Oxidation of Low Sulfur Single
Crystal Nickel-Base Superalloys

R.V. McVay, P. Williams, G.H. Meier, F.S. Pettit
Materials Science and Engineering Department
University of Pittsburgh
Pittsburgh, PA

and

J.L. Smialek
NASA Lewis
Cleveland, OH

Abstract

The influence of hafnium, yttrium and sulfur concentration on the oxidation resistance of single crystal, nickel base superalloys are compared at 1100°C in air. Both hafnium and yttrium improve oxidation resistance but the effects of yttrium are substantially greater than hafnium. Treatments to remove sulfur very significantly improve the oxidation resistance of superalloys. The effects of sulfur and oxygen active elements on superalloy oxidation resistance are examined.

Introduction

Nickel base superalloys usually contain aluminum and chromium at concentrations such that continuous scales of either Al_2O_3 or Cr_2O_3 are formed on such alloys during oxidation at temperatures between 700° and 1150°C. The alloys upon which Al_2O_3 scales are formed have better oxidation resistance than those superalloys that are Cr_2O_3-formers because transport through Al_2O_3 scales is slower than diffusion in Cr_2O_3.[1] For extended use at temperatures above about 900°C, however, all types of nickel base superalloys require coatings for protection from oxidation. Typical coatings that are used are diffusion aluminides or MCrAlY coatings deposited by physical vapor deposition or by plasma spray processes[2]. Some nickel base superalloys are now fabricated such that no grain boundaries are present in them but interphase interfaces (e.g. γ-γ') do exist. Such superalloys do not require grain boundary strengtheners such as carbon, boron or zirconium and consequently the "single crystal" superalloys usually contain fewer elements than their polycrystalline counterparts. A number of different fabricators currently produce these superalloys with slight variations in composition. Nickel, chromium, aluminum, cobalt and titanium are present at slightly different levels in all of these alloys. The elements tantalum, molybdenum and tungsten are also usually present but the concentration levels vary depending on the fabricator. The single crystal superalloys have aluminum concentrations sufficient to form external alumina scales during oxidation, and their oxidation resistances generally are superior to many of their polycrystalline predecessors[3].

In order to develop oxidation resistance in alloys it is well established[1,4,5] that an element such as aluminum in the alloy must be selectively oxidized to form a continuous external scale which is resistant to cracking and spalling. Moreover, in cases where the selectively formed oxide does spall it is necessary for selective oxidation to occur on the alloy surface exposed because of spalling. A number of factors affect the selective oxidation process[1,4,5]. The concentration of the element to be selectively oxidized is a critical factor, but other elements can also be important as well as the microstructure of the alloy itself. The adherence of the oxide scale is crucial to oxidation resistance. It is now well established that elements such as yttrium, hafnium and cerium (oxygen active elements) can be used to very substantially improve oxide scale adherence[1,5]. Yttrium is present in MCrAlY coatings to improve the adherence of Al_2O_3 scales to these coatings.

While the effects produced by oxygen active elements on oxide scale adherence are widely known, there is not agreement in regards to the mechanisms to account for how these elements influence adherence. Over the past fifty years a number of mechanisms have been formulated[6-8]. These mechanisms extended from mechanical pegs to key the oxide to the alloy substrate to stress relief mechanisms for the oxide scale. More recently some investigators[9,10] have proposed that scales such as Al_2O_3 possess good adherence to metallic substrates, and that sulfur may segregate to oxide-alloy interfaces to adversely affect this adherence. Moreover, the effect of the oxygen active elements, which also are extremely sulfur active, is to combine with sulfur and prevent it from segregating to the oxide-alloy interfaces. Some investigations have given results to support this mechanism, whereas others do not[11-14]. Hydrogen annealing has been shown to reduce the sulfur content of PWA 1480 (< 0.1 ppm), a nickel base single crystal superalloy, resulting in a dramatic increase in scale adhesion[13].

The present paper is concerned with comparing the oxidation resistances of single crystal superalloys to those with low sulfur concentrations and to those superalloys that contain oxygen active elements such as Hf and Y.

Experimental

The single crystal superalloys that were used in this investigation were prepared by Pratt and Whitney. The nominal compositions of these alloys are presented in Table I. The alloy PWA 1480 did not contain any oxygen active elements whereas PWA 1484 contained Hf and PWA 1487 contained both Hf and Y. The alloys PWA 1484 and PWA 1487 also contained Re.

Smialek[12] has developed a procedure to decrease the sulfur content of alloys by heating thin (i.e. less than 0.1 cm) specimens in dry flowing hydrogen at 1200°C. This procedure was used to remove sulfur from some of the specimens used in the present investigation. The gas flow rate was 470cc/min. and the oxygen pressure in the flowing hydrogen was estimated to be about 1.6×10^{-23} atm. The samples were annealed in four 25 hour treatments. Usually the specimens lost weight during these hydrogen anneals as shown for PWA 1480 in Figure 1. However, weight gains were observed for some samples, Table II, probably due to some moisture in the gas.

