

MULTIPHASE STRENGTHENED NICKEL BASE SUPERALLOYS

CONTAINING REFRACTORY CARBIDE DISPERSIONS

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Abstract

The feasibility of improving the mechanical properties of nickel base superalloys using multiphase particle strengthening and engineered grain structures was investigated. Five new nickel base superalloys containing dispersions of suitable combinations of  $\gamma'$ , HfC, and  $Y_2O_3$  were designed, manufactured, and evaluated. In general, the  $\gamma'$ , HfC, and  $Y_2O_3$  particle dispersions were selected to provide optimum stress rupture strength levels at low (<1073K or 800C), intermediate (1073-1223K or 800-950C), and high service temperatures (>1223K or 950C).

The best mechanical properties were obtained for Alloy 5, which was produced by incorporating fine HfC and  $Y_2O_3$  particles into the commercial  $\gamma$ - $\gamma'$  alloy MERL76 using the Rapid Solidification+Mechanical Dispersing technique. After consolidation, zone annealing heat treatments were successfully applied to the alloy to produce large columnar grains by secondary recrystallization for higher temperature stress rupture strength. The engineered grain structures that resulted had an average transverse grain size of approximately 0.7 mm and a grain aspect ratio of greater than ten. The projected 1089K (815C) 1000 hour rupture strength of this alloy was 393 MPa (57 ksi), which is a 14% increase over the 345 MPa value for MA6000. Since MA6000 and Alloy 5 contained similar  $\gamma'$  and oxide particle dispersions, the improved intermediate temperature stress rupture strength of Alloy 5 was thought to have resulted from the dispersion of fine HfC particles.

## Introduction

For nearly four decades, high temperature materials engineers have relied on the relatively simple, age-hardening gamma-gamma prime ( $\gamma$ - $\gamma'$ ) nickel base superalloy system for most commercial elevated temperature service applications. In recent years, however, conventional  $\gamma'$  superalloys have undergone increasing scrutiny when considered for use in ever more demanding service conditions. To be sure, the  $\gamma'$  phase rapidly loses coherency, coarsens, and eventually undergoes partial solutioning at the highest service temperatures. In spite of the advances obtained through controlled solidification techniques and other processing improvements such as those that have produced directionally solidified and monocrystalline grain structures, it is clear that both the coarsening and dissolution of  $\gamma'$  precipitates continue to impose an upper limit on the service temperature, stress, and exposure life of high temperature components.

By contrast, the recently developed oxide dispersed nickel base superalloys have shown considerable promise as an alternative to conventional  $\gamma$ - $\gamma'$  compositions for applications at the highest temperatures. In fact, alloys such as MA6000 (1) and IN-100+Y<sub>2</sub>O<sub>3</sub> (2,3) that contain dispersions of both  $\gamma'$  and yttrium oxide particles have demonstrated the highest temperature capability of all reported superalloy compositions. The widespread adoption of these alloys as turbine blade materials has been restricted, however, primarily as the result of inadequate intermediate temperature stress rupture strength, which is required at and near the root of turbine airfoils.

In order to meet the challenge of more demanding requirements for elevated temperature applications, it is evident that both new materials and new processing techniques must simultaneously be explored to develop advanced compositions with engineered microstructures to achieve optimal property improvements. Thus, the purpose of this study was to design, fabricate, and evaluate several new, high performance nickel base superalloys based on both multiphase particle strengthening and engineered grain structures for elevated temperature service applications.

New alloys with selected combinations of  $\gamma'$ , hafnium carbide (HfC), and yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) particle dispersions were chosen in an effort to provide optimum stress rupture strength levels at low (<1073K or 800C), intermediate (1073-1223K or 800-950C), and high (>1223K or 950C) service temperatures, respectively. Hafnium carbide was chosen based on the phase stability and the refractory nature of the monocarbide, as evidenced by thermodynamic as well as kinetic considerations, such as those indicated in Table I and Figures 1 and 2. In addition, a HfC dispersion offers the potential for coherency strengthening effects as well as an unusual degree of processing flexibility compared to most other refractory dispersoids.

