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POLYCRYSTALLINE γ-γ′-δ TERNARY EUTECTIC NI-BASE SUPERALLOYS

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Abstract

As one of the most important classes of high-temperature structural materials, Ni-base superalloys are critical to the continued development of high-performance turbine engines for propulsion and power generation. In order to accommodate the increases in engine operating temperatures required for improved performance and efficiency, higher concentrations of refractory alloying elements have been used to enhance the mechanical properties of Ni-base superalloys. However, many of these compositional modifications have also tended to result in the alloy being more difficult to manufacture into large-scale components using traditional approaches and techniques. The present investigation evaluates some of the attributes of novel Ni-Nb-Cr-Al alloys, based on the pseudo-ternary eutectic γ – γ' – δ system. Preliminary results reveal that this multi-phase pseudo-eutectic alloy system possesses high temperature properties comparable to commercial Ni-base superalloys, such as U720. A series of model γ-γ′-δ alloys with systematic changes in composition were studied to develop an improved fundamental understanding on the effect of alloying additions on these alloys. Characterization of model γ-γ′-δ alloys reveals that many of the mechanisms that govern the characteristic properties are associated with the strength at the grain boundaries and interfaces. Modification of the grain boundary attributes via the addition of minor alloying additions was found to greatly improve strength and creep resistance at elevated temperatures.

Introduction

Nickel-base superalloys are the materials of choice for structures used in the "hot section" of modern gas turbines engines, and are likely to remain so for the foreseeable future. As the fundamental understanding pertaining to the physical metallurgy of γ-γ′ Ni-base alloys matures, increasingly stringent intrinsic limitations must be overcome via changes in alloying or processing to produce modest improvements in properties. More often than not, the modest improvements in properties also accompany compromises in manufacturing, environmental resistance and cost. Additionally, the incremental improvements in mechanical properties or temperature capability are often outweighed by the compromises that are required for the insertion of the new alloy or process. For this reason, this study was aimed at investigating and developing a revolutionary new class of structural materials for high temperature applications. The innovative alloy system is based on the Ni-Al-Nb pseudo-ternary eutectic γ-γ′-δ. In addition to utilizing the ordered Ni_3Al γ′ precipitate as a strengthening phase, this alloy also contains large volume fractions of a primary intermetallic Ni_3Nb δ phase dispersed both intragranularly as well as along the grain boundaries[1]. Compared to commercial polycrystalline γ-γ′ Ni-base superalloys, preliminary results indicate that the novel γ-γ′-δ possess higher specific strengths, significantly improved temperature capability and are amenable for low cost manufacturing techniques.

Initially investigated as candidate materials for turbine airfoil applications during the 1970's and 1980's, directionally solidified γ-γ′-δ Ni-Al-Nb eutectic alloys were shown to possess excellent high temperature strength and creep resistance[2-14]. High thermal gradients combined with slow withdrawal rates during directional solidification processing of these alloys promoted the formation of an in-situ composite microstructure comprised of aligned δ lamellae contained within a γ-γ′ matrix. Despite possessing excellent mechanical properties at elevated temperature, the large degree of anisotropy and lack of transverse strength exhibited by these alloys made them unsuitable for the intended applications. Coupled with the mismatch in thermal expansion coefficients, the low interfacial strength between the δ lamellae and surrounding γ-γ′ matrix in directionally solidified structures resulted in high notch sensitivities and severely degraded fatigue resistance. As such, these intrinsic attributes exhibited by directionally solidified γ-γ′-δ eutectic alloys made them unsuitable for high temperature turbine airfoil applications. Due to the inability of these materials to meet the prescribed design criterion, a number of scientifically challenging problems were left unresolved. This includes the quantification of the deformation mechanisms operative in *polycrystalline* Ni-Al-Nb γ-γ′-δ eutectic alloys at temperatures below 800˚C. Although the properties of these alloys render them unsuitable for use at temperatures above 1000˚C, many of their unique attributes may potentially be harnessed for high performance structural applications where the temperatures are limited to below 800˚C. Since creep deformation at temperatures below 750˚C are not considered to be life limiting, columnar or single crystal grain structures are typically not required.

