OXIDE DISPERSION STRENGTHENED MAJORITY γ' PHASE NICKEL-BASE SUPERALLOY

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The objective of this work was to develop oxide dispersion strengthened (ODS) alloys, based on the Ni-Cr-Al system, which would derive a significant high temperature strength increment from the retention of high volume fractions (>50%) of γ' at 1093°C. The effects of quaternary additions of the alloying elements Ti, Ta, Nb, Mo, W, Co and Hf on the mechanical alloying and recrystallization response of a Ni-10a/oCr-17.5a/oAl ODS alloy were determined. Subsequently, data from the simple ternary and quaternary alloys were used to design more complex alloys. Promising alloys were identified which achieved the property goals of excellent 760°C rupture strength (equivalent to IN-100), combined with outstanding 1093°C rupture strength in a corrosion resistant alloy.

INTRODUCTION

Today, several distinct types of alloys with directional structures offer potential for increased operating temperatures (30-180°C) for gas turbine vanes and blades. Among these are the oxide dispersion strengthened (ODS) alloys(1-3) produced by mechanical alloying(4). The ODS + γ' nickel-base superalloys which have been produced to date offer substantial increases in high temperature strength capability over conventional nickel-base superalloys.

In these previous ODS alloy investigations, alloys with conventional volume fractions of γ' (30-50%), and low γ' solvus temperatures were studied. At intermediate temperatures ($\sim$760°C), the ODS + γ' alloys enjoy a significant strength increment over their γ'-free counterparts; e.g., TDNi and TDNi-Cr. As the use temperatures are raised, the γ' solvus is approached and the γ' strengthening increment decreases to zero. This occurs at approximately 870-1150°C for present ODS + γ' alloys.

This paper describes completed work(5-7) in an on-going program to develop ODS nickel-base superalloys with very high volume fractions (~80%) of γ'. As this work has been in progress some time, it would be beyond the scope of this paper to summarize all the alloy variations investigated. Therefore a smaller number of representative alloys which show promise have been selected for discussion in order to demonstrate developmental trends.

EXPERIMENTAL PROCEDURES

Powder batches of these alloys were mechanically alloyed in attritor mills under controlled conditions. Elemental Ni, Cr, Co, W, Mo, Ta and Nb powders were blended with preground Ni-Al-Ti and -Hf master alloys, as required, and Y_2O_3. In subsequent alloys, B and Zr were also added as preground Ni master alloy. The resultant mechanically alloyed powder was characterized using chemical and screen analyses and metallographic examination. Selected alloy compositions are given in Table 1.

Table 1. Selected Experimental Alloy Compositions in At.% (Wt.% in parentheses).

Alloy No.	Ni	Cr	Al	W	Mo	Ta	Nb	Y_2O_3
2	72.5	10	17.5	-	-	-	-	(1.1)
	(80.2)	(9.8)	(8.9)					
8	70.5	10	17.5	2	-	-	-	(1.1)
	(74.4)	(9.4)	(8.5)	(6.6)				
9	72.5	10	16.5	-	-	1	-	(1.1)
	(78.0)	(9.5)	(8.1)			(3.3)		
12	72.5	10	16.5	-	-	-	1	(1.1)
	(79.2)	(9.7)	(8.3)				(1.7)	
16	70.5	10	17.5	-	2	-	-	(1.1)
	(76.9)	(9.7)	(8.8)		(3.6)			
38&50*	66	15	15.5	2	1	0.5	-	(1.1)
	(67.8)	(13.9)	(7.4)	(6.5)	(1.7)	(1.6)		
44&49*	67	12.5	15.5	2	1	1	1	(1.1)
	(67.4)	(11.3)	(7.3)	(6.4)	(1.7)	(3.2)	(1.6)	
47&51*	68.5	10	17.5	2	2	-	-	(1.1)
	(71.1)	(9.3)	(8.5)	(6.6)	(3.4)			

* 0.15 Wt.% Zr + 0.01 Wt.% B added.

