THE ROLE OF NIOBIUM AND OTHER REFRACTORY ELEMENTS IN SUPERALLOYS

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Refractory elements are important alloying additions in both nickel-base and iron-nickel-base superalloys. They are responsible for the increased high temperature mechanical properties present in current superalloy systems.

This paper presents the results from ongoing research programs which study the effectiveness of niobium and tantalum in various nickel-base superalloys and iron-nickel-base superalloy INCONEL 718. This work not only shows the significance of niobium and tantalum as alloying additions in current superalloys, but also the necessity of these additions in the design of future superalloys demanding greater strength and temperature resistance.

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Introduction

It has long been established that nickel-base and iron-nickel-base superalloys are "super" because they are strengthened by a dispersion of fine and coherent gamma-prime (γ') and at times by gamma double-prime (γ'') precipitates within the gamma (γ) phase. These phases impart reasonably high tensile and creep strength at elevated temperatures while maintaining adequate ductility, fracture toughness, and fatigue properties. These precipitates are formed by the precipitation reaction of Ni with Al and Ti or, in the case of the iron-nickel-base superalloy (IN718), Nb and Ti (1,2).

The refractory elements, Nb and Ta, perform strengthening functions in both the γ and the precipitating γ' and γ'' phases. These elements can behave somewhat differently as carbide formers. They are also known to affect corrosion resistance and alloy stability. Both elements are bcc metals, and are highly misfitting in the fcc Ni lattice; consequently giving rise to their well deserved reputation as potent solid-solution strengthening elements in the γ as well as in the precipitating phases. Tantalum and niobium are known to partition into the strengthening γ' and γ'' phases, and are also MC- type carbide formers (3-5). Furthermore, to varying degrees these elements increase incipient melting and solidus temperatures. This results in not only a higher and broader temperature range for solutionization and homogenization, but also in segregation problems during the primary vacuum refining and melting process (VIM) and during such secondary structures refining melt processes as VAR and ESR. However, Ta is known to decrease the tendency for freckling during the directional solidification of turbine blades (6).

The detailed roles of refractory elements in superalloys are not well understood. In particular, the science-based technology for substituting one refractory element for another does not exist. For example, it is not known whether Ta and Nb are better strengtheners than other refractory elements, e.g., W and Mo. In addition, it is not known whether the large degree of misfit between the γ and precipitating phases, due to refractory element additions, affects such properties as strain strengthening and γ' and γ'' coarsening kinetics, which is an issue with respect to long term applications. In order to design and develop more enhanced superalloys, as well as to conserve on the more expensive and less abundant alloying elements, a better understanding on the role of these refractory elements on the mechanical and microstructural properties in superalloys is necessary.

This paper will present the ongoing research which addresses such questions. This paper will discuss not only the effects of refractory alloying elements in nickel-base superalloys, but also in the high niobium containing iron-nickel-base superalloy IN718, which represents roughly one-third of all superalloy sales, with emphasis on the development of a more microstructurally and thermally stable alloy. Not included in this paper is the situation with respect to the proprietary monocrystalline superalloys with high tantalum contents. However, the scientific opinions discussed below are generally applicable.

The role of refractory elements in nickel-base superalloys

Recent fluctuations in the supply of some strategic elements used in superalloys; i.e., elements in which the United States is import reliant, has resulted in the creation of government funded research programs aimed at studying the feasibility of replacing these strategic elements with more accessible refractory elements; e.g., molybdenum. The purpose of these programs is to study the characteristic and synergistic effects of alloying with various refractory elements on the mechanical, corrosive and microstructural properties in nickel-base superalloys with the intention of reducing the United States' dependence on these elements by substituting them with less strategic elements while maintaining or improving on the existing properties of these alloys.

One such program, which is sponsored by the United States Office of Naval Research, deals with understanding the roles of Ta, Nb, W, and Mo in superalloys in an effort to replace the import reliant elements, Ta, Nb, and W, with the "source-safe" refractory element, molybdenum, which the United States mines. In what follows is a brief review of our findings with an emphasis on the roles of Ta and Nb. A complete summary of our findings can be found in the articles published under this program (7,8).

When choosing an alloying system to study the role of refractory elements in nickel-base superalloys, one can either, (A) continue to investigate existing refractory metals containing superalloys in detail and compare them with each other, (B) study simpler ternary or quartenary systems, or (C) select representative alloys and systematically substitute the refractory elements with each other in each alloy. We had chosen as the research strategy approach (C), since (A) will not isolate the effects of individual elements and (B) will never yield the synergistic effects, which only studies of real systems can provide.

