly to the general dendrite growth direction. Metallographic examination was then taken at the center of the transverse plane. Standard grinding, polishing and ultrasonic cleaning procedures were practiced before microstructural analysis. A solution of 1:1:1 HCl: HNO₃: distilled water was used to dissolve the γ' precipitates, which provided good contrast of the microstructure of these γ/γ' - δ alloys. A Nikon ECLIPSE MA200 optical microscopy (OM) was used for microstructural characterization at lower magnification and a JEOL JSM-5900LV scanning electron microscopy (SEM) was used for detailed microstructural analysis. Since this study was mainly focused on the alloying effects on the solidification microstructure, analysis of γ' precipitates will not be provided here.

A SETARAM SETSYS differential scanning calorimetry (DSC) unit was used to measure the solidus and liquidus temperatures of these experimental alloys. The DSC unit was calibrated with high purity Ni (99.95%) and silver (99.9%) at scanning rates of 3, 5 and 10 °C/min, using a sapphire reference. DSC samples were sectioned near the center of the alloys with a mass of approximately 200 mg to make sure they are representative of the bulk alloys. Samples were ultra-sonically cleaned for 30 minutes in ethanol and then tested in alumina crucibles. The DSC tests were conducted under flowing argon (99.998 %) to protect both the furnace and the DSC samples from oxidation. Only the heating curve was used to determine the phase transformation temperatures to avoid undercooling effects. A heating rate of 5°C/min was chosen since it was determined to yield the best combination of peak resolution and temperature accuracy.

Compositional analysis was performed using the JEOL JSM-5900LV SEM equipped with Oxford Instruments X-Max energy dispersive spectrometer (EDS). The EDS system was calibrated using a powder alloy of similar composition (Ni-7.2Cr-6.0Al-0.7Ti-1.0Mo-0.5W-1.0Ta-11.5Nb, at. %) as standard to improve the accuracy of measurements. To ensure the consistency of the results in this study, all the experimental parameters were kept constant (accelerating voltage=20 kV, working distance=10 mm, spot size=40, acquisition time=60 s). A minimum of 10 discrete measurements were taken from representative regions of the microstructure to assure the statistical significance of the measured compositions. To confirm the subtle compositional variations, instrumental error of the EDS system was also considered in this study and reported together with the standard deviation of the measurements, as described elsewhere [26].

Quantitative area fraction measurement of γ and δ phase in experimental γ/γ' - δ alloys was performed using digital image analysis. SEM images were taken at a minimum of ten randomly selected regions that allowed for statistically significant measurements. These images were then analyzed digitally using ImageTool 2.0. Standard point count methods (ASTM E562) were also applied to assess the area fraction of γ - γ' and γ - γ' - δ eutectic qualitatively. Ten fields at 1000x magnification were counted for each alloy under light microscope with a 221-point grid to generate the averaged results. These area fraction measurements were considered to be representative of the volume information of different phases and will be referred to as volume fraction hereafter. Part of the experimental results was compared with Pandat predictions to assess the reliability of this thermodynamic database on these multi-component γ/γ' - δ eutectic alloys. Equilibrium solidification conditions were used for the predictions.

Results

1. Primary Phase Formation

Representative optical micrographs were selected from different alloys to demonstrate the microstructural variations associated with changes in alloy compositions, Figure 1. A profound influence of alloy additions was found in these γ/γ' - δ alloys, as a range of different cast microstructures were observed at different solute levels and combinations. These include the primary- γ -dominating structure in TaNb alloy, Figure 1a, the mixture of primary γ dendrites and γ/γ' - δ eutectic lamellae in 0Cr alloy, Figure 1b, the fully eutectic structure free of primary dendrites in

X1Ta alloy, Figure 1c, and the eutectic plus primary δ plate structure in E3 alloy, Figure 1d. When the micrographs of all the experimental γ/γ' - δ alloys were compared, a clear microstructural transition from primarily primary γ dendrites to large proportions of primary δ plates was observed as the level of Nb was raised, indicating a shift of the alloy compositions from the γ (Ni)-rich side (hypo-eutectic) to the δ (Ni₃Nb)-rich side (hyper-eutectic).

Figure 1. Representative micrographs of experimental γ/γ' - δ eutectic alloys revealing the as-cast microstructure of primary γ dendrites, lamellar eutectic and primary δ plates from Nb-lean alloys to Nb-rich alloys.

