Existence of Laves Phase in Nb-Hardened Superalloys

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ABSTRACT

The possibility of forming the topologically close-packed Laves phase has been investigated in various Ni-base superalloy systems that contain a significant amount of Nb. Simplified alloy compositions consisting of various combinations of major alloying elements, including Cr, Fe, and Co, were prepared; a high level of Nb was added in each alloys to simulate the dendritic segregation in the real casting process. In addition to the fcc dendrites, the as-cast microstructure through a slow solidification rate developed the regions of eutectic decomposition at the end of solidification. The eutectic regions consisted of only two phases in every alloy studied. The intermetallic phases that formed the eutectic with the fcc Ni matrix were identified by SEM-EDAX, X-ray diffraction, and DTA analysis. The results suggested that Laves phase was not expected to exist in Ni-Cr-Co base alloys, and that other Nb-hardened superalloys, especially those Ni-Cr-Fe base alloys, would likely develop Laves phase in the Nb-segregated regions during casting. Alloy chemistry theory was proposed to discuss the alloying effect on the existence of Laves phase in Ni base alloy systems. The combination of Cr and Fe alloying additions would be the essential criteria to allow Laves phase appeared in a slow solidification process. The DTA analysis indicated that the alloy with the Laves phase had a low eutectic melting point. These important results can provide a comprehensive understanding of what observed in those Nb-strengthened superalloys with complex chemical compositions.

Superalloys 718, 625, 706 and Various Derivatives
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INTRODUCTION

The addition of Nb in superalloys led to a series of important alloys being developed, and many of these alloys found some unique and important industrial applications as popular commercial materials [1]. Originally, Nb in Ni-base superalloys was considered as one of the effective solid solution strengthener, e.g. the 625 alloy. In an fcc Ni matrix (γ), Nb has a reasonably high solubility, 12 at.%, and the difference of atomic size between Nb and Ni can raise a remarkable mismatch in the γ lattice. The essential factor to be controlled in designing this type of supperalloys is how to maintain the maximum Nb content in the solid solution without forming any intermetallic phase.

The discovery of metastable γ'' - Ni_3Nb precipitates in the 718 alloy created a new branch of superalloys [2]. The coherency strains associated with the formation of γ'' particles in the γ matrix have a substantial strengthening effect. On the other hand, the sluggish aging kinetics of γ'' precipitation allow such a high strength material to be weldable. Many structural castings for gas turbine applications, especially complicate structures and large parts, have shown recently the urgent demand for strong casting superalloys with good weldability [3,4].

In both solid solution strengthened and precipitation hardened superalloys, Nb tends to segregate in the interdendritic area during solidification process. As a result, some undesirable phases may form in the casting products. In most commercial Nb-bearing superalloys, such as 718, 625, and 909 alloys, the solidification process always ends with the formation of a Nb-rich intermetallic Laves phase [5]. The γ/Laves eutectics in the cast Nb-hardened superalloys have been well documented in literature, and their detrimental effects on alloy weldability and mechanical properties have been well known.

To design a superalloy free from Laves phase is a significant challenge to metallurgists. The superalloys contain a variety of alloying elements at different concentrations, no consistent thermodynamic data or phase diagram is applicable. Through empirical approach, several new alloys strengthened by Nb show the indication of the absence of Laves phase. Among them, Rene'220C received many attentions because of its superior properties over 718 alloy [6]. In addition to offering a 50° C strength advantage, Rene'220C has excellent castability and weldability. Recent structural analysis suggested that the alloy was immune to Laves phase formation [7]. Snyder et al. also developed a "Laves Free" superalloy by modifying the alloying element contents of the 718 composition [8]. The tailored alloy is claimed to have properties comparable to 718 alloy. Further modification was made by increasing hardening element levels to improve alloy strength. However, the "High Strength" alloy, designated as PWA1472, was found to contain some trace amount of Laves phase in the as-cast condition [9].

