QUINARY ALLOY MODIFICATIONS OF THE

EUTECTIC SUPERALLOY $\gamma/\gamma' + \text{Cr}_3\text{C}_2$

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Summary

The $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ eutectic superalloy holds promise for introduction into gas turbine blade applications. Many of the difficulties which have limited superalloy eutectic use such as processability, surface and thermal stability have been successfully addressed. Due to this alloy's high chromium content, oxidation and sulfidation properties have been shown to be outstanding. Another benefit of high chromium contents is a low density of 7.5 gm/cm^3 compared to $\sim 8.5 \text{ gm/cm}^3$ for $\gamma/\gamma' + \alpha$, $\gamma/\gamma' + \delta$ and D.S. MAR-M200. Directional solidification rates as high as 125 cm/hr have yielded strong well aligned structures and thermal cycling has been shown not to deteriorate the carbide-matrix interface. In this study rhenium and yttrium additions were made to a base chemistry of 12.3 Cr, 6.9 Al, 1.5 C and bal. Ni in weight percent. Cyclic oxidation and sulfidation tests as well as stress rupture, thermal cycling and length memory testing were conducted. Rhenium additions resulted in substantially increased stress rupture lives as well as increased length memory effects. In addition to strengthening the eutectic, Re additions were also observed to enhance the cyclic oxidation and sulfidation resistance of the alloy. Yttrium was observed to be soluble in the M_3C_2 carbide and resulted in enhanced cyclic oxidation properties. On a density normalized basis this alloy system is superior to current directionally solidified and single crystal superalloys in stress rupture and also superior in uncoated oxidation and corrosion cyclic tests at 1100 and 900°C.

Introduction

Studies of the multivariant eutectic $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ within the Ni-Al-Cr-C system began at Cambridge University, England (1) under Ministry of Defense sponsorship and were continued at the National Physical Laboratory (NPL) (2,3) in conjunction with Rolls Royce. A promising application of $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ alloys derived from the latter work was stator turbine components as the elevated temperature creep-rupture properties were inferior to rotor blade alloys but their oxidation properties were outstanding.

Improvements to this alloy have been made by matrix alloying with yttrium (4,5) and both carbide and matrix alloying with rhenium (Re) (5,6) such that an improved $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ alloy, Ni-6.9 w/o Al-12.3 w/o Cr-1.5 w/o C-5.0 w/o Re-0.5 w/o Y, was identified which overcame two of the principal objections to first generation eutectic superalloys, i.e., their slow processing rates and their poor oxidation resistance. By using high temperature gradients in the melt during directional solidification it has been possible to obtain well aligned $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ microstructures at rates exceeding 30 cm/hr (5,6). This is in sharp contrast to the <3 cm/hr required to directionally solidify $\gamma/\gamma' + \alpha$ or <1 cm/hr for NiTaC-14B which represent the first generations of eutectic superalloys. Minor additions of 0.1-0.5 w/o Y to $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ resulted in dramatic improvements in the alloy's cyclic oxidation and corrosion resistance at 1100°C and 900°C, respectively. The unmodified alloy was oxidized by spallation of a chromium/nickel rich scale and by internal oxidation, the Y containing alloys formed a more protective scale of Al_2O_3 .

In the study of the TaC fiber reinforced eutectics (7), a phenomenon termed "length memory effect" was first observed in repetitive creep and heat treatment experiments. This interesting phenomenon occurred during heat treatment of precrept specimens which contracted to nearly their initial lengths (measured prior to the onset of creep). This behavior was the first experimental evidence of reversed plastic flow of the matrix due to elastic recovery of the aligned carbide fibers. Most recently this "length memory" phenomenon has been studied in the $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ system (8). It was reported that in creep tests conducted above 825°C and to strains of 3.7%, little creep strain recovery was observed. However, tests carried out at 650°C and 1.5% creep strain exhibited length recovery of 50% after heat treatment at 1100°C for 50 hrs. It is not known whether the higher temperature creep tests resulted in plastic deformation of the Cr_3C_2 fibers or whether the larger creep strain attained in this test fractured the aligned fibers or some of both modes.

The objective of this program was to provide an improved eutectic superalloy with superior oxidation/corrosion resistance and processability equivalent to current directionally solidified superalloys and to demonstrate the heat treatment conditions which permit the restoration of creep strength and recovery of strain. The investigation included characterization of the mechanical and physical properties of a rhenium and yttrium modified gamma/gamma prime plus chromium carbide eutectic, critical to its application as a gas turbine blade.