The two representative commercial nickel-base superalloys we had chosen to study were B1900 and IN738, see Table I. The B1900 alloys allow for a simple and direct comparative study between Mo and Ta on the mechanical and microstructural properties in this alloy system. The more complex IN738 alloy system which contains the four refractory elements, Ta, Nb, W and Mo, not only allows one to compare the effects of each refractory element on these properties, but also reveals any type of synergistic effect arising between the different refractory elements.

In what follows are some of the more pertinent results from the mechanical and microchemistry data. The effect of these substitutions on the alloys' incipient solidus, liquidus, gamma prime solvus and volume fraction is given in Table II. Table III presents γ/γ' partitioning behavior of each refractory element in the two alloy systems. This data was obtained from a STEM-EDS study of the microchemistry of the γ, γ' and carbide phases. Tables IV and V give the room temperature tensile and 760°C creep/stress rupture properties of these alloys.

Table I. Chemical Composition of the Alloys (Wt %)

Alloy	Ta	Nb	W	Mo	Al	Ti	Cr	Co	C	Ni
B1900	3.96	0.02	0.10	5.92	5.84	0.97	8.39	10.06	0.10	bal
Mo/Ta	0.01	0.03	0.06	8.20	5.90	1.00	8.10	10.30	0.10	bal
(Both alloys contain 0.015 pct B and 0.10 pct Zr)										
IN738	1.71	0.86	2.61	1.74	3.33	3.56	16.08	8.42	0.16	bal
Mo/W	1.70	1.00	0.10	3.10	3.40	3.30	16.20	8.70	0. 17	bal
Mo/Ta	0.10	0.94	2.53	2.65	3.51	3.43	16.20	8.50	0.18	bal
Mo/Nb	1.68	0.02	2.53	2.59	3.39	3.34	15.91	8.57	0.17	bal
(All four alloys contain ≤0.011 pct B and 0.10 pct Zr)										

Table II. Gamma Prime Fractions and Differential Thermal Analysis Results

Alloy	GP Fraction (At %)	GP Solvus (°C)	Incipient Solidus (°C)	Liquidus (°C)
B1900	62.1	1218	1280	1361
Mo/Ta	57.8	1158	1278	1372
IN738	44.8	1158	1242	1334
Mo/W	42.0	1144	1248	1333
Mo/Ta	41.7	1131	1228	1338
Mo/Nb	41.8	1143	1248	1341

The following observations were made from the results of this program:

1) The room temperature tensile tests indicate that Ta and Nb appear to be greater γ_{APB} strengtheners than Mo and W. In addition, it appears that Ta and Nb are similar γ_{APB} strengtheners. γ_{APB} is the antiphase boundary energy which controls the flow stress of superalloys up to about 760°C, at which temperature the strength decreases rapidly with increasing temperature (9).

2) Ta and Nb are greater γ' formers than Mo and W as evidenced by the changes in the γ' solvus temperature and volume fraction. As a result, it can be seen from the creep/stress rupture data that Ta and Nb are important alloying elements in producing a more creep resistant alloy.

Table III. Gamma Prime/Gamma Partitioning Ratios

Alloy	Ta	Nb	W	Mo
B1900	0.48	-	-	0.19
Mo/Ta	-	-	-	0.47
IN738	0.97	0.66	1.44	0.27
Mo/W	2.08	0.42	-	0.41
Mo/Ta	-	0.61	0.76	0.32
Mo/Nb	2.12	-	0.59	0.45

Table IV. Room Temperature Tensile Properties

Alloy	0.2 % Yield Strength (MPa)	UTS (MPa)	Elongation (%)	RA (%)
B1900	756	993	12.4	18.7
Mo/Ta	667	800	9.0	15.7
IN738	879	1061	7.7	10.6
Mo/W	894	1085	7.9	11.2
Mo/Ta	932	1031	3.3	11.5
Mo/Nb	847	1035	8.3	10.2

3) Ta and Nb have a greater affinity to occupy Al sites in the γ' phase than Mo. This tentative conclusion is based on the sharp decreases in the γ' solvus temperature when Mo replaces the other refractory elements. The yield strength values are also consistent with this conclusion.