Compared to state-of-the-art high strength polycrystalline Ni-base superalloys, this novel class of γ-γ′-δ alloys may potentially offer a number of benefits. Firstly, a substantially higher level of dispersion/precipitate strengthening is utilized in this class of materials. With up to ~40% δ and ~30% γ′ by volume, the microstructure may contain up to 70% intermetallic phases to provide high temperature strength. The high combined volume fraction of intermetallic precipitates rivals that of creep resistant single crystal Ni-base superalloys produced via investment casting and provides potent levels of Orowan and composite strengthening[15-17]. In addition to improved strength, microstructural stability after prolonged exposures to elevated temperatures is becoming increasingly important in a number of structural applications. Highly alloyed polycrystalline Ni-base superalloys are susceptible to the precipitation of topologically-close-packed (TCP) phases when subjected to high temperature service environments for extended durations[18-20]. The precipitation of TCP phases is primarily due to supersaturation of the γ matrix with refractory alloying additions that had been added to provide solid solution strengthening. Elevated levels of Cr, Mo and W combined with high equilibrium γ′ volume fractions promote the precipitation of TCP phases in γ-γ′ Ni-base superalloys. The γ-γ′-δ alloys are near eutectic alloys that possess high levels of microstructural stability even at temperatures close to the melting point. The preferred solidification sequence results in the formation of a pseudo-binary γ-δ eutectic structure from which the γ′ precipitates out in the solid state from the γ phase upon cooling. As the intermetallic δ is a primary phase that forms upon solidification, the microstructure exhibits excellent stability and additional TCP phases are unlikely to form within this class of alloys. Finally, the γ-γ′-δ alloys being proposed as part of this study possess lower densities and raw materials costs when compared to commercial high strength Ni-base superalloys. Advanced powder processed Ni-base superalloys rely on the additions of W, Mo and Ta to provide high levels of strengthening in both the γ and γ′ phases[21-25]. Not only do these refractory alloying additions increase the overall density of the alloy, they also increase the raw materials costs associated with the alloy. The pseudo-eutectic γ-γ′-δ alloys are based on ternary Ni-Al-Nb or quaternary Ni-Al-Nb-Cr systems and contain limited amounts of expensive refractory alloying additions. With up to a ~10% lower alloy density, the comparatively higher density normalized specific strength may be ideal for producing low cost, high strength structures for high performance applications. All of these reasons are motivations for investigating the γ-γ′-δ alloys as candidate materials for high temperature structural applications.

Experimental Materials and Procedure

For this investigation, a select group of high Nb containing γ-γ′-δ Ni-base superalloys were devised to highlight the dependence of high temperature mechanical properties on chemistry. Compositions of these experimental alloys investigated during these preliminary studies are listed in Table I. V204A is a simple quaternary Ni-Al-Cr-Nb alloy that possesses a composition near the pseudo-binary γ-δ eutectic. V204B is a modified variant of V204A in which 2.9wt.% Ta is substituted for Nb and contains limited levels of B and C for grain boundary strengthening. Compared to V204B, V204D contains higher levels of Nb, B and C as well as 0.2wt.% Ti. Finally, V204G has a composition with similar levels of Ta and Nb when compared to V204B, but contains additional additions of Mo, W, Hf and Zr.

All of the experimental alloys were processed into powder by first vacuum induction melting (VIM) of the alloy and then applying standard inert gas atomization techniques. Following collection of the powders, sieving was performed to remove oversized and powder fines. The -40/+270 powders were then collected in a mild steel can, vacuum sealed and hot isostatic pressed at approximately 1150˚C for consolidation of the powder into a cylindrical billet measuring approximately 75mm in diameter and 200mm in height. From the billet, cylindrical bars were excised using electro-discharge machining for assessment of both physical and mechanical properties. The γ′ solvus temperatures for the alloys were determined via heat treatment studies and differential scanning calorimetery (DSC). To optimize the mechanical properties of the alloys by refining the size and distribution of the γ′ precipitates, all of the alloys were heat treated at a temperature 10˚C above their γ′ solvus temperature for four hours and allowed cool to room temperature at a rate of 1-1.5˚C/sec. Following the γ′ solutioning heat treatment, an ageing treatment of 850˚C for 16 hours was applied to all of the alloys. Standard metallographic techniques and scanning electron microscopy (SEM) using a JEOL 5900 were used to assess the microstructure of all the alloys in the as-HIP condition and at intermediate stages during the heat-treatment.

The solutioned and aged alloys were machined into small cylinders measuring 10mm diameter and 15mm height for compression testing and standard tensile specimens with dimensions consistent with ASTM E38. The flow stresses of the alloys were measured as a function of temperature. Creep resistance of the alloys was also evaluated at 677˚C and 760˚C. Following deformation, the microstructures of the experimental alloys were carefully assessed and quantified in the SEM. Microstructural features, such as the volume fraction and size distribution of the constitutent phases were quantified using standard digital image analysis techniques. A JEOL JEM3010 transmission electron microscope (TEM) was used to identify the characteristic damage mechanisms associated with deformation in these alloys and perform selected area diffraction (SAD) to identify the characteristic crystal structures associated with selected phases that were observed in the various alloys.