Experimental Procedures

A base alloy chemistry of 12.3 Cr, 6.9 Al, 1.5 C and bal. Ni (wt%) was used. Elemental substitutions were made on a weight percent basis with refractory elements substituted for Ni. The alloy was induction melted from elemental additions and directionally solidified in a high thermal gradient water spray apparatus (5,9). This procedure typically yields thermal gradients in the liquid of approximately 300°C/cm. Excluding small end affected regions, the rate of freezing was found to be equal to the crucible withdrawal velocity over the entire specimen length. Stress rupture experiments were conducted on specimens machined from 12.5 mm diameter bars at the rates of and chemistries summarized in Table I.

Table I. Stress-Rupture Properties of Re and Y Modified
 $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ at 1040°C

<u>Alloy Modification (w/o)</u>	<u>Solidification Rate (cm/hr)</u>	<u>Stress (MPa)</u>	<u>Time to Rupture (hrs)</u>	<u>Elonga- tion (%)</u>
1.6 C, 2.5 Re	15	172	>131	12.2
1.6 C, 2.5 Re	15	207	44	12.4
1.65 C, 5 Re	5	172	245	19.6
1.65 C, 5 Re	5	172	174	21.1
1.65 C, 7.5 Re	5	172	334	11.4
1.6 C, 5 Re, 0.5 Y	5	172	115	15.2
		207	140	
1.65 C, 5 Re	15	172	62	11.2
1.6 C, 5 Re	35	172	13	
		207	13+16	10.8
1.6 C, 5 Re	50	172	59	13.8
1.6 C, 5 Re	75	172	17	12.3
1.6 C, 5 Re	100	172	56	11.2
1.6 C, 5 Re	125	172	53	9.4

Strain recovery experiments were conducted on the base alloy chemistry modified with 2.5 w/o Re. Eutectic samples grown in 9.5 mm (3/8") diameter crucibles were machined into standard creep specimens. Creep tests were performed as outlined in Table II by loading at temperature, deforming to ~ 1.4% permanent creep strain, and cooling under stress to insure no strain

Table II. Summary of Strain Recovery Experimental Conditions and Results

<u>Prior Creep Conditions</u>	<u>Final Creep Strain</u>	<u>$f_r(\infty)$ (100°C)</u>	<u>$f_r(\infty)$ (1200°C)</u>
<u>T(°C)</u>	<u>σ(MPa)</u>	<u>(%)</u>	
700	600	1.33	.440
800	338	1.43	.302
980	207	1.17	.141
1040	170	1.63	.130
			.556
			.451
			.343
			.217

recovery occurred during the thermal excursion. Near zero creep rates were observed in a number of specimens so increases in stress were made in order to achieve the desired creep strain in reasonable periods with the primary consideration that the specimen be well into secondary creep before the test termination. Specimen lengths were measured before and after creep deformation to ± 0.0076 mm (± 0.0003 ") followed by heat treatment at 1100°C in an Ar atmosphere. Specimen lengths were again measured after various time intervals during the heat treatment to observe creep strain recovery. By assuming that all creep strain and subsequent recovery occurred in the specimen gage section, total specimen lengths can be used in determining recovered strain.

Both cyclic oxidation and sulfidation experiments were conducted on the base $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ alloy as well as with Y and Re modifications. Tests were conducted such that specimens were cycled 200 times through a 55 min soak at 1100°C and 900°C for oxidation and sulfidation experiments respectively and withdrawn for 5 min at room temperature. Sulfidation tests included a $1 \text{ mg/cm}^2 \text{ Na}_2\text{SO}_4$ application every 20 cycles and surface area normalized.

Experimental Results and Discussion

Physical Metallurgy of Alloy Modifications

Rhenium Modifications. A differential thermal analysis (DTA) of $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ alloys containing 2.5-7.5 w/o Re was undertaken in order to better understand the effect of Re on the freezing range and coupled eutectic growth region. The resulting data yielded γ' solvus, eutectic solidus, eutectic liquidus and primary Cr_3C_2 liquidus temperatures with variations in Re content.