Table V. 760°C Creep/Stress Rupture Properties

Alloy	Stress (MPa)	Minimum Creep Rate ($X 10^{-8}$)	Rupture Life (Hours)	Elongation (%)
B1900	641.2	6.0	120.0	7.0
Mo/Ta	641.2	26.7	40.5	11.4
IN738	600	8.8	100.8	6.6
Mo/W	600	44.3	42.0	14.9
Mo/Ta	600	11.2	70.0	7.6
Mo/Nb	600	11.1	72.0	6.4

4) Ta is a greater MC-type carbide former than Mo and Ti. When Ta was replaced in the B1900 alloy with Mo, a semi-continuous Mo_2C grain boundary carbide formed in the alloy. In addition, the concentration of Ti dramatically increased in the MC carbide phase when Ta was removed. This extra Ti was found to come from the strengthening γ' phase, which, in turn, caused a weakening of the alloy.

5) Ta and Nb were found to be more hot corrosion resistant than Mo in IN738 and B1900.

The role of refractory alloying elements in the iron-nickel base superalloy IN718

The presence of refractory elements in Inconel 718, as in nickel-base superalloys, increases the strength of the alloy's matrix and γ' phases (10,11). In addition, the presence of Nb promotes the precipitation of an additional strengthening phase known as γ''. Gamma double-prime is a metastable, ordered, and coherent body-centered tetragonal Ni_3Nb phase which precipitates either in the matrix or on γ' particles (12). It has been argued that most of the strength associated with this alloy results from the distortion of the matrix caused by this phase (13).

As mentioned, Inconel 718, one of the most widely used superalloys in the jet engine industry, accounts for approximately 35% of all wrought superalloy production. IN718's exceptional fabricable and weldable properties, as well as its adequate strength at temperatures up to 650°C, make this alloy a favorable material to use in the medium temperature regions of the jet turbine engine; e.g., the turbine disk and shaft. The alloy's high Nb content of approximately 5.3 wt.% also makes it a major consumer of Nb.

However, associated with these favorable attributes, IN718 possesses a problem which not only restricts its use to the medium and lower temperature regions of jet turbine engines, but also threatens its existence in many of the components in the next generation of high performance jet engines. The problem arises from overaging of the γ'' particles and the formation of a more stable, but needle-like, Ni_3Nb (δ) phase at the expense of the strengthening, but metastable, γ'' phase at elevated temperatures. It is believed that the high concentration of Nb in the alloy is responsible for the formation of this δ phase. Both reactions result in a degradation of the alloy's heat resistant mechanical properties (14,15). In addition, the rates of these reactions increase with higher temperatures. This results in an operating ceiling temperature of about 650°C , and a limited service lifetime for the IN718 component parts.

Recent advances in the jet engine industry are placing new demands for an alloy which exhibits the excellent fabricability and heat resistant properties of IN718, but which is not hampered by the alloy's relatively low temperature ceiling. Alternative nickel-base superalloys are currently being developed to satisfy these demands. This, in turn, would reduce the role of IN718 in these engines (16).

One of the problems with these new alloys, many of which are powder metallurgical systems, is their relatively high processing expense compared to IN718. Cleanliness associated with powder production and processing, as well as prior powder boundary problems are still of some concern with respect to P/M superalloy uses. Therefore, the development of a more stable IN718-type alloy is still under active pursuit by many laboratories..

In order for IN718 to continue satisfying the requirements imposed by the superalloy industry, its composition must be modified for increased strength and thermal stability at higher temperatures. Adding more niobium will increase the strength by producing more γ'', yet it will also result in a decrease in thermal stability and lower the temperature ceiling for δ.

Another argument entails adding more fcc elements (Ni, Co) into the alloy. This may stabilize the γ'' (and prevent δ formation), but may not boost the mechanical properties at any temperature.

The most promising modification points toward varying the alloy chemistry in such a way as to increase the amount of the more stable γ' phase. Preliminary experimental results (17) suggest that allowing the atomic percent of aluminum and titanium to equal that of niobium may result in a more thermally stable γ'', due to the greater fraction of γ'' particles coarsening on γ'. Increasing the amount of Al, and possibly Ti, should result in more γ' and especially more γ' surface area for the γ'' to nucleate and grow. By increasing the number of γ'' nucleation sites, more γ'' particles should form. In doing so, this would produce finer sized γ'' particles upon reaching equilibrium, which could result in a reduction in the driving force to form δ.