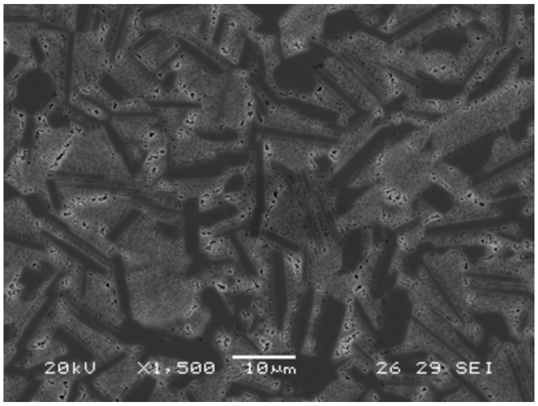
Results

As expected, the compositional changes in the series of γ-γ′-δ alloys investigated resulted in some modest changes in both the microstructure and characteristic phase transformation temperatures, Table II. Compared to V204A, which contains no Ta, the γ′ solvus temperatures of V204B, V204D and V204G are all approximately 20˚C higher. The addition of Ti in V204D and V204G also resulted in a modest increase in the γ′ solvus temperature when compared to V204B. These results are consistent with existing knowledge of conventional γ-γ′ Ni-base superalloys in which both Ta and Ti tend to segregate preferentially to the γ′ phase and increase its solvus temperature. All of the powder processed alloys exhibit a three phase microstructure following the γ′ solutioning heat treatment and ageing. Large, elongated blocky δ phases are distributed within a matrix of equiaxed grains comprised of cuboidal γ′ precipitates contained within a γ matrix. Average grain sizes are on the order of 10μm for all four of the powder processed alloys. The δ phases are distributed both along the grain boundaries as well as transgranularly. Representative micrographs showing the characteristic three phase microstructure in V204B is shown in Figure 1. At higher magnifications, an additional phase was found to develop in alloys containing Ta, V204B, V204D and V204G, after ageing for 16 hours at 850˚C. This phase exhibited a very fine lenticular morphology and resided within the γ channels, Figures 1c and 2. Selected area diffraction (SAD) in the TEM was used to generate diffraction images that revealed these precipitates are coherent with the matrix and exhibit a body centered tetragonal crystal structure characteristic of γ′′, Figure 2.

With respect to the microstructure, compositional changes were found to induce differences in volume fraction of the constituent phases, Table III. For V204A, the comparatively high level of Nb resulted in the formation of approximately 43% by volume of

Table I: Nominal Compositions of the Experimental Alloys (wt.%)

	Ni	Al	Cr	Ti	Nb	Ta	Mo	W	B	C	Hf	Zr
V204A	Bal.	2.4	6	-	20.3	-	-	-	-	-	-	-
V204B	Bal.	2.3	5.8	-	17.5	2.9	-	-	0.0017	0.017	-	-
V204D	Bal.	2.5	5.9	0.2	20.2	2.5	-	-	0.005	0.03		
V204G	Bal.	2.6	6	0.5	17.2	3	1.5	1.5	0.005	0.04	0.15	0.03- 0.05



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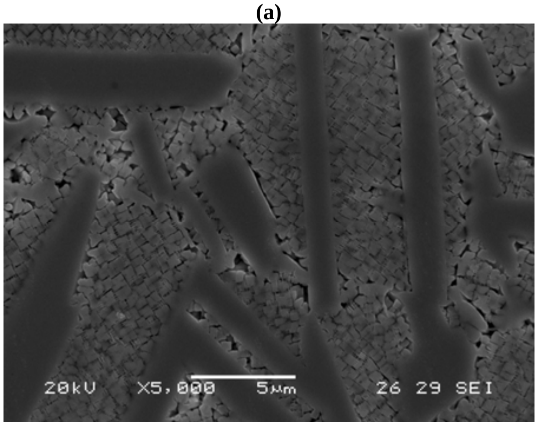

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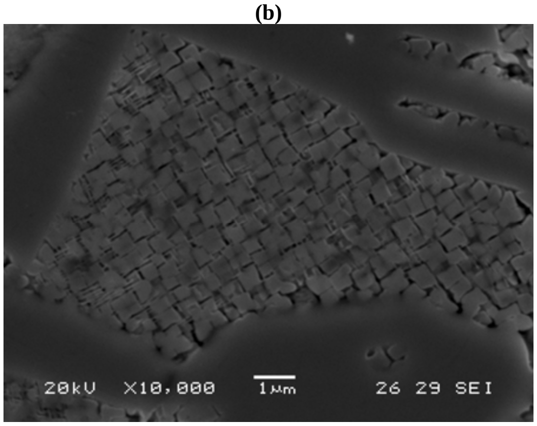

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Figure 1: Microstructure of γ-γ′-δ alloys at various magnifications revealing (a) blocky δ precipitates, (b) cuboidal γ′ precipitates distributed within a γ matrix and (c) fine lenticular phases contained within the γ channels.

δ phase. Reducing the Nb level in V204B to 17.5 wt.% led to a 10% decrease in the overall δ volume fraction. The addition of Ta and Ti coupled with a high level of Nb in V204D resulted in a microstructure that consists of 54% δ by volume. Interestingly, alloy V204G contains approximately the same δ volume fraction as V204A despite having nominally the same level of Nb as V204B. This suggests that additions of Mo, W and Ti also modify the microstructure of these alloys. Sizes of the γ′ and δ phase precipitates were also quantified. Although all of the γ′ precipitates were cuboidal in shape, the size or edge lengths of the γ′ varied as a function of the measured volume fraction with higher volume fractions resulting in smaller γ′ precipitates. Within the γ-γ′ grains, the normalized volume fraction of γ′ ranged from between 72 to 80%. This would suggest that a high degree of precipitate strengthening exists within these alloys as the interparticle spacings are small and the Orowan resistance is high. Finally, the aspect ratios (length/width) of the δ precipitates were quantified and found to vary between 4.9 and 8.2 with fairly large standard deviations.

