THE EFFECTS OF YTTRIUM AND SULFUR ON THE OXIDATION RESISTANCE OF AN

ADVANCED SINGLE CRYSTAL NICKEL BASED SUPERALLOY

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Abstract

The oxidation resistance of nickel based superalloys is strongly dependent on the composition and adherence of the oxide scale formed during exposure to an oxidizing environment. Cyclic oxidation testing was conducted on advanced nickel based superalloy single crystal test bars, modified with additions of elemental yttrium. A significant improvement in the oxidation resistance of the single crystal test bars was achieved with yttrium additions greater than 200 ppm. The retained yttrium content of the test bars was directly related to the concentration of yttrium added. These results can be explained based on the interactions of yttrium and sulfur at the oxide/alloy interface as well as sulfur being tied up as innocuous compounds in the alloy.

Background

The oxidation resistance of nickel based superalloys is strongly dependent on the composition of the oxide scale formed during exposure to an oxidizing environment. For adequate protection from the atmosphere of a gas turbine engine, alumina (Al_2O_3) forming superalloys are preferred over chromia (Cr_2O_3) formers. Alumina will not volatilize at typical gas turbine operating temperatures (i.e., > 1100°C) and will strongly bond to the underlying superalloy. However, even low concentrations of tramp elements such as sulfur in the alloy can severely degrade oxidation resistance. (1,2) At elevated temperatures, diffusion of these elements to the oxide/alloy interface will severely weaken the bond at this interface causing rapid scale exfoliation. Yttrium additions have been shown to dramatically improve the oxidation resistance of nickel based superalloys, although the exact mechanism is not fully understood. (3-5) It has been theorized that yttrium reacts with sulfur in the alloy forming innocuous compounds which prevent the diffusion of these elements to the oxide/metal interface. (5) Consequently, it is the objective of this research to characterize the interactions between yttrium, sulfur, and phosphorous during cyclic oxidation of an advanced nickel based superalloy.

Materials and Procedures

Single crystal test bars (1.27 cm dia.) of an advanced nickel based superalloy, PWA 1484, were cast using conventional foundry ceramics and equipment. The nominal composition of PWA 1484 is shown in Table I. Elemental yttrium was added to the alloy ingots at the casting unit prior to melting in the following concentrations: 0, 20, 200, 500, 1000, 1500, and 2000 ppm. The molten alloy was heated to 1510°C and then poured into a mold which was also heated to 1510°C. The mold was withdrawn from the hot zone at 25.4 cm/h. Chemical analyses were performed on representative test bars from each mold. All material was solution treated and aged using conventional parameters for this alloy.

Table | Nominal Composition of PWA 1484

Alloy Elements	Ni	Со	Та	W	Αl	Cr	Re	Мо	Hf
Nominal Composition(wt.%)	Bal	10.00	8.70	5.90	5.65	5.00	3.00	1.90	0.10

Cyclic oxidation tests were performed on the alloy ingots and fully heat treated castings using the following cycle: 1177°C/23h/air + 23°C/1h/air. Four samples per condition were evaluated. Samples from the alloy ingots measured approximately 0.95 cm x 0.95 cm x 2.54 cm., while those from the castings were 1.27 cm dia. x 2.54 cm long. Test specimens were weighed and visually inspected every 24 hours. The cyclic oxidation tests were continued until the specimens had been exposed for 504 hours. Weight change (mg/cm²) versus time plots were developed from the data.

Electron microprobe evaluations were also conducted to characterize the effects of sulfur in the castings. X-ray mapping was used to determine the interactions between yttrium, sulfur, and other alloying elements.

<u>Results</u>

Chemical analyses showed that all single crystal test bars met current specifications for PWA 1484. Table II lists the results of the chemical analyses for yttrium and sulfur. In all the test bars, only 10% of the yttrium added to a given ingot was retained in the final casting. The average sulfur contents were unaffected by the concentration of yttrium added or retained and did not appreciably increase as a result of processing with conventional ceramics and equipment.

Table II Chemical Analyses of PWA 1484
Alloy Ingots and Castings

	 			
ppm Y		ppm Y	ppm S	
Added	Location	Retained	Present	
0	Тор	<1	2	
	Middle	< 1	1	
ł	Bottom	< 1	4	
	Average	<1	2	
20	Тор	2	1	
1	Middle	3	4	
	Bottom	2	1	
	Average	2	2	
200	Тор	17	2	
	Middle	12	3	
	Bottom	27	1	
	Average	19	2	
500	Тор	70	1	
	Middle	61	5	
	Bottom	38	1	
	Average	56	2	
1000	Тор	111	1	
	Middle	100	2	
	Bottom	79	1	
	Average	97	1	
1500	Тор	214	1	
	Middle	215	3	
	Bottom	155	2	
	Average	195	2	
2000	Тор	197	1	
	Middle	220	1	
	Bottom	182	11	
	Average	200	11	
Ingot		<1	2	

Figure 1 illustrates the results from the 504 hour cyclic oxidation testing on the yttrium modified PWA 1484 castings. Excellent oxidation resistance was observed for those specimens with a 200 to 2000 ppm Y addition, while test bars with a 0 or 20 ppm Y addition showed significant weight losses. The oxide scale formed on the former specimens had a blue tint and was adherent. The scale on the latter specimens was black, spalled readily, and had areas which appeared glassy. These glassy areas were found to be predominantly nickel and chromium rich and spalled rapidly.