After screening to remove the coarse +12 mesh particles, powder batches of each composition were cone blended for 2 hours and packed into mild steel 89 mm O.D. extrusion cans which were then sealed in air. Extrusions were made after preheating the billets for 1-2 hours at temperatures in the range 1010-1205°C. Conical extrusion dies were used yielding round bar (20.4 mm ϕ) at an 18:1 ratio, while rectangular dies were used to extrude bar (30.2 mm x 20.4 mm) at a 10:1 ratio for subsequent hot rolling trials. Rectangular extruded bar of selected alloys was preheated 1 hour and hot rolled at temperatures in the range 1120-1230°C with thickness reduction levels of 20, 40 and 60%. The hot rolled bars were then pickled to remove the can material.

The objective of the extrusion studies was to determine the conditions required to yield a coarse elongated grain structure, in each alloy, upon heat treatment. The necessity of obtaining this structure to achieve maximum high temperature strength in ODS alloys is well documented(8,9). Stationary gradient anneals were used to determine the recrystallization behavior as a function of annealing temperature. The grain aspect ratio (GAR) and hence the high temperature strength(1,10) of the alloys was then increased by zone annealing bars in the same furnace at 70 mm/h and maximum zone temperatures ranging from 1260°C to 1330°C.

Metallographic and Differential Thermal Analyses (DTA) studies were used to determine the γ' solvus temperature. Appropriate solution and aging heat treatments were then applied to the alloys. Specimens having a 19 mm gage length and 3.5 mm gage diameter for mechanical testing were ground from bar with its axis parallel to the direction of structural elongation. Mechanical tests in air included 760°C, 1093°C and 1150°C stress rupture with room temperature and 760°C tensile tests.

Oxidation tests were performed at 1093°C for 504 hours in air-5% H_2O flowing at 250 cc/min. Sulfidation tests were conducted at 930°C for 168 hours in a rig corresponding to the G.E. Lynn low velocity burner rig(11). Conditions for the oxidation and sulfidation tests are identified in Figure 1.

Microstructural examination was made using optical and electron microscopy. Phase identification was achieved using electron microprobe analysis and x-ray diffraction.

RESULTS AND DISCUSSION

Quaternary Alloys

Gradient annealing has been used extensively in this work to measure the recrystallization response vs. composition and thermomechanical processing conditions. The feasibility of producing 90% γ' ODS Ni-Cr-Al alloys by mechanical alloying was established(5). Then, follow-on work(6) on the effects of quaternary addition elements on the directional recrystallization response of a Ni-10^{W}/oCr-9^{W}/oAl-1.1^{W}/oY_2O_3 alloy (Table 1, Alloy 2) set two guidelines for subsequent alloy design. Firstly, elements which mainly partition to the γ' phase (Ti, Ta, Nb, Hf) tended to decrease recrystallization response when added above 1 at.%. Secondly, elements which mainly partition to the γ phase (Cr, Mo, W, Co) tended to increase recrystallization response when added up to approximately 20 at.% Cr, 2 at.% Mo, 3 at.% W and 10 at.% Co, respectively.

The mechanical property results of these quaternary alloys indicated that, of the elements examined, W, Mo and, to a lesser extent Nb and Ta, were the most effective elements for improving the rupture strength of the simple Ni-Cr-Al ODS alloy as shown in Table 2. Some variable recrystallization response was obtained in alloys containing Ti and Co respectively which precluded these elements from the alloy design at the time.

Table 2. Effect of Quaternary Alloy Additions on Rupture Strength and %γ' of Ni-Cr-Al ODS Alloy.