On the other hand, when these alloys were compared within each alloy series, varying the concentration of individual alloying elements, such as Cr, Ta, Mo and W, was also shown to significantly impact the primary phase formation. Trends observed in the different alloys series were quantified via image analysis and are summarized in concentrations of Ta tend to promote higher volume fractions of primary γ during solidification. A considerable amount of primary γ dendrites was also observed in the Cr alloys, but Cr additions tended to have a modest and steady effect in suppressing the primary γ phase formation from 34 % to 23 %. Mo and W additions were both found to trigger the formation of primary δ phase as their concentration Figure 2. For the level of alloying investigated, elevated increased. It is worth mentioning that as in the pseudo-binary γ - δ eutectic system, the reduction of primary γ formation associated with increasing Cr additions is essentially equivalent to the increase of the primary δ formation in the XMo and XW series of alloys, suggesting a possible similarity between these alloying additions. In addition, Ta, Mo and W were found to have a stronger influence on the primary phase formation of this γ/γ' - δ eutectic system than Cr, based on the different slopes in Figure 2. Interestingly, an increase of primary phase volume fraction was observed in XTa, XMo and XW alloy series, which all started with a fully eutectic microstructure. When the concentration of solute atoms increases to above 2 at. %, a much more pronounced change in the microstructure occurs. This may imply that the γ - δ eutectic structure is unable to accommodate excess levels of solute supersaturation.

Figure 2. Variations of primary phase volume fraction with different levels of alloying elements.

Measurements of primary phase volume fraction of experimental γ/γ' - δ alloys are summarized in Figure 3, and compared with the Pandat calculations to assess its predictive ability at different solute levels. The alloys are plotted in the order of ascending Nb concentration, with levels of different solutes increasing within each alloy set. Consistent with the qualitative microstructural observations in Figure 1, higher levels of δ -forming elements (Nb) suppress the formation of primary γ and gradually promotes larger proportions of primary δ . Several interesting phenomena can be found from these comparisons. First of all, Pandat is generally capable of predicting the qualitative trends of primary phase

formation within each alloy series. However, discrepancies exist between the measured and calculated results in all alloy series, which tend to escalate as the concentration of alloying addition increases. This trend can be clearly seen in the Cr, XTa and XW alloy series. Additionally, slightly better agreement between experimental and calculated results was found in alloys with near-eutectic microstructures. With alloys containing considerable amounts of primary γ phase (intermediate Nb levels), Pandat calculations deviate substantially from the experimental measurements.

2. δ Volume Fraction

The volume fraction of δ phase is of significant importance to this class of eutectic alloys, since the mechanical properties are directly governed by the amount of reinforcing phase. Due to the intrinsically sluggish diffusivity of transition metals (Nb, Ta, W and Mo) in the Ni matrix [27], attaining a near equilibrium microstructure via a homogenization heat treatment has been proven to be impractical for these alloys, particularly at intermediate to low temperatures. Here, the overall δ volume fraction within the as-cast microstructure was measured and assumed to be proportional to the equilibrium δ volume fraction of each alloy at the solidus temperature. These δ volume fraction data were plotted against the Nb content within each alloy, Figure 4. As expected, a strong increasing trend of the overall δ volume fraction was found as Nb content was raised in these γ/γ' - δ alloys.

Figure 3. Comparison between the measured primary phase volume fraction and the calculated results from Pandat software of various experimental alloys.

To better assess the reliability of Pandat in estimating the δ volume fraction in multi-component γ/γ' - δ alloys, representative alloys at different Nb levels (from 6.0% to 15.5%) were selected to compare with thermodynamic calculations, Figure 5. Since the microstructures of these cast alloys are not expected to vary substantially during cooling after solidification, predictions at the solidus temperature of each alloy were used to compare with experimental results. For the composition range investigated in this study, these predictions are generally capable of capturing the overall trend in the variations of the overall δ volume fraction associated with subtle differences in chemistry from alloy to alloy. It is consistent with all the alloys investigated that the measured δ

volume fractions always appear to be higher than the calculated results. This can be most likely attributed to the non-equilibrium solidification of the experimental alloys.

Figure 4. Relationship between the measured overall δ volume fraction and the Nb content in γ/γ' - δ eutectic alloys.

Figure 5. Comparison between the experimental measurements of the overall δ volume fraction of selected alloys and the corresponding Pandat predictions at the solidus temperature of different alloys.