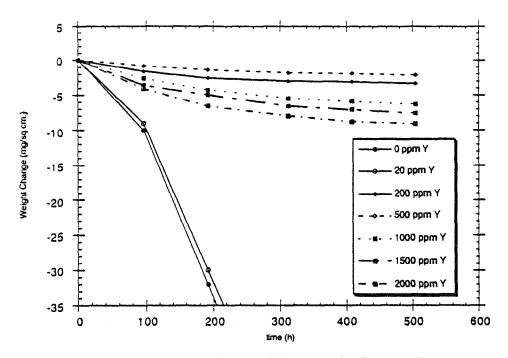


Figure 1 - 1177°C cyclic oxidation results for single crystal cast yttrium modified PWA1484 test bars

Figure 2 illustrates the effect of the added and retained yttrium content of the alloy on the average weight change of the specimens at 504 hours. As suggested in Figure 1, there is a pronounced improvement in the oxidation resistance of the castings with greater than 200 ppm Y addition (19 ppm Y retained). The data indicate a minimum 200 ppm Y addition is required to significantly improve the oxidation resistance of PWA 1484.

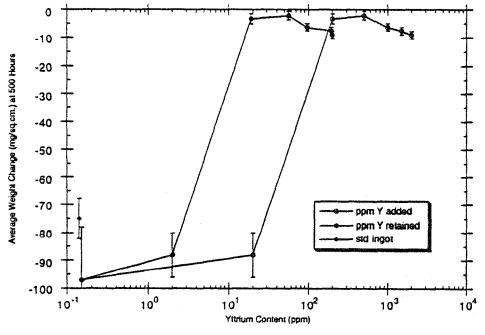


Figure 2 - Average weight change at 500 hours for ingots and test bers

Electron microprobe evaluations on representative yttrium modified PWA 1484 test bars following cyclic oxidation testing are shown in Figure 3. In test bars which did not contain

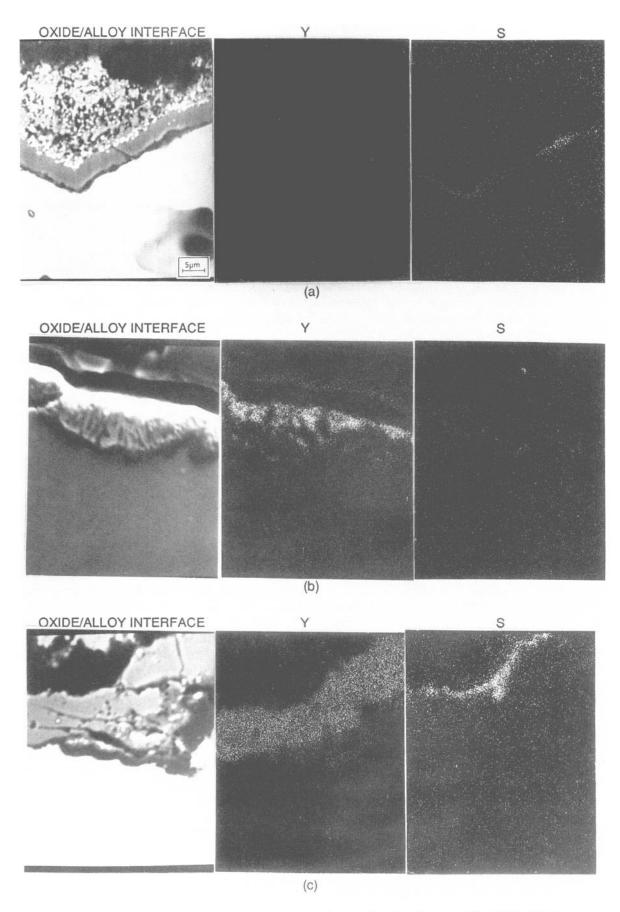


Figure 3 - Oxide/Alloy interfaces at 504 hours for test bars with (a) 0 ppm, (b) 1000 ppm, and (c) 1500 ppm yttrium additions.

yttrium additions or had an addition below 200 ppm, sulfur was observed to be present at the oxide/alloy interface, Figure 3a. In the micrograph shown, the oxide is almost completely separated from the alloy and ready to spall off. Conversely, significant yttrium diffusion to the oxide/alloy interface was observed in test bars which had yttrium additions greater than 200 ppm, Figure 3b. Where sulfur had diffused to the oxide/alloy interface in these test bars, Figure 3c, yttrium was found to have tied up this element. The oxide scales in these latter test bars are adherent.