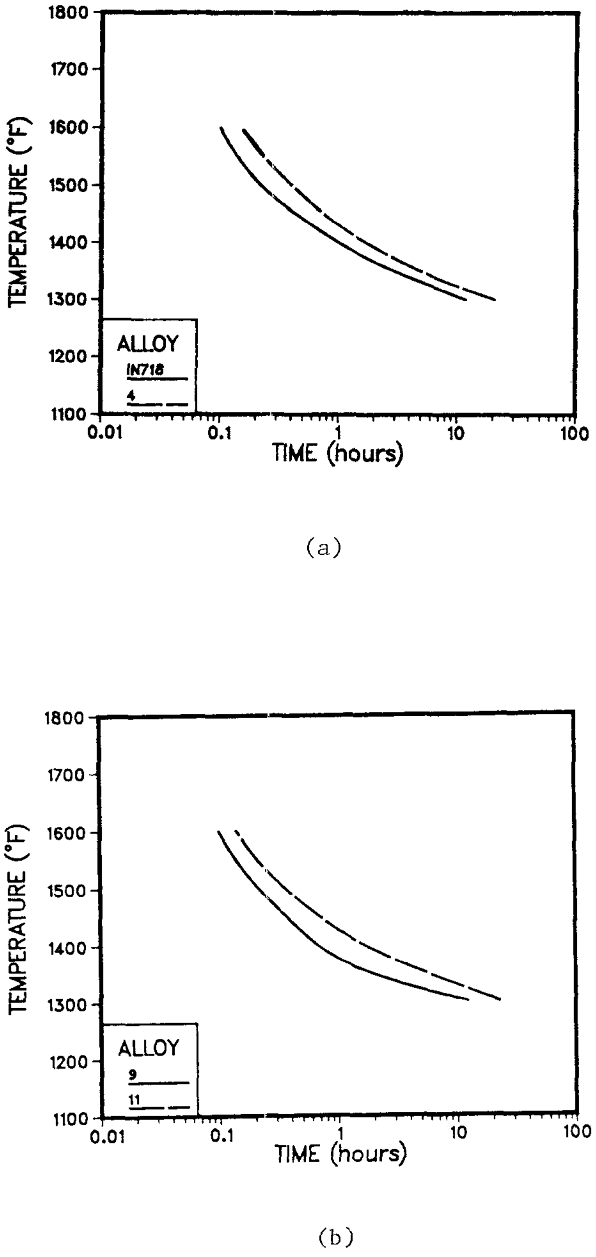
In our research program, which is funded by The Niobium Products Company (a subsidiary of Companhie Brasileira de Metallurgia e Mineracao [CBMM]), we chose to study the effects of modifying the alloy chemistry of IN718 following this latter approach. Three sets of alloys were produced, see Table VI. The first alloy series examines the effect of increasing the (Al+Ti)/Nb ratio by increasing the Al+Ti content, while maintaining the niobium level at 5.25 wt. %. The second alloy series compares the effects of Al and Ti on the stability of each phase by increasing the Al/Ti ratio from 0.86 to 1.67 while maintaining the (Al+Ti)/Nb ratio and Ti content. The third set, which was produced after an intensive investigation of the first two sets, follows the strategy of the second series by increasing the Al/Ti ratio to 1.78; however, this series also studies the effect of reducing the Ti content in the alloy.

Table VI. Chemical Composition of the IN718-type Alloys (Wt%)

								(Al+Ti)	Al
Alloy	Al	Ti	Nb	Ni	Fe	Mo	Cr	Nb	Ti
IN718-1	0.46	0.95	5.26	bal	18.25	3.05	18.00	0.65	0.86
4	0.63	1.34	5.28	bal	18.30	3.05	17.80	0.90	0.83
9	0.53	0.96	4.32	bal	18.30	3.02	18.15	0.85	0.98
10	0.68	0.97	4.91	bal	18.30	3.03	18.10	0.86	1.24
11	0.87	0.96	5.42	bal	18.00	3.02	17.80	0.90	1.61
12	0.94	0.96	5.72	bal	17.83	3.05	17.53	0.89	1.74
13	0.87	0.90	5.38	bal	18.05	3.04	17.80	0.88	1.72
14	0.86	0.86	5.66	bal	17.95	3.06	17.70	0.82	1.78

* Also contains approximately: 0.032 C, 0.02 Mn, 0.11 Si, 0.02 Ta, 0.003 B,
0.002 S, 0.006 P, 0.006 Cu, 8 ppm Mg, 20 ppm Sn

In what follows is an abbreviated summary of our results. More extensive results and discussion are published elsewhere (18,19). Figure 1 shows the effect of these modifications on the transformation time for the δ phase. It can be seen that increasing the (Al+Ti)/Nb and Al/Ti ratios in the alloy resulted in an increased time to form the embrittling δ phase. Table VII gives the lattice parameters of the γ' and γ" phases, while Tables VIII and IX show their sizes and volume fractions following a 100 hour heat treatment at 760°C. The effect of increasing these ratios also resulted in a greater misfit between the matrix and γ" phase, which, in turn resulted in the smaller γ" particles. On the other hand, the decrease in misfit between the matrix and γ' phase resulted in an increase in ~~the~~ the size of the more stable γ' particles. Table IX shows that increasing these ratios also produced more of the stable γ' compared to the metastable γ" counterpart.