Table I: Standard Gibbs Free Energy of Formation of Ni<sub>3</sub>Al, HfC, and Y<sub>2</sub>O<sub>3</sub> at 1300°K (1027°C).

Phase	$\Delta G_f^\circ$ at 1300°K (kJ/mole)
Ni <sub>3</sub> Al	-133
HfC	-221
Y <sub>2</sub> O <sub>3</sub>	-1,531

References: (6,7)

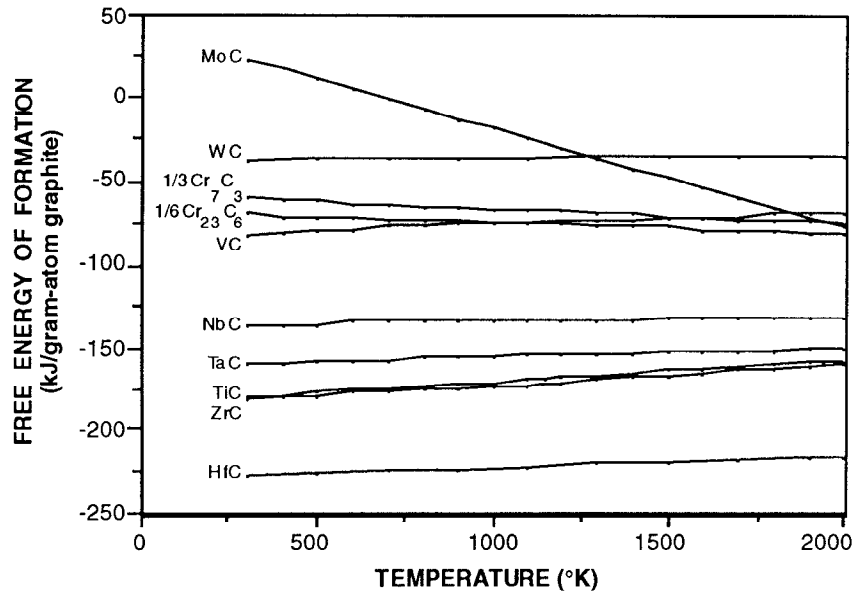


Figure 1: Standard Gibbs Free Energy of Formation as a function of temperature for several carbides. References: (6, 7, 11, 12).

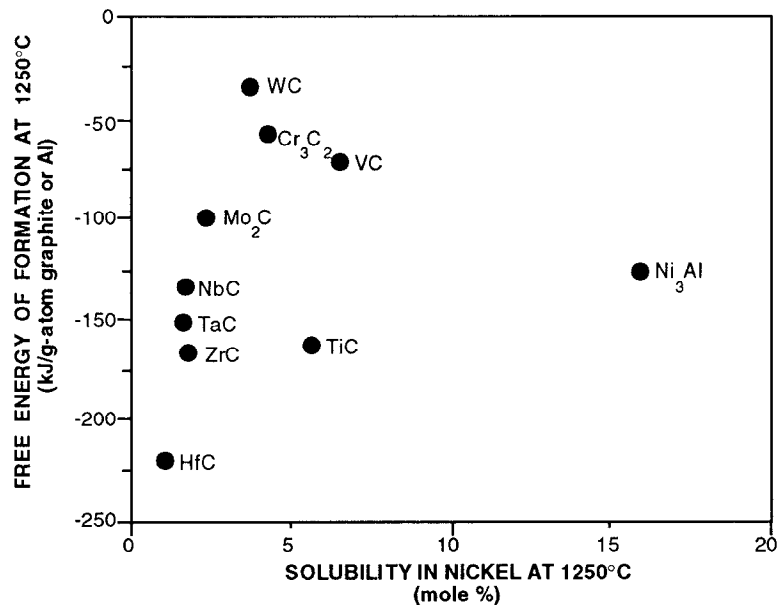


Figure 2: Standard Gibbs Free Energy of Formation as a function of solubility in Ni at 1523°K (1250°C) for selected phases. References: (6, 7, 9, 10, 11, 12, 13, 14)