Alloy	Quaternary Addition (At.%)	100 h Rupture Strength MPa(ksi) 760°C	1093°C	1150°C	%γ' at 1093°C
2	-	503(73)	103(15)	79(11.5)	60
8	2W	510(74)	131(19)	103(15)	60
9	1Ta	505(73)	97(14)	72(10.5)	60
12	1Nb	503(73)	103(15)	83(12)	60
16	2Mo	586(80)	117(17)	90(13)	65

Hot corrosion studies showed that the quaternary alloys had excellent high temperature oxidation resistance equivalent to IN-100. Sulfidation resistance was also better than IN-100 and Alloy 713 but below the more sulfidation resistant alloys such as IN-738. Raising the Cr to 15 wt.% in the ternary Alloy 2 reduced the sulfidation attack by 50%. Corrosion data for the stronger quaternary alloys (NAVAIR precursor alloys), given in Table 2, are compared in Figure 1 with other well-known superalloys.

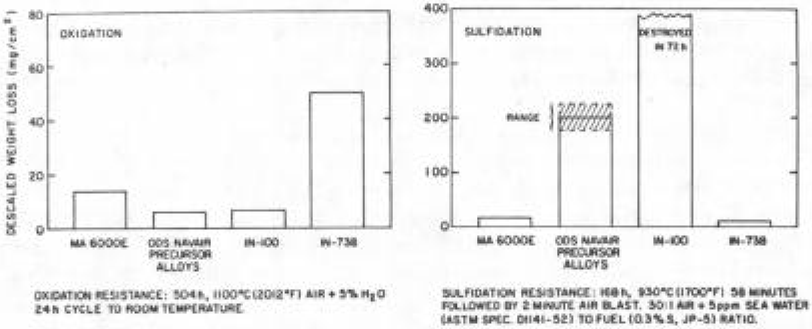

Figure 1. Comparison of Oxidation and Sulfidation Resistance of ODS NAVAIR (Precursor) Alloys with Other Superalloys.

Quinary and Higher Order Alloy Design

Data from the simple ternary and quaternary alloys were used to design more complex alloys. Specifically, the effects on properties of W, Mo, Ta and Nb combinations, substituted, as in previous work(6), on an atomic weight basis into each of three Ni-Cr-Al ternary systems were determined. The Cr:Al levels of 15:16, 12.5:17.5 and 10:17.5 at.% were chosen which represented a range in sulfidation resistance due to Cr, while maintaining the Al level at a maximum for γ' strengthening consistent with phase diagram considerations(12). Alloys 38, 44 and 47 (Table 1) gave the best directional recrystallization response with GAR's generally >15 (Figure 2). Screening

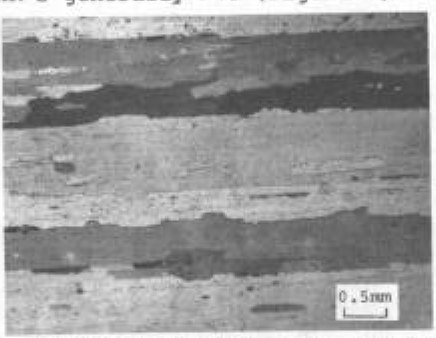

Figure 2. Extruded and Zone Annealed Alloy 47.

tests indicated that the 760°C/100-hour rupture strength of all three alloys was at least equal to that of MA 6000E(13), i.e., 552 MPa(80 ksi), and could be further improved by minor additions of B and Zr (Alloys 49-51). Since these alloys represented a desirable range of potential corrosion resistance and strength, they were selected for more detailed characterization studies which are discussed from here on.

Thermomechanical Processing

The optimum directional recrystallization response was obtained from material preheated 1 to 1-1/2 h at 1175°C and extruded at ratios equal or greater than 18:1. Reducing the ratio, and thereby the degree of primary deformation, generally decreased the recrystallization response. Hot rolling of the 10:1 ratio sheet bar introduced sufficient energy to progressively improve the directional recrystallization response as shown in Figure 3. Note, also how increasing additions of γ' and carbide forming elements such as Ta and Nb reduced the extent of directionally recrystallized grain growth.