(a)

(b)

Figure 1. Time-Temperature-Transformation curves for alloys (a) 1 and 4 and (b) 9 and 11.

Table VII. X-Ray Lattice Parameters of the matrix, γ', and γ'' phases (following 760°C - 600 hr heat treatment)

Alloy	γ a-axis (Å)	γ' a-axis (Å)	γ'' a-axis (Å)	γ'' c-axis (Å)
IN718-1	3.6008	3.606	3.626	7.416
4	3.5986	3.607	3.625	7.416
9	3.5956	3.606	3.625	7.410
10	3.5964	3.607	3.626	7.417
11	3.5991	3.607	3.626	7.423
12	3.6007	3.608	3.627	7.429
13	-	3.606	3.625	7.422
14	-	3.607	3.629	7.418

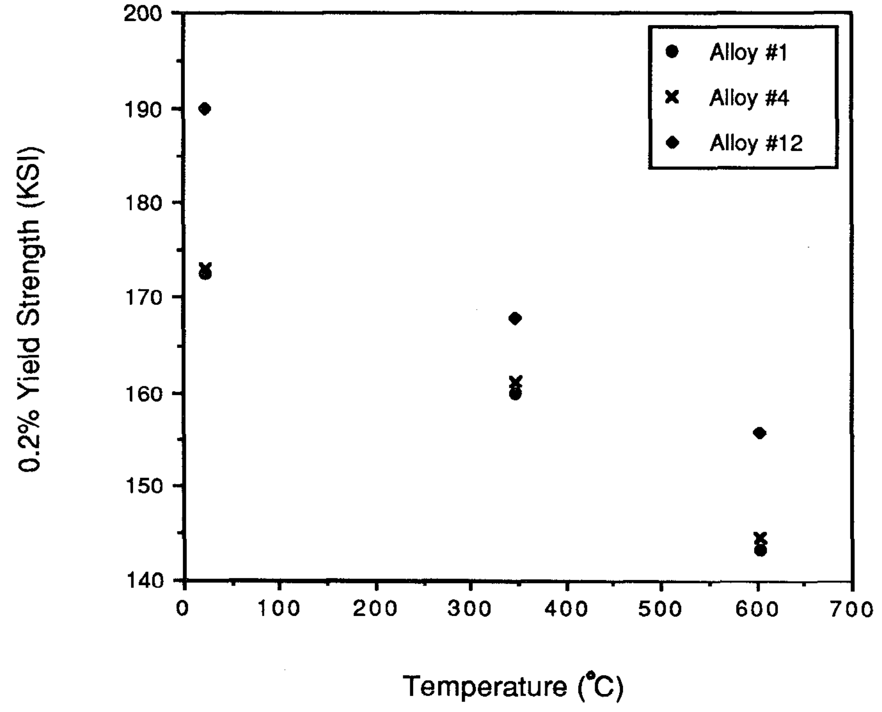


Figure 2. Room temperature and elevated temperature 0.2% yield strengths of alloys 1, 4, and 12.

Figure 2 shows the effect of these modification on the room temperature and elevated temperature tensile properties. The results from the abbreviated thermal stability test are given in Table X. In this test samples were creep/stress rupture tested a) in their initially heat treated condition and b) following an aging treatment at 732°C for 1000 hours, which was designed to overage the γ'' and force the formation of δ phase. Not only did these modifications produce a stronger alloy at ambient and elevated temperatures, but also resulted in a more thermally and microstructurally stable alloy, see Figure 3.