While the concentration of Nb was shown to have a substantial influence on the as-cast microstructures, experimental observations suggest that other alloying additions can also trigger a profound variation in the δ volume fraction, as significant scatter in δ vol. % was seen for alloys having similar Nb levels, Figure 4. To investigate the microstructural variations associated with these elements, the δ volume fraction within the γ - δ eutectic regions of Cr, XTa, XMo and XW alloys were measured via quantitative image analysis, Figure 6. All four elements were found to promote higher δ volume fractions within the eutectic regions. W and Mo were again shown to be more effective than Cr in altering the microstructure of these γ/γ' - δ eutectic alloys.

Figure 6. Variations of eutectic δ volume fraction with different concentration of alloying elements.

3. γ - γ' and γ - γ' - δ eutectic

Closer examination of the as-cast microstructure at higher magnification reveals that different eutectic structures were formed in some alloys at the end of solidification. In the XTa series of alloys, pools of γ - γ' eutectic were found at the boundaries of different γ/γ' - δ eutectic colonies, Figure 7 (a). In the Cr series of alloys, structures with fine granular δ phase embedded within a continuous γ - γ' eutectic matrix was observed in the interdendritic regions, indicating the formation of γ - γ' - δ ternary eutectic from the liquid, Figure 7 (b). These structures were determined to have substantially different compositions when compared to the bulk alloy, Table II. In both eutectic structures, the concentration of Cr and Al were found to be notably higher than the bulk alloy.

Although only a limited amount of these eutectic structures were observed in the as-cast microstructure of the experimental alloys, qualitative microstructural analysis reveals that the tendency to form γ - γ' or γ - γ' - δ eutectic is closely related with the level of different alloying additions. These tendencies were quantified by the standard point-counting technique at 1000X magnification under light microscope on selected alloys, Table III. In spite of the relatively large standard deviations associated with the measurements of these highly localized structures, qualitative trends can be effectively assessed using this technique. While higher Ta levels were found to suppress the occurrence of γ - γ' or γ - γ' - δ eutectic, Mo and W additions were shown to modestly promote the occurrence of these structures. The E series of alloys in Table III were selected mainly to examine the effect of Cr and Al, since the γ - γ' or γ - γ' - δ eutectic structures were found to be enriched in these two elements. From the results in Table III, it is quite clear that both Cr and Al have the effect of promoting the formation of these eutectic structures. This phenomenon can be better shown in Figure 8. Al additions exhibit a much stronger impact on the formation of γ - γ' - δ eutectic than Cr additions, as significantly higher proportions of these eutectic structures were induced by only 2 at. % increase of Al. This is also reflected by the more pronounced increasing trend of these eutectic structures associated with Cr additions at higher Al level, as shown in Figure 8.

Table II. Composition of γ - γ' and γ - γ' - δ eutectic regions in X2.5W and 10Cr alloy. (at. %)

Alloy	10 Cr	Ni	Cr	Co	Al	Ti	Mo	W	Ta	Nb
X2.5W	bulk alloy	Bal.	2.0	2.0	5.0	0.5	1.0	2.5	1.0	12.7
	γ - γ' eutectic	Bal.	4.4	3.0	13.5	0.4	1.6	1.3	0.5	9.9
10 Cr	bulk alloy	Bal.	10.0	-	5.5	-	-	-	-	13.5
	γ - γ' - δ eutectic	Bal.	17.4	-	8.2	-	-	-	-	15.5

Figure 7. SEM image revealing the morphology of (a) γ - γ' binary eutectic in X1Ta alloy and (b) γ - γ' - δ ternary eutectic in 10Cr alloy.**Table III.** γ - γ' or γ - γ' - δ eutectic volume fraction in selected alloys.

Alloy	γ - γ' / γ - γ' - δ Vol. % (%)	Alloy	γ - γ' / γ - γ' - δ Vol. % (%)	Cr %	Al %
X1Ta	0.9	0Cr	0	0	5.5
X3Ta	0	4Cr	0	4.0	5.5
X5Ta	0	8Cr	0.5	8.0	5.5
X2Mo	2.7	10Cr	1.8	10.0	5.5
X3Mo	4.1	E6	0	0	7.2
X1.5W	2.7	E10	17.2	5.0	7.2
X2.5W	5.4	E9	19.9	10	7.2
		E12	1.8	6.0	4.6
		E13	8.6	6.0	5.6
		E14	14.0	6.0	6.6
		E15	23.5	6.0	7.5

Figure 8. 3-D plot showing the influence of Cr and Al concentration on the initiation of γ - γ' or γ - γ' - δ eutectic formation in experimental alloys.