Table II: γ′ solvus temperatures for the powder processed alloys

Alloy	**γ′ Solvus Temperature (˚C)**
V204A	1195
V204B	1213
V204D	1218
V204G	1220

The flow stresses of the samples were measured as a function of temperature for both the compression and tensile samples. At room temperature, the flow stress of V204G is highest followed by V204A, V204B and V204D, respectively, Figure 3. All of the alloys were found to exhibit significant decreases in strength at temperatures above 750˚C. At 800˚C, the 0.2% flow stresses of the alloys ranged from 744 to 850MPa. The degree of temperature dependent softening was found to vary for the different alloys as V204G possessed the highest strength at 800˚C followed by V204D, V204B and V204A. The observed differences in strength among these alloys do not appear to be related to either the composition or obvious microstructural characteristics detailed in Table III. Nevertheless, compared to the properties of fine, grained U720, V204G was found to be significantly stronger at all temperatures, while V204A, V204B and V204D exhibited equivalent or higher strengths at temperatures above 750˚C.

Creep properties of the powder processed alloys were also evaluated at two conditions, 677˚C/724MPa and 760˚C/560MPa. The creep curves for the four γ-γ′-δ alloys at 677˚C/724MPa is shown in Figure 4. Under these conditions, V204G exhibited the highest resistance to deformation while V204A was the worst performing alloy among the set of four alloys. The creep response

Table III: Microstructural parameters of the powder processed alloys.

Alloy	Average γ′ Precipitate Size (μm)	Aspect Ratio of δ	Volume Fraction γ	Volume Fraction γ′	Volume Fraction δ	γ′/γ+γ′ ratio
V204A	0.7±0.2	5±2	0.15	0.42±0.05	0.43±0.02	0.74
V204B	0.5±0.1	5±2	0.19	0.48±0.06	0.33±0.03	0.72
V204D	1.0±0.2	8±3	0.09	0.37±0.05	0.54±0.02	0.80
V204G	0.7±0.2	8±3	0.15	0.44±0.02	0.41±0.02	0.75

Table IV: 0.2% Flow stresses as a function of temperature (MPa)

Temperature (˚C)	V204A	V204B	V204D	V204G	U720
25	1187	1085	985	1268	1205
700	982	1040	926	1117	1060
750	900	983	921	1015	900
800	744	759	830	850	-

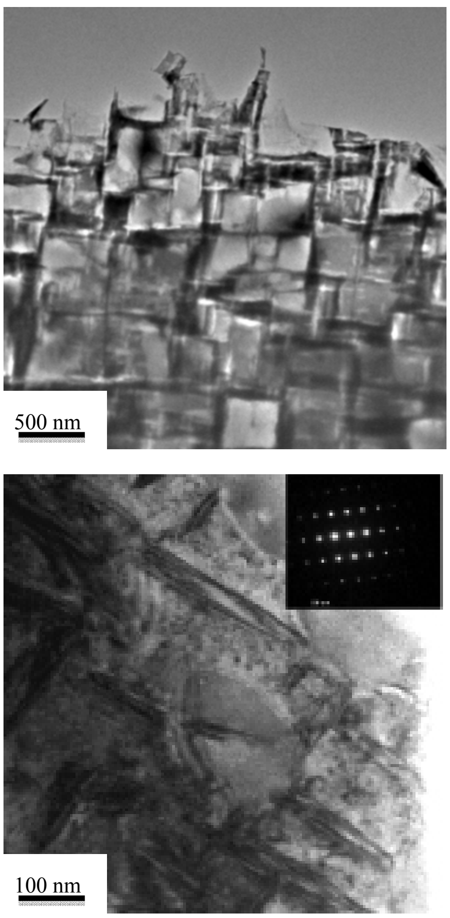


Figure 2: TEM micrographs showing the presence of a body centered tetragonal γ′′ phase within the γ channels.

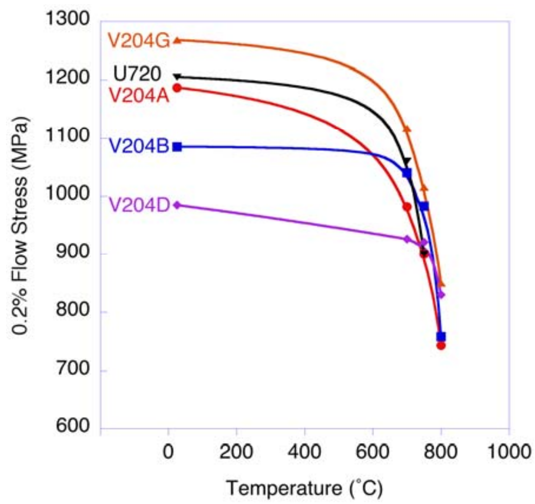


Figure 3: Temperature dependent 0.2% flow stresses of the powder processed γ-γ′-δ alloys.