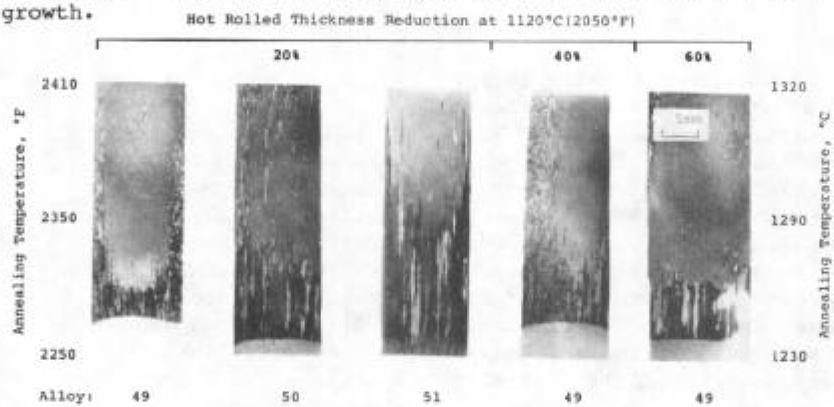

Figure 3. Gradient Annealed Bars Showing Effects of Hot Rolling and Composition on Directional Recrystallization Response.

Stress Rupture Properties

Stress rupture tests of up to 500-hour duration on extruded and zone annealed bar indicated significant improvements in 760°C/100-hour rupture strength due to $0.01^{W}/oB + 0.15^{W}/oZr$ additions as shown in Table 3. In particular, Alloy 49 strength (621 MPa/90 ksi) showed (i) significant improvement over MA 6000E (552 MPa/80 ksi), (ii) was equivalent to high strength cast alloys such as IN-100 (627 MPa/91 ksi) and (iii) approached directionally solidified MAR-M200 + Hf (724 MPa/105 ksi)(14). Some minor strength improvements in the high temperature region, i.e., 1093°C and above, where ODS rather than γ' strengthening predominates, were obtained through improved grain shape control. The density-corrected 100-hour rupture strengths of various materials are given for comparison in Figure 4. This plot shows that experimental ODS Alloy 49 has an excellent combination of intermediate and high temperature strength.

Table 3. Effect of B&Zr Additions on 100-Hour Rupture Strengths of Experimental Alloys.

Alloy	B&Zr Addition	Strength MPa(ksi) 760°C	1093°C
38	No	552(80)	103(15)
50	Yes	579(84)	110(16)
44	No	586(85)	131(19)
49	Yes	621(90)	135(19.5)
47	No	558(81)	127(18)
51	Yes	593(86)	135(19.5)

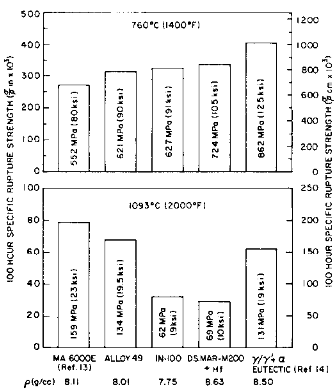

Figure 4. Comparison of 100-Hour Specific Rupture Strength Capability of Various Materials Systems.

Tensile Properties

Room temperature (RT) and 760°C tensile test results on all the experimental alloys indicated superior strength advantages over DS MAR-M200 + Hf(15), as shown in Table 4, although ductilities were lower.

Table 4. Tensile Test Results of Experimental Alloys

Alloy No.	Temp. °C	0.2% Y.S. MPa	(ksi)	U.T.S. MPa	(ksi)	El. %	RA %
49	RT	1165	(169)	1262	(183)	3.5	8.0
	760	1151	(167)	1151	(167)	1.0	2.5
50	RT	1089	(158)	1213	(176)	3.5	8.5
	760	1055	(153)	1055	(153)	2.0	3.0
51	RT	1034	(150)	1172	(170)	2.0	3.5
	760	1041	(151)	1103	(160)	3.5	6.5
DS MAR-M200 +	RT	869	(126)	1089	(158)	13.1	16.7
Hf (Ref. 15)	760	910	(132)	1145	(166)	11.7	22.8