4. Liquidus and Solidus Temperature

Liquidus and solidus temperatures of experimental γ/γ' - δ alloys were determined by DSC analysis, Table IV. These results were plotted together with Pandat predictions, Figure 9. Effects of the various alloying additions on the phase transformation temperatures were found from the experimental results. Cr was found to suppress the liquidus and solidus temperature, and this effect becomes much more pronounced at higher Cr levels. Ta additions, on the other hand, increased both these temperatures. Higher levels of Mo and W tended to lower the solidus temperature of these γ/γ' - δ alloys, but modestly increased the liquidus temperature. When these DSC measurements were compared with predicted results from Pandat, different degrees of discrepancies, both qualitative and quantitative, were found within different alloy series, Figure 9. In general, a better agreement between experiment and calculation was found for the solidus temperatures for the alloys inspected, except for alloys with considerable amount of primary γ (Ta/Nb alloy). While higher Ta levels raised the solidus and liquidus temperatures in XTa alloys, higher concentrations of other solutes were generally found to lower the solidus temperature of these γ/γ' - δ alloys.

Table IV. Measured and calculated liquidus and solidus temperature of experimental γ/γ' - δ alloys. (Unit: °C)

Alloy	T_{solidus}	T_{liquidus}	T_{solidus}	T_{liquidus}
	DSC		Pandat	
0Cr	1295	1316	1288	1300
2Cr	1287	1310	1282	1289
4Cr	1276	1304	1274	1280
6Cr	1258	1295	1266	1272
8Cr	1238	1283	1257	1269
X1Ta	1268	1313	1282	1298
X3Ta	1278	1325	1280	1298
X5Ta	1293	1336	1281	1308
X2Mo	1261	1309	1274	1297
X3Mo	1255	1317	1263	1294
X1.5W	1267	1318	1280	1295
X2.5W	1265	1319	1277	1297
TaNb	1317	1356	1300	1335
E1	1295	1309	1288	1315
E2	1290	1305	1280	1313
E3	1268	1289	1268	1300
E4	1255	1283	1258	1290
E5	1248	1275	1250	1270
E7	1217	1249	1210	1255
E8	1240	1271	1248	1293
E10	1248	1275	1249	1295
E11	1233	1270	1228	1270

Figure 9. Liquidus and solidus temperatures of different sets of γ/γ' - δ alloys. The solid dots represent the measured results via DSC, and the hollow dots represent Pandat predictions.

Discussion

Over the years, the continuous development of high temperature structural materials has largely been directed towards discovering new classes of structural materials that are capable of maintaining their mechanical properties at ever increasing temperatures. γ/γ' - δ eutectic alloys have been shown to exhibit excellent microstructural stability at temperatures at around 1000°C [18-21], which provides this class of materials tremendous advantage over conventional γ/γ' - δ alloys. Recently, powder processed complex polycrystalline γ/γ' - δ alloys, with densities of $\sim 8.5 \text{ g/cm}^3$, were demonstrated to possess attractive mechanical properties at intermediate temperatures (700–800°C) [28]. However, a

fundamental understanding of the relationship between chemistry, solidification and microstructure of this alloy system is still lacking.

The characteristic in situ composite microstructure of directionally solidified γ/γ' - δ alloys is based on the invariant eutectic reaction $L \rightarrow \gamma(\text{Ni}) + \delta(\text{Ni}_3\text{Nb})$ in the Ni-Nb binary system [29,] with $\gamma'(\text{Ni}_3\text{Al})$ precipitates forming within the γ matrix in the solid state. In Ni-Nb-X ternary systems, such an invariant eutectic reaction is extended from the Ni-Nb binary side to higher solute (X) level along a monovariant eutectic trough, Figure 10 [30]. Alloys with these eutectic compositions may potentially be of significant industrial importance, as they can be solidified with minimal degrees of chemical segregation and usually lead to the formation of a fine composite microstructure, which is generally considered as beneficial to the structural integrity and mechanical properties [22]. However, small deviations in alloy chemistry away from the eutectic trough can significantly alter the microstructure of these γ/γ' - δ eutectic alloys, resulting in different levels of primary phase formation. In this study, since only one alloying element was systematically varied within each alloy series, these complex eutectic alloys can be simply treated as Ni-Nb-X (X being the varying alloying addition) pseudo-ternary eutectic alloys when analyzing the effect of individual alloying element. The trends in the ternary alloy systems can thus be used to compare with trends observed in multi-component eutectic alloys.