This study tends to identify the basic control of alloying with respect to the formation of Laves phase. The interdendritic segregation of Nb is known to dominate the solidification behavior. The equilibrium phases that make the final eutectic with γ can be readily determined if the alloys contain an excessive amount of Nb and the ingots are prepared through a reasonably slow casting rate. Different γ matrix compositions that simulate various Nb-strengthened superalloys are designed for investigation.

EXPERIMENTALS

Table 1 lists commercial superalloys that contain a certain amount of Nb as the strengthening element. Generally, the major alloying additions include Cr, Fe, Co, and their combinations. To

Table 1 Nb-strenghtened superalloys

Designation	Composition, wt.%	Nb Effects
625 alloy	Ni-21.5Cr-2.5Fe-9Mo-3.6Nb-.2Ti-.2Al-.06C	solid solution
706 alloy	Ni-16Cr-40Fe-2.9Nb-1.75Ti-.25Al-.03C	γ'' precipitates
718 alloy	Ni-19Cr-18.5Fe-3Mo-5.1Nb-.9Ti-.5Al-.04C	γ'' precipitates
725 alloy	Ni-21Cr-9Fe-8Mo-3.5Nb-1.5Ti-.25Al-.01C	γ'' precipitates
909 alloy	Ni-13Co-42Fe-4.7Nb-1.5Ti-.35Si-.01C	γ'' precipitates
Rene'220C	Ni-19Cr-12Co-3Mo-5Nb-3Ta-1Ti-.5Al-.03C	γ'' precipitates
PWA 1472	Ni-12Cr-18Fe-3Mo-6Nb-2Ti-.6Al-.04C	γ'' precipitates

Table 2 Alloy compositions (wt.%)

Alloy	Ni	Cr	Fe	Co	Nb
MRL-1	Bal.	20.0	--	--	15.0
MRL-2	Bal.	20.0	18.0	--	15.0
MRL-3	Bal.	20.0	--	12.0	15.0
MRL-4	Bal.	--	18.0	12.0	15.0
MRL-5	Bal.	20.0	--	24.0	15.0
MRL-6	Bal.	20.0	10.0	--	15.0
MRL-7	Bal.	12.0	18.0	--	15.0

Table 3 Effects of major alloying on eutectic secondary phases in Ni-Nb systems

Alloy	Major Alloying	Secoundary Phase	Eutectic Amount
MRL-1	high Cr	δ - Ni_3Nb	Moderate
MRL-2	high Cr, high Fe	Laves	Rich
MRL-3	high Cr, low Co	δ - Ni_3Nb	Moderate
MRL-4	high Fe, low Co	δ - Ni_3Nb	Little
MRL-5	high Cr, high Co	δ - Ni_3Nb	Moderate
MRL-6	high Cr, low Fe	Laves	Moderate
MRL-7	low Cr, high Fe	δ - Ni_3Nb	Moderate

approach the issue quantitatively, each alloying element was selected at two levels: Cr, 12 and 20 wt.%; Fe, 10 and 18 wt.%; Co, 12 and 24 wt.%. A fixed Nb concentration of 15 wt.% was the only hardening element added. In total there were 7 compositions selected, and their nominal chemistries are given in **Table 2**.

Raw materials of high purity laboratory grades were employed to prepare the heat of each alloy by vacuum induction melting (VIM). Conditioned ingots were charge into a directional solidification (DS) furnace that had the thermal control to produce single crystal superalloys. A slow draw speed of 15 cm/hr was used, and all crystals produced had large elongated grain structure. Such a structure could be considered as the near equilibrium state during the solidification process. Minimum grain boundaries in the as-cast structure could simplify the analysis of phase relationship.

DS crystals were cut in both transverse (T) and longitudinal (L) cross sections for microstructural characterization and phase identification. Polished samples were examined under a Cambridge scanning electron microscope equipped with secondary electron (SE) and X-ray energy dispersion detectors. Eutectic decomposition in each alloy generated constituent phases that had a significant difference on Nb concentration. The contrast between eutectic phases in SE images was apparent because of the heavy atomic weight of Nb. The intermetallic phases such as Laves or Ni_3Nb phases were much brighter than the Ni-rich γ phase. Energy dispersion analysis of X-ray (EDAX) was carried out in coupling with the SE images to further differentiate the type of intermetallics. Quantitative chemical analysis performed by employing a microprocessor aimed at the participation of major alloying elements, Cr, Fe, and Co.