## Experimental

Five new alloy compositions were selected to investigate the potential mechanical property improvements obtained when multiphase dispersions of fine  $\gamma'$ , carbide, and oxide particles are combined in typical, fully alloyed nickel base superalloy compositions. The compositions selected are shown in Table II. The multiphase dispersions were produced in the alloys by new processing techniques including Rapid Solidification+Mechanical Dispersing (RS+MD) and Rapid Solidification+Precipitation Hardening (RS+PH) (16). RS+PH was employed to produce fine dispersions of HfC particles by precipitation from rapidly solidified supersaturated solid solutions in Alloys 1, 2, and 3. Alternatively, with the RS+MD technique, ultrafine powders of  $Y_2O_3$  (in Alloy 2), HfC (in Alloy 4), or both dispersoids (in Alloy 5) were mechanically incorporated into rapidly solidified, fully alloyed nickel base superalloy powders by high energy attrition and ball milling techniques (2,16). The average particle size of the HfC powders that were incorporated into Alloys 4 and 5 by mechanical dispersing was approximately 30 nm. The  $Y_2O_3$  powder that was incorporated into Alloys 2 and 5 had an estimated particle size of approximately 1  $\mu m$ , but these irregularly shaped and fissured particles were subsequently fractured into extremely fine particulates during the mechanical dispersing process. The dispersions of fine  $\gamma'$  particles in Alloys 3, 4 and 5 were obtained by conventional solution treatment and aging techniques.

Table II: Compositions of Alloys Investigated

Alloy		1	2	3	4	5
<b>Base Composition</b>		$\gamma$ + HfC	Alloy 1 + $Y_2O_3$	$\gamma + \gamma'$ + HfC	IN-100 + HfC	MERL 76 + HfC + $Y_2O_3$
<b>Desired Phases (vol. %)</b>	$\gamma'$	-	-	40	60	60
	HfC	9	9	11	4	1
	$Y_2O_3$	-	1.5	-	-	1.5
<b>Elements (wt. %)</b>	Ni	bal	bal	bal	bal	bal
	Co	16.5	16.5	19.4	14.0	18.6
	Cr	13.9	13.9	17.4	10.0	12.2
	Mo	7.9	7.9	8.1	3.0	3.2
	Al	-	-	3.9	5.5	5.0
	Ti	-	-	2.0	4.6	4.3
	C	0.73	0.73	0.67	0.16	0.023
	Hf	13.6	13.6	13.1	-	0.41
	B	0.031	0.031	0.024	0.012	0.020
	Nb	-	-	-	-	1.3
	Zr	0.25	0.25	0.25	0.04	0.07
<b>Powder Additions (wt. %)</b>	HfC	-	-	-	6.4	1.6
	$Y_2O_3$	-	0.8	-	-	0.9

All alloys were consolidated by hot extrusion at 1448-1473K (1175-1200C) using a 2.85 MN (320 ton) extrusion press with an extrusion ratio of 16.6:1. The extruded bars of each alloy were subjected to zone annealing treatments (1,2,3,16) to obtain large, columnar engineered grain structures via secondary recrystallization for optimal elevated temperature stress rupture strength.