Figure 10. Superimposed liquidus projections of various Ni-Nb-X ternary phase diagrams (Ni-rich corner), revealing different trends of γ - δ eutectic trough in different systems [30]. (X=Cr, Co, Mo, W, Ti and Ta)

Different alloying additions were found to have dissimilar effects in altering the primary phase formation of this γ/γ' - δ eutectic system, Figure 2. Interestingly, Cr, Mo and W additions were observed to shift the primary phase formation in the same direction. This is in agreement with the ternary phase diagram, where increasing levels of Cr, Mo and W shift the γ - δ eutectic trough in the iso-Nb direction, suggesting their tendency of substituting for Ni atoms in the γ - δ eutectic reaction, Figure 10. In fact, the various effects of alloying elements on shifting the primary phase formation in multi-component γ - δ eutectic system can be qualitatively predicted by examining various liquidus

projections. For example, when concentration of Ta is raised in substitution for Nb (along the iso-Ni line) in XTa alloys, an initial increase of primary γ phase is predicted by the Ni-Nb-Ta eutectic trough, which is consistent with the experimental observation. Similar analysis suggests that agreement between ternary and multi-component system can also be found in Cr and XMo alloys.

Figure 11. Superimposed isothermal sections of various Ni-Nb-X ternary phase diagrams (Ni-rich corner) at 1000°C, showing different level of solubility associated with various alloying elements in γ and δ phase [30]. (X=Cr, Co, Mo, W, Ti and Ta)

γ/γ' - δ eutectic alloys owe many of their extraordinary attributes to the reinforcing δ phase. Understanding the relationship between alloying additions and δ volume fraction is of critical importance in developing this in situ composite material. In this study, the δ volume fraction was found to be strongly dependent on the concentration of Nb, as supported by the results in Figures 4 and 5. However, although Cr, Ta, Mo and W additions were all observed to promote higher amount of δ phase, Figure 6, compositional analysis suggests that the Nb concentrations within these eutectic areas are relatively unchanged at different solute levels. In fact, such increases in the eutectic δ phase are likely triggered by subtle solubility changes of Nb in γ (or Ni in δ) when alloying levels are varied. This is again consistent with trends in ternary systems, Figure 11 [30]. In Ni-Nb-X ternary systems, the relative proportion of $\gamma(\delta)$ phase could be determined by the length of the tie-line that connects the γ and δ phase fields (lever rule). When alloying additions are added in substitution for Ni (along the iso-Nb line), higher concentrations of Cr gradually lower the solubility limit of Nb in γ phase, while higher level of W tends to lower the solubility limit of Nb in δ phase, both of which favor a higher proportion of the δ phase. These proposed effects are consistent with those reported previously for the Cr series of alloys [26]. Mo additions sharply suppress the solubility limit of Nb in both γ and δ at the same time and induce a higher δ volume fraction in Ni-Nb-Mo system. This is consistent with the results in the current study as the Mo series of alloys exhibit the strongest effect in altering the amount of δ , Figure 6, among the solute elements investigated. Segregation measurements and compositional analysis in the XTa alloys confirm that higher levels of (Ta+Nb) within eutectic regions were responsible for

inducing the formation of higher δ volume in this alloy series [31].

The formation of γ - γ' and γ - γ' - δ eutectic as terminal structures during solidification are generally considered as being undesirable in these γ/γ' - δ eutectic alloys. Their presence may jeopardize the microstructural integrity of the material as they retain large amount of solute atoms from the matrix, substantially lower the solidus temperature and can be very difficult to eliminate by homogenization heat treatments. In this study, these terminal structures were found to be rich in Al and Cr. Similar segregation behavior has been reported in directionally solidified γ/γ' - δ eutectic alloys, where Al and Cr tend to segregate to the end of solidified ingot, a phenomenon possibly caused by their tendencies of lowering the melting point of this alloy system [11]. The sharp increase of γ - γ' - δ ternary eutectic associated with higher Al content, as shown in Figure 8, is somewhat expected, since Al is a strong γ' -former and triggers the formation of γ - γ' - δ ternary eutectic in Ni-Nb-Al system when its concentration reaches 7.3 at. % [11, 32]. Cr additions may be indirectly promoting the formation of γ - γ' - δ ternary eutectic by increasing the volume fraction of δ phase, which consequently enhances the level of Al supersaturation within the γ phase, leading to the occurrence of ternary eutectic formation.