Rhenium was observed to have two strong effects on phase equilibria in the $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ system as shown in Fig. 1. The first is to raise the γ' solvus for increasing Re contents. The base alloy has a γ' solvus of 1208°C which was increased to 1250°C with the addition of 7.5 w/o Re. The second effect was to linearly raise the primary carbide liquidus temperature from that of the bivariant eutectic, 1310°C , to 1341°C at 7.5 wt% Re. The pseudo-binary eutectic solidus and liquidus were very close and not distinguishable within 3°C accuracy.

The Re concentration was found to have a substantial effect on the carbide morphology. The as-directionally solidified material is shown in both transverse and longitudinal views with varying concentrations of Re in Fig. 2. Increasing Re concentration resulted in two effects. The first was to cause the solidification of primary carbides, similar to raising the carbon concentration, and the second was to break down the planar front solidification interface. This morphological effect is especially apparent in Fig. 2c and d where the carbides are seen growing as much as 30° from the growth direction. Raising the Re concentration above ~ 2.5 wt% produces an uncoupling of the bi-phase growth from the melt.

Figure 1. Phase diagram for Re modified $\gamma/\gamma' + \text{Cr}_3\text{C}_2$

Figure 2. Longitudinal and transverse microstructures of $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ as function of Re content.

Yttrium Modifications

Since Y has been shown to be very beneficial to both oxidation and sulfidation (6), knowledge of its distribution in the eutectic would be

very useful. It is known that Y losses in Ni-base superalloys readily occur due to mold-metal interactions in their original melting and subsequent solidification processing. A wet chemical analysis becomes difficult especially when such small amounts of Y are of interest. To alleviate this problem X-ray microprobe maps were made of a base alloy plus 0.5% Y and 5.0% Re. Figure 3 shows the secondary electron image along with its corresponding Y and Re maps. From these maps it is clearly seen that Re and Y have greater concentrations in the carbide than in the matrix. Since the level of Y was so small, its detection in the eutectic carbides was difficult due to their small diameters, but the primary carbides were plainly seen to be enriched in Y.

Figure 3. Microprobe maps of directionally solidified $\gamma/\gamma' + \text{Cr}_3\text{C}_2 + \text{Re} + \text{Y}$

Of equal importance is the ease of processability for this alloy system. Rupture lives for specimens grown at rates through 125 cm/hr show little debit at rates between 15 and 125 cm/hr while at slower rates substantial increases were observed. These results are consistent with the aligned microstructures observed previously (4). It is interesting to note, however, that the strongest microstructures were grown at slow rates and that increasing the solidification rate decreased properties. This is the opposite effect described by Bullock, et al. (3) where increased growth rates yielded finer carbides which were hypothesized to be stronger. With Re addition however, this trend was reversed.

A Larson-Miller plot of the rupture lives for $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ (3), Re modified $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ and other advanced directionally solidified alloys is presented in Fig. 4 for comparative reasons. The alloy developed in this study possesses rupture lives comparable to COTAC 3 and superior to D.S. MAR-M200. Rhenium additions are seen to increase the temperature capability of the $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ eutectic by 125°C (260°F).

Stain Recovery

The partial recovery of creep strain in fibrous in situ composites where the matrix is plastically deformed while the reinforcing fibers are only elastically deformed has been previously observed, and referred to as

Figure 4. Comparison of stress rupture properties for several directionally solidified superalloys.

the "length memory effect" (7). In particular, this effect has been shown to occur in the $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ system, to a limited extent by McLean (8). It was shown that an appreciable percentage of prior creep strain could be removed if the initial deformation temperature was held below 750°C. A heat treatment of 1100°C for 100 hrs was given to specimens strained in creep at 650°C to 1.5%, 750°C to 1.5% and 825°C to 3.7% yielded strain recoveries of 44.7, 22.6 and 5.9%, respectively. These results showed a strong temperature and prior creep strain dependence. The only partial recovery of prior creep strain can be attributed to plastic deformation of the carbide fibers at high temperatures or the creeping of the fiber-matrix interface. It was anticipated that by modifying the Cr_3C_2 chemistry with Re, enhanced strain recovery results could be obtained.

The results of the strain recovery experiments outlined in Table II are given as the fraction of prior creep strain recovered, $f_r(t)$, vs time at aging temperature. The time dependent fraction recovered is defined as:

$$f_r(t) = \frac{\epsilon_c - \epsilon_r(t)}{\epsilon_c} \quad (1)$$

where $f_r(t)$ = time dependent fraction of creep strain recovered
 $\epsilon_r(t)$ = time dependent strain after recovery
 ϵ_c = initial prior creep strain
 t = heat treatment time at 1100°C.