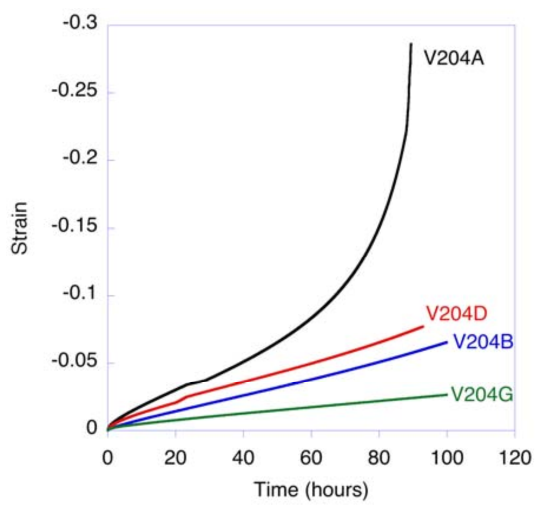


Figure 4: Creep curves of γ-γ′-δ alloys at 677˚C/724MPa.

of V204B and V204D were revealed to be nearly identical under these conditions. Figure 5 shows the creep response of the alloys at 760˚C/560MPa. Interestingly, the creep properties of V204G and V204D appear similar and are approximately equivalent to the creep performance of U720 at 760˚C/560MPa. Conversely, V204A exhibits a relatively poor creep capability under these conditions and V204B is only modestly better than V204A.

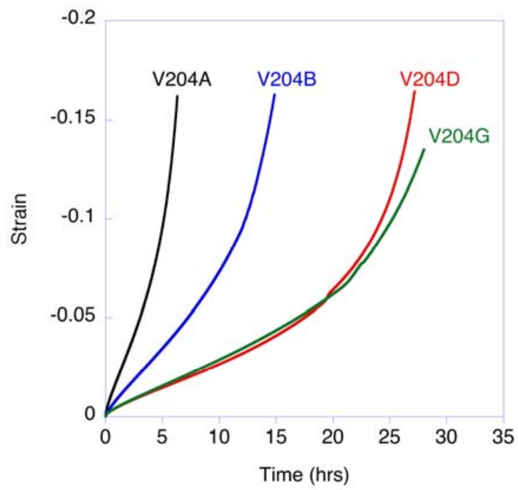
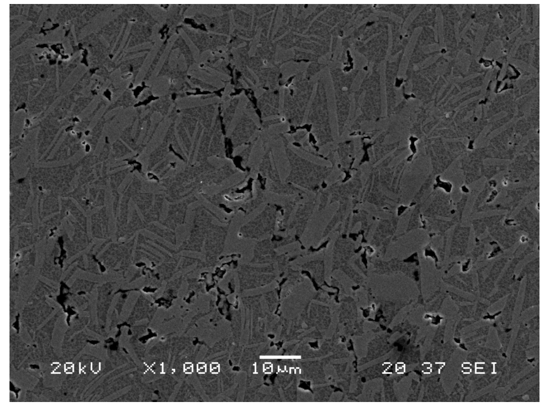


Figure 5: Creep curves of γ-γ′-δ alloys at 760˚C/560MPa.

Microstructures of the samples after creep deformation were characterized in detail in an attempt to understand the mechanisms governing their behavior. Both SEM and TEM were performed. Due to the lack of grain boundary strengthening elements (C, B, Hf and Zr) in V204A, cavitation damage was observed to occur readily during deformation at high temperatures. Since alloy V204B also only contained limited quantities of C and B, creep at 760˚C/560MPa resulted in substantial decohesion of the grain boundary interfaces and accumulation of cavitation damage, Figure 6a and 6b. For alloys V204D and V204G, in addition to adding Zr and Hf, the C and B levels were increased over those in V204B. This resulted in a much more resilient grain boundary and little to no cavitation damage was observed within the microstructures of V204D and V204G after creep at 760˚C/560MPa, Figure 6c. TEM analyses of the interfaces between the δ and γ-γ′ matrix showed little damage in V204D and V204G. Deformation of the δ phase precipitates was apparent particularly at elevated temperatures. Many of the blocky precipitates with large aspect ratios were plastically deformed during creep at elevated temperatures, Figure 7a. During compression of tensile testing at room temperature, the δ phase precipitates were observed to accommodate strain via twinning, Figure 7b.

Discussion

Nickel-base superalloys are the materials of choice for both static and rotating structures used in the "hot section" of modern gas turbines engines, and are likely to remain so for the foreseeable future. However, as the service temperatures and loads for each particular component are quite different form one another, this has led to the development of distinctive alloy specifications (differing in composition, processing and resulting microstructure) to satisfy the disparate operational requirements. Recent advances in the development of computational alloy design tools and thermodynamic database models have enabled incremental improvements mechanical properties and temperature capability via refinement of alloy compositions and/or optimization thermal-mechanical treatments[26-28]. As the fundamental understanding pertaining to the physical metallurgy of γ-γ′ Ni-base alloys matures, increasingly stringent intrinsic



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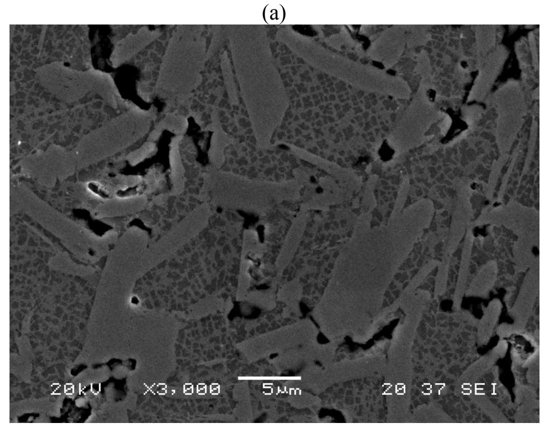