The process of developing and selecting promising alloys with attractive physical and mechanical properties among the vast quantity of possible compositions via the traditional trial-and-error route is impractical. In recent years, thermodynamic database models such as Pandat from CompuTherm, have become increasingly popular for optimization of alloy compositions. Many of the commercially available thermodynamic software models have been demonstrated to be quite reliable in predicting phase stability and volume fractions in traditional γ/γ' Ni-base superalloys [33-35], where significant amounts of high fidelity experimental data were used to validate the free energy curves. When these thermodynamic models are extended to multi-component γ/γ' - δ alloys, many of the qualitative trends are captured, but the accuracy of the predictions remains uncertain. Different degrees of discrepancy were observed when predicted results were compared with experimental measurements. Besides the possible errors introduced by compositional inhomogeneities within these arc melted ingots, some inherent difficulties related with modeling γ/γ' - δ eutectic alloys might have contributed to the observed differences. To successfully predict the properties of equilibrium phase in an alloy system, the free energy curves assigned to each constituent phase needs to accurately describe its thermodynamic properties [33-35]. The observed discrepancies can likely be attributed to the relatively limited amount of thermodynamic information of higher order Nb-containing sub-systems that exists within the thermodynamic database.

Careful examination of the experimental results and model predictions reveal a number of interesting tendencies for this γ/γ' - δ eutectic system. First of all, the discrepancy between experimental results and predictions within each alloy series tends to escalate as the level of solute additions increases, Figure 3, which is likely due to the higher level of elemental interactions. Secondly, the predicted trends within each alloy set are often more pronounced than experimental observation, as seen in Figure 3. This can be mostly attributed to the non-equilibrium solidification condition of arc melting. In principle, the influence of various alloying additions on the solidification behavior and microstructural

features is determined by their ability in shifting the equilibrium solutal partitioning behavior within these alloys. It is likely that the solute separation between different phases and regions during solidification is suppressed to some degree by the relatively fast cooling rate of arc melting, making the experimental observation less pronounced than predicted trends [36]. Thirdly, when comparing between different alloys sets, better agreement between experimental results and thermodynamic calculations seems to exist within alloys possessing fully eutectic structure, Figure 3. This is most likely related to the limited degree of chemical segregation associated with these eutectic structures, which leads to a close-to-equilibrium phase volume relationship in the as-cast microstructure.

Conclusion

Based on the experimental observation of this investigation, the following conclusions can be drawn to the γ/γ' - δ eutectic alloys at the composition range considered.

1. The volume fraction of primary phase and overall δ in these multi-component γ/γ' - δ alloys strongly depend on the Nb concentration, yet they can also be effectively modified by additions of other alloying elements.
2. While Cr, Mo and W tend to promote the formation of primary δ , additions of Ta favor the formation of primary γ . With their different influence on the eutectic δ volume fraction and potential elemental partitioning behavior, this confirms the possibility of maintaining a fully eutectic microstructure with different combinations of constituent alloying additions, which could then provide variation of other microstructural attributes of interests.
3. Additions of Cr, Mo and W were shown to have qualitatively similar behaviors in altering the solidification characteristics and as-cast microstructure of this γ/γ' - δ alloy system.
4. Mo and W slightly increase the tendency to form a terminal γ - γ' eutectic during solidification, while Ta additions suppress the occurrence of this structure. Al and Cr were observed to both promote higher volume fractions of the γ - γ' - δ ternary eutectic, although the effect of Cr is much less pronounced and tends to be more effective at higher Al levels.
5. The thermodynamic database model, Pandat, is capable of predicting qualitative trends resulting from compositional changes in these multi-component γ/γ' - δ alloys. Although good agreement was observed with the comparisons of the predicted and measured solidus temperatures, discrepancies in the equilibrium volume fractions and liquidus temperatures become increasingly larger with higher solute levels. Interestingly, the best agreement between the experimental observations and predictions were found in alloys with near eutectic microstructures.

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