## Results and Discussion

The best mechanical properties were obtained for the MD processed Alloy 5 produced by incorporating approximately 1.0 vol% HfC and 1.5 vol% Y<sub>2</sub>O<sub>3</sub> into the commercial alloy MERL76 that had been rapidly solidified by ultrasonic gas atomization. After consolidation, the alloy was found to have an ultrafine, equiaxed grain size of approximately 0.28 μm, as well as multiphase dispersions of γ', HfC, and mixed (Y,Hf)-oxide particles, as shown in Figure 3. Using transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), the average sizes of the particles were measured to be 29, 48, and 23 nm, respectively, in the as-extruded condition. The combined strengthening effects of these fine, multiphase particle dispersions and an ultrafine grain size resulted in extremely high 298K (25C) yield and ultimate tensile strength levels of 1875 and 1889 MPa (272 and 274 ksi), respectively, and elongation and reduction-in-area values of approximately 3 and 4%, respectively.

Zone annealing treatments were successfully applied to the MD processed alloys to produce large columnar grains by secondary recrystallization for improved elevated temperature strength. The alloy displaying the best secondary recrystallization response was Alloy 5, which was the MERL76+HfC+Y<sub>2</sub>O<sub>3</sub> composition. This alloy recrystallized to an average transverse grain size of approximately 0.7 mm and a grain aspect ratio greater than 10, as shown in Figure 4. The projected 1089K (816C) 1000 hour rupture strength of this zone annealed alloy was 393 MPa (57 ksi), which was a 14% increase over the 345 MPa (50 ksi) value for MA6000, as indicated in Figure 5. Since MA6000 and the experimental alloy contained similar amounts and sizes of γ' and oxide particles, the improved intermediate temperature rupture strength of the experimental alloy was thought to have resulted from the incorporation of the fine HfC dispersion.

A potential objection to carbide dispersion strengthened nickel base superalloys is that the high carbon level could significantly depress the incipient melting temperatures of the alloys. In fact, the melting temperatures of the carbide dispersed alloys produced by incorporating ultrafine carbide particles into commercial compositions were found using differential scanning calorimetry (DSC) to be approximately 30-35K higher than those of the conventionally processed commercial alloys without the carbide dispersoids. The increased melting temperatures were believed to have resulted chiefly from the high solidification rates associated with the gas atomization techniques. The carbide dispersions in the MD processed alloys apparently caused little, if any, depression of the melting temperature because these carbide dispersions were produced mechanically rather than by precipitation, which generally results in significantly higher carbon levels in the matrix.

A possible advantage of producing a HfC dispersion via precipitation hardening techniques was that the fine carbide precipitates produced using this method could be coherent or semi-coherent, thereby conferring true coherency strengthening effects to the alloy rather than the much more modest strength

increases resulting directly from incoherent particles. Indeed, transmission electron microscopy of Alloy 3 after rapid solidification revealed the presence of coherent or semi-coherent HfC particles that probably shared a cube-cube orientation relationship with the matrix, as is typically observed for coherent MC type carbides in nickel base superalloys. After consolidation, however, evidence of HfC coherency was no longer observed in the alloy.