The crystal structure of phases existing in every alloy was verified by the X-ray diffraction method. The radiation employed was Cu K_α (=1.54060), and the diffraction angle 2θ for the observed peaks in each spectrum were examined and indexed numerically and graphically. To avoid the ambiguity caused by the texture of crystal growth, X-ray diffraction was done on both transverse (T) and longitudinal (L) cross sections.

Phase transition temperatures, specifically the liquidus and the eutectic temperatures, were investigated by differential thermal analysis (DTA). The DTA cell was calibrated for temperature with pure Al and Si, and the experimental accuracy was within 2°C. The heating and cooling rate was set at 10 °C/min. Duplicate tests were done on some alloys to check the variation of samples associated with the macrosegregation.

RESULTS

SEM and EDAX

The as-cast structures examined by the secondary electron (SE) image under a scanning electron microscope are shown in **Figure 1**. A controlled slow cooling of directional solidification generates a crystal growth structure that is convenient for phase analysis. The preferred orientation for crystal growth in all alloys studied is <100>, similar to that in other superalloys. The dendrite morphology with 90° intercepting dendrite arms appears clearly on the cross section of alloy crystals at low magnifications. As expected, the secondary phase with a high Nb content forms in every alloy, and their morphology is ready for observation with a bright atomic weight contract by SE imaging.