Discussion

Table II indicates that only 10% of the yttrium added to the alloy was retained in the test bars with no appreciable variation in sulfur content. Previous research suggests that yttrium is reacting with and being absorbed by the ceramic mold but is not removing sulfur from the alloy. The low yttrium also could result from volatilization of this element during vacuum induction melting. Thermodynamic calculations indicate that the equilibrium yttrium vapor pressure above the liquid is approximately 17 μ m. However, since the casting chamber is continually evacuated, equilibrium would not be reached. Consequently, yttrium volatilization would occur continuously during single crystal solidification.

Figures 1 and 2 show that a minimum 200 ppm yttrium addition is required to improve the cyclic oxidation resistance of PWA 1484 test bars. Figure 3 indicates that yttrium improves oxidation resistance by tying up sulfur at the oxide/alloy interface and/or improving the bond between the alloy and the protective oxide scale. Thermodynamic data indicate that yttrium oxysulfide (Y_2O_2S) is the most stable sulfur bearing compound formed by these elements ⁽⁸⁻¹⁰⁾. Therefore, to completely tie up all the sulfur in the alloy would require a retained yttrium content equal to six times the sulfur concentration of the alloy (on a weight percent basis). Based on the chemical analysis results, the minimum required yttrium addition would be 60 times the sulfur content. Since the average sulfur content is 2 to 3 ppm, the minimum yttrium addition required is approximately 120 to 180 ppm. This is consistent with the data presented above.

Figures 1 through 3 and Table II also suggest that the retained yttrium content of the test bars is more important than the amount of yttrium added during casting. The oxidation results for the test bars with additions of 20 ppm (2 ppm retained) and 200 ppm (19 ppm retained) yttrium indicate a significant improvement in the oxidation resistance of the latter test bars. Since yttrium appears to be tying up sulfur at the oxide/alloy interface, having sufficient retained yttrium (i.e., six times the sulfur content) in the alloy would be necessary for excellent oxidation resistance. If, on the other hand, a yttrium addition equal to six times the sulfur content was sufficient to tie up all the sulfur at the oxide/alloy interface, then the oxidation resistance of these two groups of test bars would be expected to be similar. Clearly, this is not the case, indicating the retained yttrium content is of greater importance.

Conclusions

- 1. Yttrium retention in single crystal PWA 1484 test bars was extremely low (<10%). This is the result of reactions between the molten alloy and foundry ceramics and yttrium volatilization during melting and solidification.
- 2. The oxidation resistance of PWA 1484 test bars is dramatically improved by the addition of greater than 200 ppm yttrium. The minimum yttrium addition required is approximately equal to sixty times the sulfur content of the alloy.
- 3. The retained yttrium content of the test bars is of greater importance than the amount of yttrium added during casting. This is evidenced by the difference in oxidation resistance of the PWA 1484 test bars modified with 20 and 200 ppm yttrium additions.

<u>Acknowledgements</u>

This work was supported by Howmet Corporation internal research and development funds. Also, thanks to D. Parille and D. Duhl (Pratt & Whitney) for technical discussions during the course of this work.

References

- 1. J.G. Smeggil, A.W. Funkenbusch, and N.S. Bornstein, Met. Trans. A, 17, (1986), 923 -932.
- 2. P.D. Mercia and R.G. Waltenburg, U.S. Nat. Bur. Std. Tech. Paper No. 281, 1925.
- 3. J.K. Tien and F.S. Pettit, Met. Trans., 3, (1972), 1587-1595.
- 4. F.A. Golightly, F.H. Scott, and G.C. Wood, Oxid. Met., 10, (1976), 163-168.
- 5. J.G. Smeggil, A.W. Funkenbusch, and N.S. Bornstein, Met. Trans. A, 16, (1985), 1164-1170.
- 6. M.J. Straszheim, private communication with author, Howmet Corporation, 1988.
- 7. E.A. Brandes, 6th ed., <u>Smithell's Metals Reference Book</u>, (London, England, Butterworths, 1983), 8-56.
- 8. K.A. Gshneidner and N. Kippenhan, <u>Thermochemistry of the Rare Earth Carbides</u>, <u>Nitrides</u>, and <u>Sulfides for Steelmaking</u>, <u>IS-RIC-5</u>, Rare Earth Information Center, Ames, lowa, (1973), 17-21.
- 9. K.A. Gshneidner, N. Kippenhan, and O.D. McMasters, <u>Thermochemistry of the Rare</u> Earths, IS-RIC-6, Rare Earth Information Center, Ames, Iowa, (1973), 7-45.
- 10. J.J. Pak and R.J. Fruehan, Met. Trans. B, 18, (1987), 687-693.