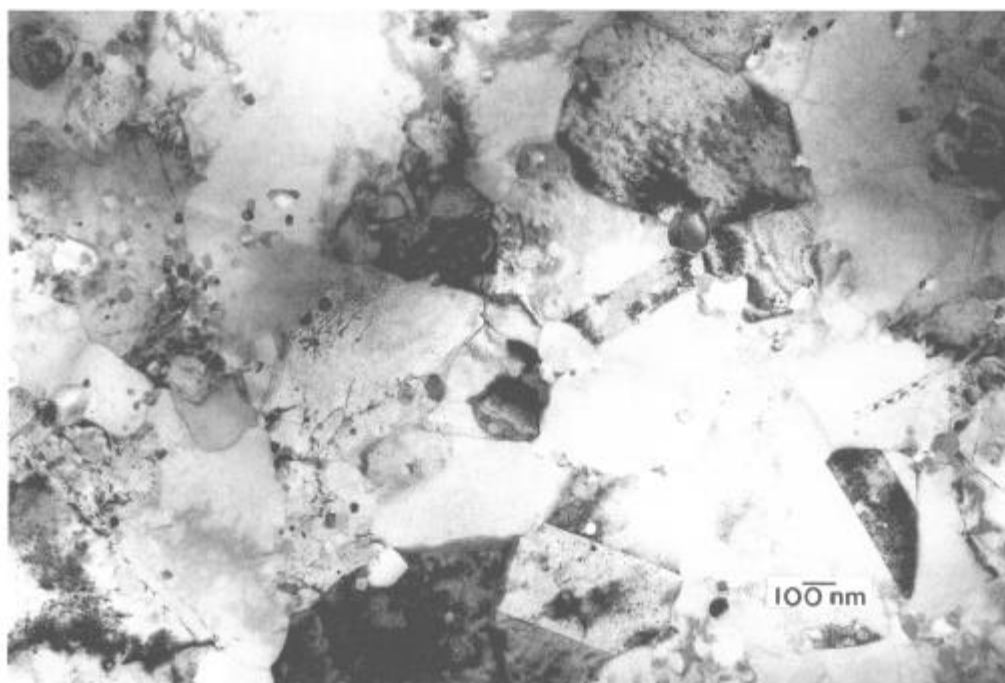


Figure 3: As-extruded microstructure of Alloy 5.

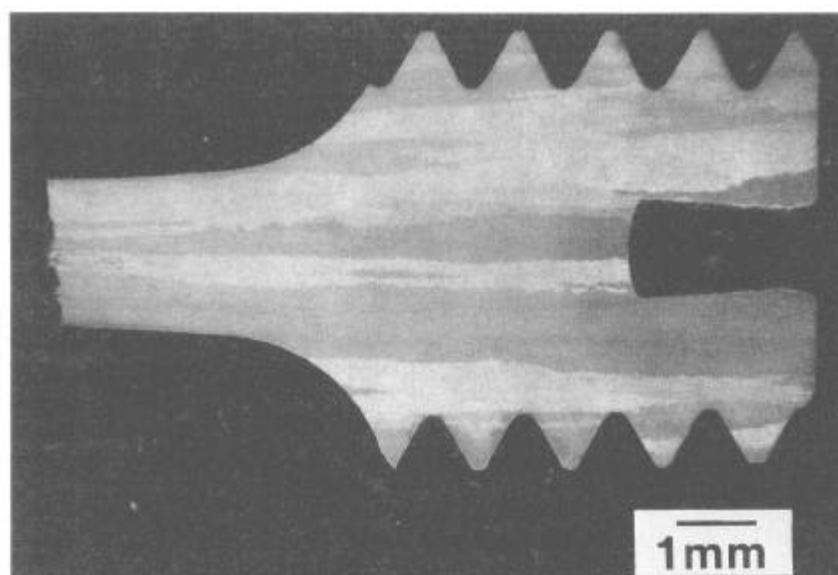


Figure 4: Columnar recrystallized grains in Alloy 5 after zone annealing at 1508°K at a rate of 7.6 cm/h.