Figure 1 As-cast structures of Ni-Nb alloy systems

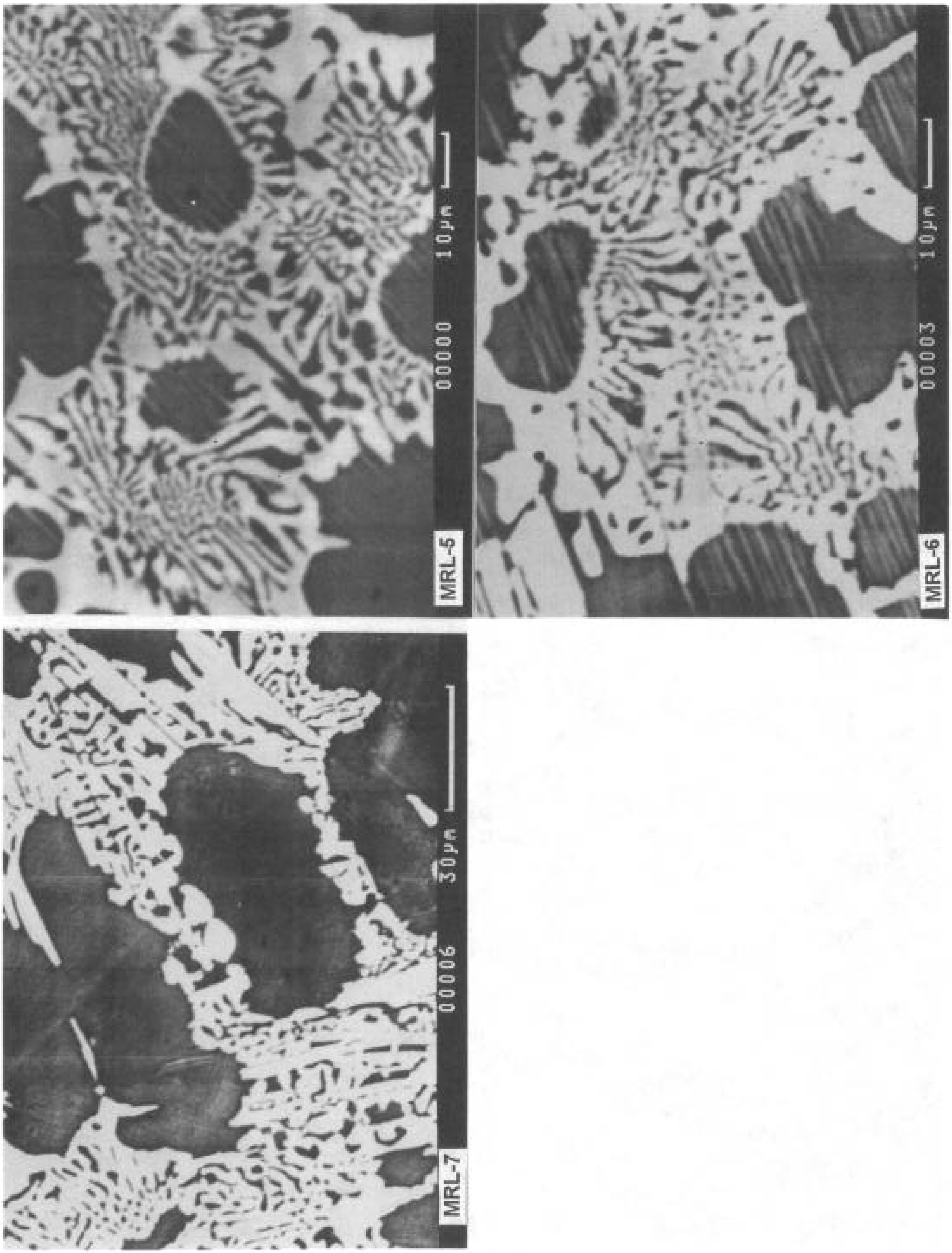


Figure 1 (conti.)

Figure 1 shows that the eutectic decomposition takes place in the interdendritic regions at the end of solidification. All alloys in this study contain 15 wt.% Nb that is definitely above the solubility of Nb in the γ matrix, but the eutectic reaction in each alloy and the correspondent composition of each phase are unknown. A qualitatively volume fraction of eutectic regions in every alloy is described in **Table 3**. Except alloy MRL-4 with a eutectic area less than 10%, the rest alloys exhibit a substantial volume fraction of decomposed eutectic. The major eutectic constituent in alloys MRL-1 and MRL-2 is the γ phase, which forms a continuous network around the isolated Nb-rich phase in bright contrast. The rest alloys, including MRL-3, MRL-5, MRL-6, and MRL-7, have connected bright phases, and the fcc γ phase becomes the secondary phase in the eutectic.

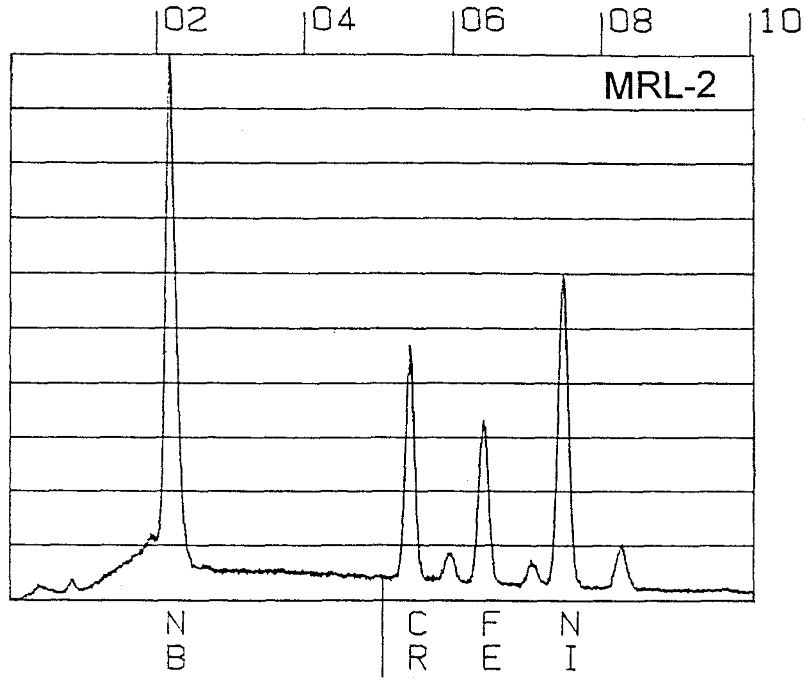
To identify Nb-rich secondary phase that forms eutectic constituents with the fcc γ matrix was performed by employing the energy dispersion analysis of X-ray (EDAX). Two types of EDAX spectrums were observed for those secondary phases, and both revealed a high Nb peak at about 20 - 30 at.% as seen in **Figure 2**. The major difference was Cr (and/or Fe) concentration that was balanced by Ni. In the case that Cr is lean, the secondary phase is apparently the binary Ni_3Nb (δ). The Cr solubility in the δ phase never exceeds 5 at.%, and so is Fe. The other type of Nb-rich secondary phase was a ternary intermetallic compound consisting of at least 3 different elements. The Cr content in this phase is above 10 at.%. The crystal structure of the high Cr secondary phase was identified as Laves phase by X-ray diffraction, as reported in details later. **Figure 2** compares the EDAX spectrums for alloy MRL-2 and MRL-7. A reduction of Cr from 20 wt.% (MRL-2) to 12 wt.% (MRL-7) in a high Fe (18 wt.%) alloy changed the secondary phase of eutectic.