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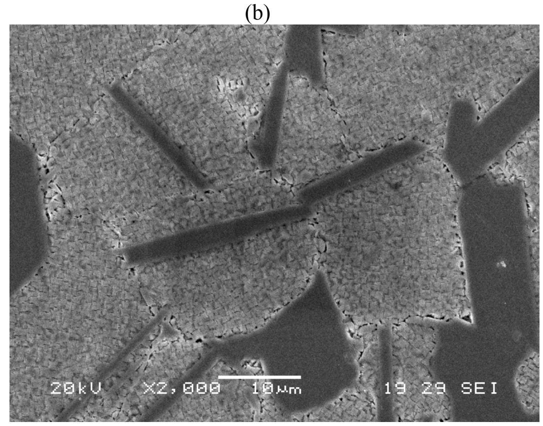

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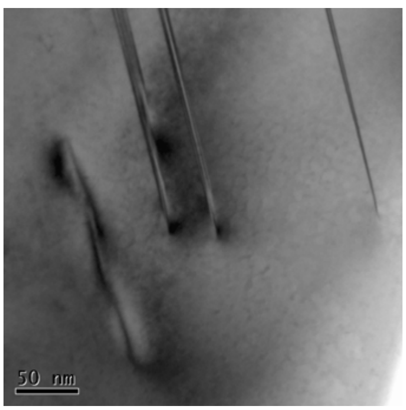
Figure 6: Micrographs showing cavitation damage in (a) V204B after creep at 760˚C 560MPa. (b) Cavitation occurs at both the grain boundaries and δ/γ-γ′ interfaces. Microstructure of V204G after creep at 760˚C 560MPa revealing limited damage at grain boundaries and interfaces.

limitations must be overcome via changes in alloying or processing to produce modest improvements in properties. More often than not, the modest improvements in properties also accompany compromises in manufacturing, environmental resistance and cost. Additionally, the incremental improvements in mechanical properties or temperature capability are often outweighed by the compromises that are required for the insertion of the new alloy or process. For this reason, new classes of structural materials are required in order to meet the design requirements for advanced gas turbine engines. The innovative alloy system is based on the Ni-Al-Nb pseudo-ternary eutectic γ-γ′-δ. In addition to utilizing the ordered Ni_3Al γ′ precipitate as a strengthening phase, this alloy also contains large volume fractions of a primary intermetallic Ni_3Nb δ phase dispersed both intragranularly as well as along the grain boundaries. Compared to commercial polycrystalline γ-γ′ Ni-base superalloys, these preliminary results clearly indicate that the novel γ-γ′-δ possess higher specific strengths, significantly improved temperature capability and are amenable for low cost manufacturing techniques[1].



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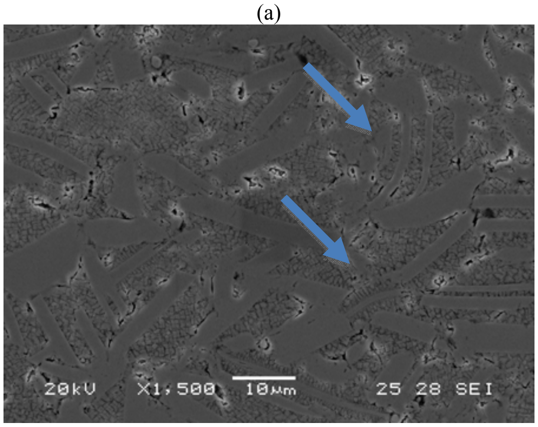

(b)

Figure 7: (a) TEM micrograph showing the formation of twins in the δ phase precipitates after plastic deformation at room temperature. (b) SEM micrograph revealing the plastic deformation of V204D following creep at 760˚C 560MPa.

Similar to conventional γ-γ′ Ni-base superalloys, solid-solution strengthening occurs in both the disordered FCC γ phase as well as the ordered $L1_2$ γ′ phase. However, the presence of the intermetallic Ni_3Nb δ phase offers an additional degree of dispersion strengthening not encountered in γ-γ′ alloys. Ti and Ta may also substitute for Nb in the δ phase and provide solid solution strengthening within the $D0_a$ structure[29-33]. Precipitation/dispersion strengthening is the primary mode of strengthening utilized in high temperature alloys. As temperatures exceed 750°C, diffusive processes become operative and dislocations are no longer constrained onto their respective glide planes[34-35]. Under these conditions, the Orowan resistance associated with bowing of dislocations between non-shearable precipitates becomes the dominant mode of strengthening. For this reason, the volume fraction of precipitates in γ-γ′ Ni-base superalloys has gradually increased over the years with improved temperature capability. Currently, advanced high strength polycrystalline Ni-base superalloys, such as Rene 104, RR1000, Alloy 10 and LSHR, contain on average ~55% volume fraction of γ′ precipitates at room temperature. Increasing the equilibrium volume fraction of γ′ precipitates in these alloys may potentially improve their strength and temperature capability, but the degree to which the compositions can be modified is limited by existing manufacturing techniques and processes. Due to the high levels of refractory alloying additions, conventional casting of high strength superalloy ingots is prone to segregation related solidification defects[36-37]. Costly powder metallurgy processes are typically required for production of large, high strength γ-γ′ superalloy ingots. Furthermore, increasing the volume fraction of the γ′ phase often renders the alloy to be more susceptible to microstructural instabilities and less ductile, thereby making it more difficult to forge[38]. Consequently, most of the efforts aimed at improving the temperature capabilities of high strength polycrystalline Ni-base superalloys have been dedicated towards modification of the grain structure and heat treatments to control the γ′ precipitate size and morphology. These novel γ-γ′-δ alloys adopt a different approach as the resulting microstructure utilizes potent strengthening mechanisms stemming from both the high volume fraction of meso-scale δ phase structures as well as from the intragranular submicron γ′ precipitates contained within the γ phase. The intermetallic Ni_3Nb δ phases provide composite strengthening, whereas the γ′ phase offers precipitate strengthening.