## Conclusions

1. HfC dispersions offer an unusual degree of processing flexibility compared to most other refractory dispersoids because a suitable particulate dispersion can be obtained using either precipitation hardening or mechanical dispersing methods.
2. The RS+MD method was favored over the RS+PH method for the production of HfC dispersion strengthened nickel base superalloys. The RS+PH alloys were found to be highly resistant to secondary recrystallization grain growth treatments, and thus, the stress rupture strength levels of these relatively fine grained alloys were less than those obtained with the RS+MD technique.
3. The  $Y_2O_3$  particles that were incorporated into Alloys 2 and 5 were found to be extremely fine and resistant to coarsening, but not chemically inert. After consolidation, no "pure"  $Y_2O_3$  particles were identified. Instead, the  $Y_2O_3$  particles had combined with some of the Hf in the alloys to produce mixed (Y,Hf)-oxides.
4. Given the demonstrated propensity of oxide dispersed alloys manufactured with  $Y_2O_3$  to form complex oxides during consolidation, an appropriate improvement to the manufacture of oxide dispersed alloys would be to incorporate more stable, mixed oxides from the start. This would avoid stripping the composition of useful alloying elements to produce the mixed oxide particulates.
5. Extremely high 298K (25C) yield and tensile strength values of 1875-1896 MPa (272-274 ksi) were found for the RS+MD processed Alloy 5 in the as-extruded condition as the result of combined effects of the ultrafine grain size of 0.28  $\mu m$  and the multiphase dispersion strengthening by  $\gamma'$ , carbide and oxide particles.
6. The projected 1089K (816C) 1000 hour rupture strength of Alloy 5 was 393 MPa (57 ksi), which is 14% greater than the 345 MPa (50 ksi) value for MA6000. Since the alloys contained similar dispersions of  $\gamma'$  and oxide dispersoids, the improved intermediate temperature strength of Alloy 5 was thought to have resulted from the dispersion of the HfC particles that were incorporated into Alloy 5.
7. No measurable melting point depression was detected in the HfC dispersed alloys as the result of the addition of the carbide particulates.