The SEM/EDAX results on the secondary phase of all alloys studied are summarized in **Table 3**. Five of seven alloys have the binary δ phase in their eutectic constituents, while the other two, MRL-2 and MRL-6 are Laves phase. Alloy MRL-1 demonstrated that only Cr by itself did not cause Laves phase in the Ni-Nb alloy system. A combination of high-content Cr and Fe is necessary for Laves phase formation, and Cr has more pronounced effect than Fe as referred to MRL-6 and MRL-7. The Co addition within 24 wt.% simply substitutes Ni and does not affect the secondary phase (δ-Ni_3Nb).

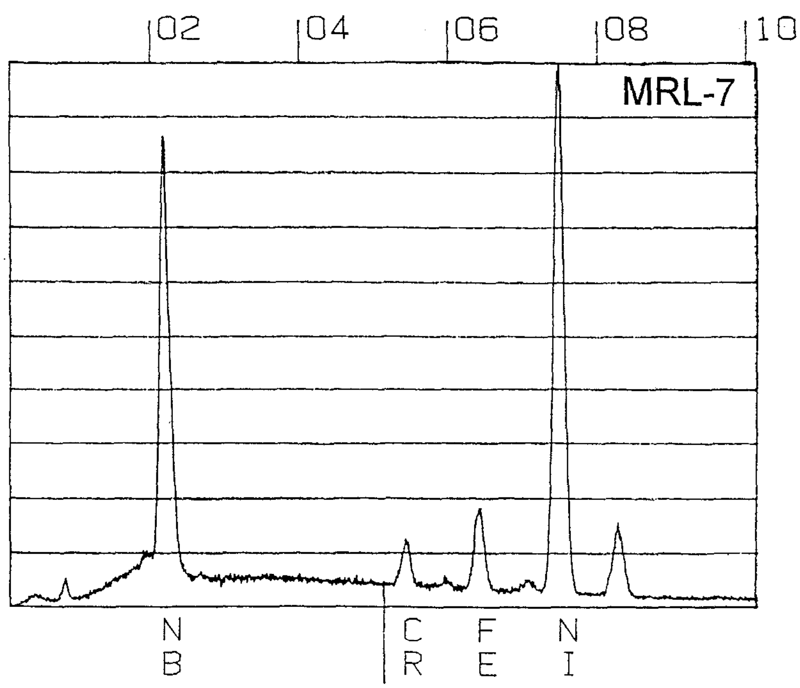
<u>X-ray Diffraction and DTA</u>

Identifying the crystal structure of phases through X-ray diffraction offered additional evidences that the solidification process in 7 alloys studied was terminated by two-phase eutectic decomposition. **Table 4** summarizes the observed peaks in the diffraction spectrums for all runs and the lattice plane indices of their corresponding phases. Only two intermetallic phases were identified, i.e., the hexagonal (C14 type) Laves phase and the othorambic ($D0_a$ type) δ-Ni_3Nb phase. In addition to the fcc γ matrix phase, there was a single intermetallic phase detected in each alloy. Alloy MRL-2 that represented alloy 718 and alloy MRL-6 that contained a low level Fe formed Laves phase. The δ-Ni_3Nb phase was found in the rest alloys. No attempt was done in this work to determine the accurate lattice parameters of individual phases. The texture of crystal growth as reflected by the relative intensity of different peaks for a phase agreed with SEM morphology observation.

Differential thermal analysis has been extensively used to investigated the solidification behavior of Nb-bearing superalloys [10,11]. Unlike most previous studies in which there was only a little fraction of secondary phases existed, every alloy in this investigation contained a substantial amount of intermetallic phases. As a result, the DTA thermogram on cooling showed two



(a) Laves phase



(b) δ-Ni_3Nb

Figure 2 EDAX spectrums of eutectic secondary phase

Table 4 Eutectic Phases identified by X-ray diffraction

			ALLOYS												
Phase	Indices	**2θ**	1 T	1 L	2 T	2 L	3 T	3 L	4 T	4 L	5 T	5 L	6 T	6 L	7 T
δ	200	34.9	√				√		√	√					√
Laves	*110*	*37.4*			√								√	√	
δ	002	39.8		√				√							√
δ	201	40.4	√	√			√	√	√	√	√	√			√
Laves	*103*	*40.7*			√	√							√	√	
δ	020	42.5		√					√	√					√
γ	**111**	**43.6**	√	√	√	√	√	√	√	√	√		√	√	√
Laves	*112*	*44.1*			√	√							√	√	
Laves	*201*	*44.9*			√	√							√	√	
δ	012	45.3	√	√				√		√		√			√
δ	211	46.0	√	√			√		√	√					√
Laves	*004*	*46.3*			√								√	√	
γ	**200**	**50.8**	√	√	√	√	√	√	√	√	√	√	√	√	√
δ	022	59.6		√						√	√	√			√
δ	221	60.2		√					√						
Laves	*213*	*69.5*											√		
Laves	*302*	*71.9*											√		
δ	203	72.5						√		√		√			√
δ	400	73.9	√				√		√						
γ	**220**	**74.7**	√	√	√	√	√	√	√	√	√		√		√
δ	231	80.0		√				√	√	√		√			√

2θ is the diffraction angles for the Cu K_{α} (=1.54060) radiation.
T: transverse section; L: longitudinal section.

Table 5 Effects of major alloying on eutectic secondary phases in Ni-Nb systems

Alloy	**Eutectic Constituents**	**Liquidus Temperature**	**Eutectic Temperature**
MRL-1	γ/δ	1308°C	1256°C
		1299°C	1240°C
MRL-2	γ/Laves	1292°C	1193°C
MRL-3	γ/δ	1301°C	1227°C
MRL-4	γ/δ	NA	1226°C

NA: data are not available.

distinct exothermic peaks, which corresponded to the liquidus and the eutectic temperatures. The data are listed in **Table 5**. While all alloys exhibit similar liquidus temperatures, the eutectic temperature of those alloys that form Laves phase (MRL-2) is low in comparison to that of other alloys. This observation definitely provides the fundamental explanation for the low incipient melting of Laves phase in the complicate compositions of commercial superalloys.

DISCUSSION

Phase Diagram

Laves phase does not appear in the binary Ni-Nb phase diagram but exists in Co-Nb, Cr-Nb, and Fe-Nb binary systems [12]. It is difficult to figure out the occurrence of an intermetallic phase in the Ni-X-Nb system based on the binary phase diagrams. As suggested by Sim, a polar phase diagram of Nb versus first long-period elements provides a consistent picture of various phase regions across the periodic table [13]. The individual alloying effect on a specific alloy system requires empirical data to set up ternary phase diagrams.