Heat Treatment Studies and Structural Analyses

Mechanical property results hereto were determined on extruded, zone annealed bar which was then given a simple 1/2 h heat treatment at the zone anneal temperature and air cooled. A typical microstructure produced by this heat treatment is illustrated by Figure 5 for Alloy 49 which was zone annealed at 1280°C and shows ∿80 vol.% primary γ' of 1-2 μm size with some in-fill of secondary γ' that precipitated on air cooling. The effect of B and Zr additions was to increase grain boundary γ' precipitation producing more contiguous grain boundaries in this alloy. This may account for the increase in rupture strength and ductility over Alloy 44. Similar effects have been observed elsewhere(16). Metallographic and D.T.A. studies on Alloy 49 indicated the γ' solvus temperature to be ∿1280°C. Results of a solution and aging treatment survey, based on the γ' solvus temperature, showed slightly improved rupture elongation (from 2 to 4%) but generally lower strength. The heat treated material had a less desirable γ' morphology which was attributed to incomplete solutioning of the γ' during the 2 h/1295°C/AC solution anneal. Subsequent studies showed that 4-8 h soaks at temperatures approaching the solidus ∿1310°C were necessary to resolution the very high γ' content characteristic of these alloys.

X-ray diffraction and microprobe analyses studies on 760°C/100 h rupture samples identified the phases present in the promising Alloy 49 as a γ/γ' matrix containing Ta/Nb-rich grain boundary MC carbides, W/Mo/Cr-rich grain boundary and matrix M_6C and $M_{23}C_6$ carbides with M_3B_2 borides and a Y_2O_3/Al_2O_3 combination dispersoid (predominantly as $3Y_2O_3 \cdot 5Al_2O_3$). No traces of σ, β or α'(Cr) phases were detected.

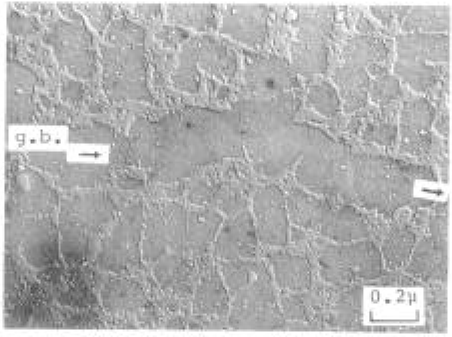

Figure 5. Replica Electron Micrograph of Alloy 49 Showing γ' Morphology (g.b. = grain boundary).

Effect of Alloy Content on Recrystallization Response

From the gradient annealing studies it was apparent that secondary recrystallization occurred at or above the γ' solvus temperature. This implies that a proportion of the γ' must redissolve before growth of the recrystallized grains can proceed and that the redissolution rate is, in turn, proportional to the γ' volume fraction. Since the γ' solvus temperature and volume fraction are both functions of alloy composition, it is possible to extend the temperature range of directional recrystallization response in a given alloy by minor compositional modifications, as indicated in Figure 3. Thus a composition modification may, inter alia, be desirable in Alloy 49, the best 760°C strength alloy developed to date, to improve grain shape control particularly for better 1093°C strength.

SUMMARY AND CONCLUSIONS

Development of a series of high volume %γ' Ni-base ODS superalloys confirmed that the high %γ' characteristic is an effective means of improving the intermediate temperature strength. An alloy having 100-hour rupture strengths of 621 MPa(90 ksi) at 760°C and 134 MPa(19.5 ksi) at 1093°C, respectively, was identified. Hot corrosion data indicated that the compositional range of the series had excellent oxidation resistance (generally better than IN-100) and much superior sulfidation resistance than IN-100 and Alloy 713. Directional recrystallization response was improved by secondary hot working. Maximum strength was developed with a simple heat treatment. Correlation between the γ' content, γ'solvus temperature and directional recrystallization temperature of the series suggested minor compositional changes to optimize the properties of a single alloy.

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