The alloys investigated in this study possess compositions that were carefully selected such that the characteristic effects of the various alloying additions may be elucidated. V204A is a quaternary Ni-Nb-Cr-Al alloy that contains no grain boundary strengthening elements. Due to the relatively high level of Nb and Al, large volume fractions of δ and γ′ formed within the microstructure. This imparted a high level of strength to V204A at room temperature, but both the strength and creep resistance were the poorest of all the alloys investigated due to the lack of grain boundary strengthening elements. This is evident in the high degree of softening that occurs at temperatures above 700˚C, Figure 3. The 1187MPa yield strength measured at room temperature decreases drastically to 744MPa at 800˚C. Moreover, the creep properties of V204A at 677˚C/724MPa and 760˚C/560MPa, Figures 4 and 5, both progress into tertiary creep at comparatively low times and the resulting microstructures after deformation exhibit extremely high degrees of cavitation damage. These findings clearly suggest that in order to enhance the high temperature strength of these polycrystalline γ-γ′-δ eutectic alloys, the grain boundaries and interfaces must be strengthened.

The composition of V204B was designed to substitute Ta for Nb and incorporate a modest amount of grain boundary strengthening elements. Since a continuous δ (Ni_3Nb or Ni_3Ta) phase spans across the Ni-Nb and Ni-Ta axes in the ternary Ni-Nb-Ta system, it was expected that Ta would partition preferentially to the δ phase and provide solid solution strengthening. However, the Ta addition was found to shift the composition of the alloy off the γ-δ pseudo-binary eutectic trough and decrease the volume fraction of δ phase in the powder processed from 43% in V204A to 33% in V204B. The substitution of 2.9 wt.% Ta for Nb resulted in an increased γ′ volume fraction and solvus temperature, Tables II and III. Although this compositional change resulted in a ~100MPa decrease in the 0.2% flow stress at room temperature when compared to V204A, the strength of V204B at elevated temperatures is noticeably higher, Figure 2. Some of the improvements in high temperature strength and creep resistance of V204B can be attributed to the additions of C and B, but significant cavitation damage was also observed after creep deformation, Figure 6a and 6b. Results from V204B indicate that Ta additions to these polycrystalline γ-γ′-δ eutectic alloy systems stabilize the γ′ phase over the δ phase.

Based on the findings from V204A and V204B, the composition of V204D was designed to maintain a sufficiently high level of Nb to achieve a pseudo-binary γ-δ eutectic microstructure during solidification while adding both Ta and Ti to strengthen and stabilize the γ′ phase. As a result, alloy V204D contained the highest volume fraction of δ (54 vol.%) and had the highest proportion of γ′ in the γ-γ′ matrix (80.4%). B and C concentrations in V204D were also increased in an attempt to impart a higher degree of grain boundary strengthening at elevated temperatures. Although the 0.2% flow stress of V204D was modest at room temperature (985MPa), this alloy was able to maintain much of it strength at elevated temperatures and experienced only a 155MPa decrease in strength at 800˚C. This resulted in alloy V204D being significantly stronger than both V204A and V204B at 800˚C. For comparison, V204A and V204B experienced decreases in strength of 443MPa and 326MPa, respectively, when going from room temperature to 800˚C. The high combined volume fractions of δ and γ′ combined with the increased content of B and C were observed to greatly improve the creep properties of V204D at 760˚C/560MPa. The creep life of V204D was five times greater than V204A and two times better than V204B. Although the compositional changes to V204D were found to improve the high temperature strength and creep resistance, strength at lower temperatures were compromised, possibly due to the excessively high combined volume fraction of intermetallic strengthening phases present in the microstructure. This suggests that both the grain boundary strength and microstructure need to be optimized in order to achieve a balance of properties throughout the temperature range.

The composition of V204G contains nominally the same levels of Nb and Ta as V204B, however, V204G also contains Ti, Mo, W, Hf and Zr. The levels of C and B in V204G are also equivalent to those in V204D. These alloying changes resulted in a more balanced microstructure in which the δ and γ′ volume fractions were 41% and 44%, respectively. Microstructurally, V204G appears to be similar to V204A. In designing the composition of V204G, Mo and W were added to provide solid solution strengthening of the γ phase while Ti was utilized to make the γ′ precipitates more resistant to dislocation shear. More importantly, minor additions of Hf and Zr were added to enhance the grain boundary strength of these alloys. These alloying changes resulted in a substantial improvement in mechanical properties for V204G. On the basis of strength, V204G exhibited the highest yield strength at all temperatures from 25˚C to 800˚C. The creep properties of V204G were also far superior to the other alloys at 677˚C/724MPa, Figure 4. Moreover, despite having a significantly lower combined volume fraction of δ and γ′ in its microstructure, V204G has an equivalent creep resistance as V204D at 760˚C/560MPa and no obvious signs of cavitation damage were observed along the grain boundaries, Figure 6c.