In the Ni-Cr-Nb ternary phase diagram [14], the Ni-rich γ phase forms tie-lines with α-Cr and δ-Ni_3Nb but not Lave phase Cr_2Nb. The two-phase region of α-Cr + δ-Ni_3Nb divides the ternary triangle into two parts, and γ and Laves phases stay in different parts. It is impossible to have the γ/Laves eutectic in the Ni-Cr-Nb ternary system, in spite of a high solubility of Ni in Laves phase. The results from alloy MRL-1 in which the δ-Ni_3Nb was detected re-verify the absence of Laves phase eutectic.

Quaternary Ni-Cr-Fe-Nb system was the key issue for the formation of Laves phase in Ni-base superalloys. Alloys MRL-2, MRL-6, and MRL-7 made the possible combinations of Cr and Fe alloying at high and low levels. A high level of Cr and a certain amount of Fe is the necessary condition for Laves phase (MRL-2 & MRL-6). If Cr addition is reduced to 12 wt.%, then Laves phase can be avoid. A similar empirical observation has been reported in alloy 718 [8].

Based on the polar phase diagram of Nb, Laves phase is expected at 24 wt.% Co but not at 12 wt.% Co in the ternary Ni-Co-Nb system. A high level of Cr in alloys MRL-3 and MRL-5 definitely promotes Laves phase. However, the eutectic in both alloys only consists of δ-Ni_3Nb. The Co solubility in the HCP δ phase is known to be very high and may substitute for more than 60% Ni. The Ni-rich γ and Nb-rich δ phases are **separated** by the δ phase whose Ni/Nb ratio (~3) is higher than that of Laves phase (~2).

Alloy MRL-4, a Ni-Fe-Co-Nb quaternary system, develops the least fraction of γ/δ eutectic. Isolated δ particles in the as-cast structure suggested a high solubility of Nb in the Cr-free Ni-base matrix. Laves phase is unlikely to form unless the alloy becomes a Fe-base system (e.g., alloy 909).

Alloy Design

The formation of TCP phases has been a critical topic for designing a useful superalloys. Because of chemistry complex, the base thermodynamic information, such as binary or ternary phase diagram, can only provide a simple reference as the starting point. Empirical trial is the most effective method to develop a new alloy for specific purposes. Nevertheless, some of empirical rules can be summarized and rationalized in conjunction with alloy chemistry theory.

The main reason why alloy 718 contains a high level (~18 wt.%) of Fe is to achieve a high strength at low and intermediate temperatures up to 650°C [2]. The strength enhancement is directly related with the precipitate coherency determined by the lattice mismatch between γ/γ'' phases. A low Fe version of alloy 718 was reported to have better stress rupture strength, but the improvement of temperature capability was limited. Complete Fe-free 718 might get rid of Lave phase; how ever its strength becomes too low to be practically useful.

One of effective approaches to eliminate Laves phase is the reduction of Cr alloying (12 wt.%). The Cr addition in superalloys provides high temperature oxidation and corrosion resistance as well as the solubility control of precipitation elements. More additions of precipitation elements can compensate the strength loss caused by Cr reduction as done in PWA 1472 [9].

A novel approach taken in Rene'220C replaced Fe by an optimum level of Co. The data of this study strongly support that Lave phase would not appear in this type of alloys. Another important consequence of Co alloying that has little relation with Laves phase is the significant improvement of stress rupture life at temperatures above 650°C.

CONCLUSIONS

The terminal solidification constituent of a series of Ni-base alloys containing various combinations of major alloying elements and excessive Nb has been investigated. The additions in two levels of major alloying, including Cr, Fe, and Co, resulted in two types of eutectic decomposition to finish alloy solidification process. A high level of Cr (20 wt.%) together with a certain amount of Fe (10 wt.% or above) will cause the formation of Laves phase. Otherwise the binary γ/δ eutectic will appear at a high Nb concentration. The substitution of Co for Ni (up to 24 wt.%) has little effect on the phase formation.

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