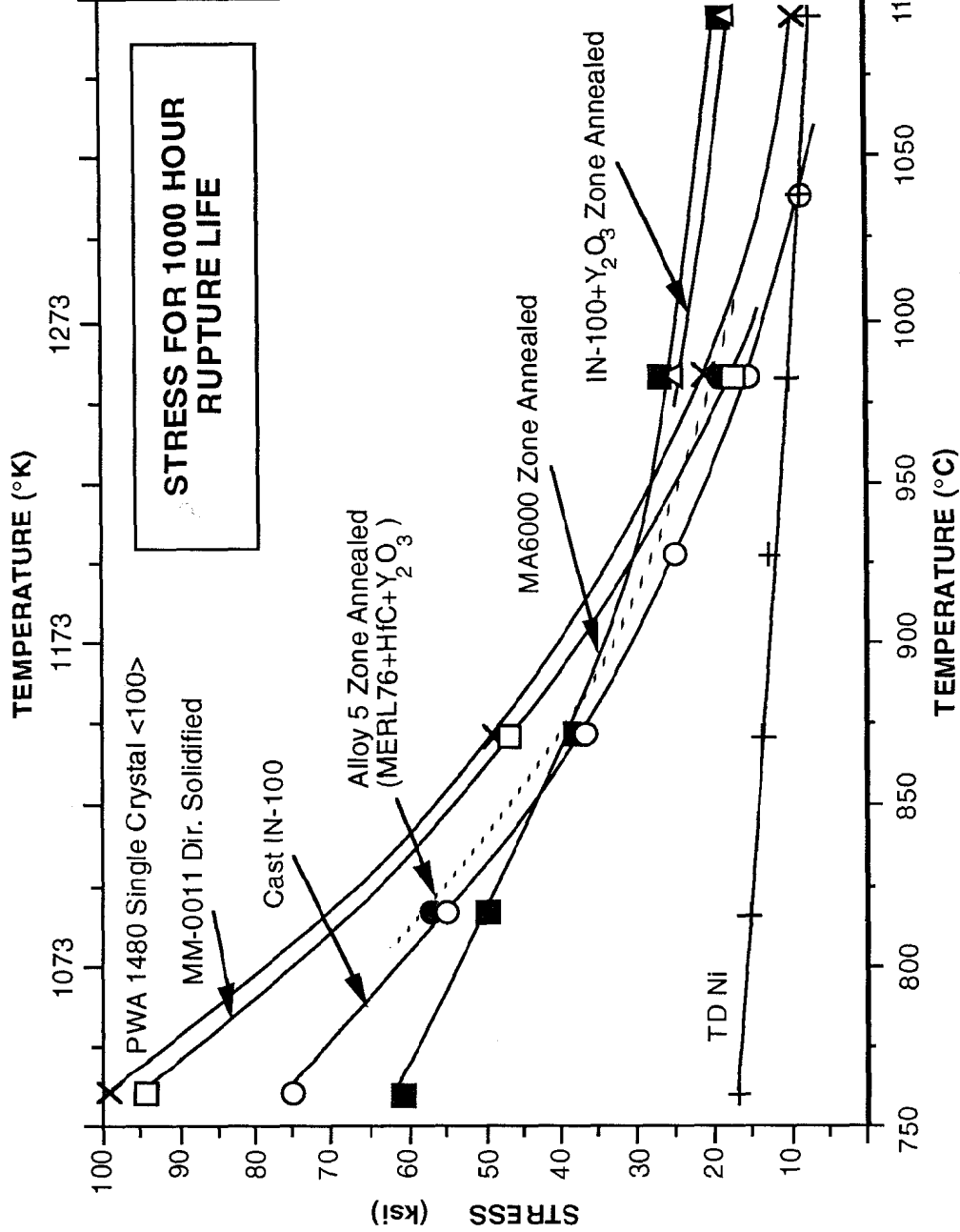


Figure 5: Stress for a 1000 hour rupture life as a function of test temperature for zone annealed Alloy 5 and selected nickel base superalloys. References: (2, 3, 4, 5, 8, 15).



## References

1. G.H. Gessinger, Powder Metallurgy of Superalloys, (Boston, MA: Butterworth & Co., 1984).
2. C.H. Smith and N.J. Grant, "An Alternative Approach to Processing Dispersion-Stabilized Superalloys," Mat. Sci. and Eng., 89 (1987), 129.
3. C.H. Smith, "Process Development and Characterization of an Oxide Dispersion Stabilized Nickel Base Superalloy," (Sc.D. Thesis, M.I.T., 1982).
4. C.T. Sims, N.S. Stoloff, and W.C. Hagel, eds., Superalloys II, (New York, NY: J. Wiley & Sons, 1987).
5. High Temperature High Strength Nickel Base Alloys, International Nickel Co., Inc., Third Ed. (1977).
6. I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, (New York, NY: Springer-Verlag, 1973).
7. I. Barin, O. Knacke, and O. Kubaschewski, Thermochemical Properties of Inorganic Substances: Supplement, (New York, NY: Springer-Verlag, 1977).
8. C.Y. Li and R.A. Oriani, "Some Considerations on the Stability of Dispersed Systems," Oxide Dispersion Strengthening, G.S. Ansell et al. eds., (New York, NY: Gordon and Breach Science Publ., 1968), 431.
9. H.B. Ageev, ed., Diagrammy Sostoianiiia Metallicheskih Sistem, (USSR, 1974), 191.
10. C.J. Smithells, ed., Metals Reference Book, Fourth Ed., (Plenum Press, 1967), 411.
11. J.F. Elliott and M. Gleiser, Thermochemistry for Steelmaking, Vol. 1, (Reading, MA: Addison-Wesley, 1960), 147.
12. M.W. Chase et al., J. Phys. Chem. Ref. Data, 4 (1) (1975) JANAF Thermochemical Tables, 1975 Supplement, 51.
13. H.E. Exner, "Physical & Chemical Nature of Cemented Carbides," Int. Met. Rev., 4 (1979), 149.
14. H.B. Ageev, ed., Diagrammy Sostoianiiia Metallicheskih Sistem, (USSR, 1962).
15. R.C. Benn, "Oxide Dispersion Strengthened Superalloys for Long Term Service," (Proc. Third Intl. Conf. on Creep and Fracture of Engineering Materials and Structures, U. College of Swansea, Swansea, U.K., April 5-10, 1987).
16. J.M. Nell, "Multiphase Strengthening of Rapidly Solidified Nickel Base Superalloys," (Ph.D. Thesis, M.I.T., 1989).