Table VIII. Average γ' and γ'' Precipitate Sizes After 100 Hour Heat Treatment at 760°C

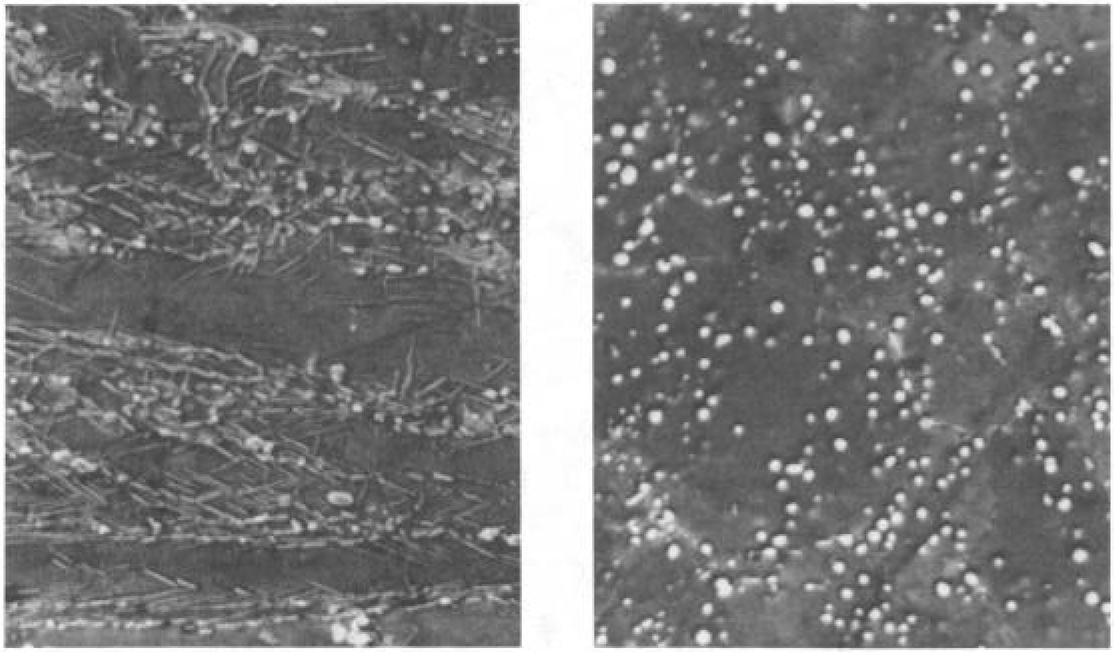
Alloy	γ' Diameter (mm)	γ'' Length (mm)	γ'' Thickness (mm)
IN718-1	0.045	0.090	0.016
4	0.048	0.064	0.011
9	0.032	0.084	0.011
10	0.044	0.065	0.008
11	0.051	0.052	0.006
12	0.052	0.048	0.006
13	0.048	0.050	-
14	-	0.048	-

Table IX. γ' and γ'' Volume Fractions After 100 Hour Heat Treatment at 760°C

Alloy	γ' (%)	γ'' (%)
IN718-1	3.5	10.1
4	5.3	6.5
9	-	-
10	4.9	3.8
11	8.1	3.0
12	9.1	2.6

Table X. 705°C Creep/Stress Rupture Results

	(70 KSI)			
	[Initial Heat Treatment]		[+ 732C - 1000 Hour Exposure]	
Alloy	Rupture Life (Hours)	ε (%)	Rupture Life (Hours)	ε (%)
IN718-1	210.9	13.3	3.0	21.8
4	187.6	16.7	20.6	21.6
11	185.8	17.2	18.2	36.6



(a) (b)

Figure 3. Scanning electron micrographs of alloys (a) 1, and (b) 11 after 1000 hour exposure at 732°C.

These preliminary results indicate that increasing the Al/Ti and/or the Al+Ti content above that of the original IN718 results in a more thermally and mechanically stable alloy. This could be due to the higher volume fraction of γ, the smaller and more misfitting γ" particles, and/or the reduced amount of δ in the alloy. These results also indicate that more of the high temperature heat resistant Nb can be added into the alloy without any corresponding loss in stability.

The second phase of this alloy design program, which is currently under way, will more extensively study the properties of a larger, commercial-sized ingot of the most stable alloy, alloy 12. The results of this program, to date, indicate a promising future for IN718 in the jet turbine engines.

Concluding remarks

Refractory elements, in particular Nb and Ta, are important alloying additions in nickel-base and iron-nickel-base superalloys. They are responsible for much of the strength associated with these heat resistant alloys. The work performed at Columbia University's Center for Strategic Materials shows the significance of Nb and Ta as alloying additions in current superalloys. In addition, these elements have been proven to be necessary additions in the design of future superalloys demanding greater strength and temperature resistance.

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