The term $f_r(0)$ is equal to zero since $\epsilon_r(0) = \epsilon_c$.

In the specimens tested, almost all of the strain recovery occurred during the first few moments at temperature. Only slight recovery continued until a stable specimen length was achieved after approximately 10

hrs of aging. The maximum fraction of creep strain recovered, $f_r(\infty)$ is then given by:

$$f_r(\infty) = \frac{\epsilon_c - \epsilon_r(\infty)}{\epsilon_c} \quad (2)$$

where $f_r(\infty)$ = maximum fraction of prior creep strain recovered

$\epsilon_r(\infty) = \epsilon_r(t)$ at a time, t , great enough to achieve a stable specimen length (~ 100 hrs).

The maximum fraction of recoverable strain, $f_r(\infty)$, is dependent on the temperature at which prior creep deformation (T_c), the temperature at which recovery occurred (T_r) and the amount of prior creep strain (ϵ_c). Figure 5 illustrates how T_c influenced $f_r(\infty)$ for specimens strained to constant ϵ_c of $\sim 1.4\%$ and aged identically. High temperature creep deformation caused either plastic deformation of the Cr_3C_2 fibers or the matrix-fiber interface is allowed to slide by a diffusional process thereby allowing relaxation of the internal stresses developed between the matrix and fiber during creep. At this time the mechanism in operation is not known. Data from Ref. 8 for Re free $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ are also given in Fig. 5. In this previous study, poorer results were obtained which are directly attributable to the Re modifications of this study.

Figure 5. Fraction of prior creep strain recovered, $f_r(\infty)$ vs creep temperature for 2.5% Re modified $\gamma/\gamma' + \text{Cr}_3\text{C}_2$.

An additional recovery heat treatment of 1200°C for 50 hrs was made on all specimens to determine if any additional prior creep strain could be recovered. The results of this experiment along with the heat treatment of a undeformed specimen are given in Table II as $f_r(T_r)$ for both 1100 and

1200°C heat treatments. Comparison of these data shows that significant increases in recovered creep strain were realized after apparent stabilization at 1100°C. The further recovery was enhanced in specimens crept at higher temperatures. In the case of a specimen originally deformed at 980°C, for example, a 143% increase in recovered strain was realized upon treating at 1200°C.

The results obtained in this study are comparable to those reported by McLean (8) at the lowest creep temperature of 700°C while at the higher creep temperatures of 800 and 980°C the results presented here are much superior to those of Ref. 8. This would be the expected result if carbide strengthening were occurring due to Re additions at high temperatures.

Environmental Attack

The cyclic oxidation resistance of the $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ alloys was excellent. Alloys with rhenium additions to 5 wt% and yttrium additions to 0.3 wt% were tested. No observable change in cyclic oxidation response was observed with Re modifications to the base eutectic alloy. In both cases stable weight gains were obtained and measured at 3 mg/cm². No surface instabilities were observed. Yttrium had the effect of reducing even these small oxide coatings to near immeasurable thicknesses again resulting in a stable oxide layer.

The unmodified alloy displayed surface instabilities upon cyclic sulfidation testing after 140 temperature cycles. Additions of 2.5 wt% Re or 0.5 wt% Y completely stabilized the surface for 200 test cycles. No measurable weight gains or losses were observed illustrating the exceptional oxidation and corrosion resistance of the high chromium alloy.

Future Perspectives

Rhenium and yttrium modifications to the eutectic $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ in situ composite have resulted in improvements in both mechanical properties and surface stability. The optimized creep properties have been shown to be slightly inferior to those of current advanced superalloys such as single crystal PWA 1480. On a density normalized basis, however, $\gamma/\gamma' + \text{Cr}_3\text{C}_2$ is superior. This is important especially when one considers rotating parts such as turbine blades. These improvements in strength resulted from material solidified at rates much greater than those used in single crystal superalloy fabrication and approaching those of conventional columnar grain D.S. This may lead to very economical blade or vane fabrication techniques.

The surface stability of this alloy is superior to any alloy now used or planned for use at temperatures > 1000°C. This stems from the use of high chromium concentration to produce a strengthening phase; the opposite effect of Cr additions to conventional superalloys. From these findings it is expected that the $\gamma/\gamma' + \text{Cr}_3\text{C}_2 + \text{Re} + \text{Y}$ in situ composite will find acceptance in high temperature stressed components under harsh environmental conditions.

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