Compared to the original directionally solidified counterparts, polycrystalline variants of Ni-Al-Nb γ-γ′-δ pseudo-binary and ternary eutectic alloys possess a comparatively lower temperature capability but do not appear to exhibit the same shortcomings. By breaking the up the continuous δ lamellae into shorter particles and segments that are contained within an equiaxed polycrystalline structure, both the degree of anisotropy and the magnitude of internal stresses contained within the microstructure can be significantly reduced. As seen from the results of this study, the resulting microstructure utilizes potent strengthening mechanisms stemming from both the high volume fraction of meso-scale δ phase structures as well as from the intragranular submicron γ′ precipitates contained within the γ phase. Currently, the measured flow stresses as a function of temperature for some of these model polycrystalline γ-γ′-δ alloys are comparable to those of advanced, high strength powder processed polycrystalline Ni-base superalloys. These preliminary results are extremely promising as the potential for achieving transformational property improvements over conventional Ni-base superalloys improves along with our fundamental understanding of the mechanisms that govern deformation in these alloys. Once these mechanisms are identified, the chemistries and processing routes may then be carefully optimized to fully exploit the attributes of these novel Ni-Al-Nb γ-γ′-δ alloys.

In addition to exhibiting promising high temperature properties, the formation of γ″ occurs in these alloys after a post-solution heat treat age at 850˚C. In conventional Ni-base superalloys, the post-solution heat treatment age is intended to coarsen and refine the morphologies of the γ′ precipitates. In these novel Ni-Al-Nb γ-γ′-δ alloys, however, γ″ was found to form in-between the cuboidal γ′ precipitates within the γ phase in alloys containing both Nb and Ta. No γ″ was observed to occur in V204A, which had no Ta additions. These precipitates were extremely fine and uniformly dispersed throughout the regions where γ and γ′ were observed, Figures 1 and 2. Selected area electron diffraction using a TEM was performed on the samples to identify the composition and the characteristic body centered tetragonal crystal structure of these γ″ precipitates. The occurrence of γ″ in these alloys is rather interesting as this metastable precipitate typically forms in Ni-Fe superalloys containing Nb, such as IN718. For these alloys, γ″ likely forms as a result of Nb and Ta supersaturation in the γ phase. Despite the substantial precipitation of δ (Ni_3Nb) and γ′ phases that consume the large majority of the Nb and Ta, excessively high concentrations of these elements may become supersaturated within the γ phase. During ageing, sufficient thermal energy is provided for the γ″ to precipitate out from the γ matrix. These observations are consistent with studies on a high strength, Ni-base superalloy containing both Nb and Ta, Rene 220[39], which also contains γ′ and γ″. At the moment, it is unclear as to whether the γ″ is beneficial or detrimental to the mechanical properties of these alloys and experiments are being designed to elucidate their role in modifying the properties of Ni-Al-Nb γ-γ′-δ alloys. Such investigations are currently in progress.

In summary, polycrystalline Ni-Al-Nb γ-γ′-δ alloys exhibit tremendous potential as candidate materials for high temperature structural applications. Preliminary measurements of the temperature dependent strength and creep properties for selected model alloys are comparable to existing commercial Ni-base superalloys and have the potential to greatly exceed their performance. To truly optimize the composition, microstructure and processing routes for these innovative alloy systems, a fundamental understanding of the mechanisms responsible for their characteristic deformation behavior needs to be developed.

Conclusions

Based on the results presented in this investigation, the following conclusions can be drawn:

1. Polycrystalline Ni-Al-Nb γ-γ′-δ alloys can be can be designed to exhibit 0.2% flow stresses that are substantially higher than U720 at temperatures between 25˚C and 800˚C.
2. The solubility of Ta appears to be limited in the Ni_3Nb δ phase within these alloys as Ta additions promoted the formation of γ′.
3. The mechanical properties of the γ-γ′-δ alloys are strongly dependent upon the composition and resulting proportion of constituent phases present in the microstructure. Grain boundary strengthening elements, such as B, C, Hf and Zr, were observed to minimize cavitation damage at grain boundaries and are required to maintain strength and creep resistance at elevated temperatures.
4. Large proportions of intermetallic phases (γ′ + δ) are desirable to maintain creep resistance at temperatures above 750˚C.
5. The elevated levels of Nb + Ta contributed to the supersaturation of the γ phase and resulted in precipitation of γ″ within the γ channels.
6. Development of these polycrystalline Ni-Al-Nb γ-γ′-δ alloys requires a number of trade-offs in terms of balancing the need for improved high temperature properties with those of alloy density, cost and manufacturing. Understanding the fundamental mechanisms controlling their characteristic behavior and linking the properties, chemistry, microstructure and processing is necessary for truly optimizing these alloys for high temperature structural applications.

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