Prior to the sulfur removal treatment all of the specimens were polished through 600 grit SiC paper. After the sulfur removal treatment the specimens were polished again with 600 grit paper and washed with soapy water and rinsed in methanol. Cyclic oxidation was performed in laboratory air at 1100°C. A cycle consisted of 45 minutes in the furnace hot zone and 15 minutes in the cold zone. Weight change versus time measurements and visual examination of the exposed specimens were performed at various time intervals. Initially the time intervals were small (e.g. 1, 2, 4, 8, 16, 24 hours) but once it was determined that adherent Al_2O_3 scales had developed, the observation intervals were usually every week (~ 160 hours). All specimens were disk-shaped (~ 1 cm in diameter). Specimens given the desulfurizing treatment were less than 0.1 cm thick and should have had the sulfur reduced to < 0.1 ppm[13]. The other untreated specimens were about 0.1 to 0.3 cm in thickness. The cyclic tests were continued until the weight change data and visual examinations showed that the specimens were no longer Al_2O_3 formers. Some isothermal experiments were performed at 1100°C to obtain the rate constants for oxidation. After exposure all specimens were examined in detail using optical metallography, the SEM, and XRD.

Results and Discussion

The weight change versus time measurements for all of the alloys during isothermal oxidation in air at 1100°C approached a parabolic rate law, after a transient period, with parabolic rate constants in good agreement with those for growth of α-Al_2O_3 scales[1] (e.g. 1.5×10^{-13} $g^2/cm^4 \cdot s$). Visual examination of the specimens after oxidation showed that the oxidation products defined the cast microstructure of the alloys, Figure 2. Such structures show that the alloys had undergone transient oxidation prior to the development of a continuous Al_2O_3 layer over the surfaces of the specimens. More transient oxidation had occurred over the dendrite-shaped phase.

The results obtained from the weight change versus time measurements during the cyclic oxidation tests are presented in Figures 3 and 4 for PWA 1480, PWA 1484 and PWA 1487. These results show the following:

- The oxidation resistance of PWA 1487 is better than that of PWA 1484 which in turn is better than PWA 1480.

- The treatment to remove sulfur from these alloys has very substantially improved the oxidation resistances of PWA 1480 and PWA 1484, Figure 3. The cyclic oxidation test was not performed long enough to determine if the hydrogen pretreatment affected the oxidation resistance of PWA 1487.

All of the cyclically oxidized specimens were examined metallographically upon conclusion of this test. A cross-section of an exposed specimen typical of low sulfur PWA 1480, PWA 1484 and PWA 1487, as well as untreated PWA 1487 is presented in Figure 5. A protective scale of Al_2O_3 was evident. These scales exhibited an outer zone of Al_2O_3, containing both chromium and nickel, and an inner zone of virtually pure Al_2O_3. In the case of those alloys containing Hf and Y protrusions of the oxide scale into the alloy were evident. These protrusions were found to contain yttrium, hafnium and aluminum. All of these specimens also contained voids in the alloy substrate, Figure 6. In the case of the thin low sulfur specimens the voids extended completely through the specimens but were located in the alloy just beneath the external scale in the thicker specimens. These voids were not present in the specimens prior to oxidation, nor in the specimens from the shorter time isothermal experiments. The voids had to be formed during oxidation. The specimens that exhibited large weight losses in the cyclic oxidation, namely untreated PWA 1480 and PWA 1484 were also examined metallographically. Continuous scales of Al_2O_3 were not evident. The oxide scales were composed of discontinuous Al_2O_3 and Cr_2O_3 as well as a substantial amount of NiO.

The results that have been obtained show that the oxygen active elements Hf and Y improve the oxidation resistances of these type superalloys by inhibiting spalling of Al_2O_3 scales from these alloys. The results also show that the pretreatment used to attempt to remove sulfur from these alloys very significantly improves oxidation resistance. For example pretreated alloys of PWA 1480 and PWA 1484 have better oxidation resistance than PWA 1480 with a diffusion aluminide coating, Figure 7. This pretreatment causes the adherence of Al_2O_3 to be improved and the alloy can also reform Al_2O_3 when spalling of the scale occurs, although this condition may be due to less aluminum depletion of the alloy resulting from less spalling of the oxide scales.

The fact that the oxidation resistance of PWA 1480 is increased by the hydrogen anneal strongly supports the argument that sulfur has been removed from the alloy, which otherwise would have segregated to the Al_2O_3 - alloy interface to enhance cracking and spalling. The cause of the improvement of the oxidation resistance of PWA 1484 is less clear. Hafnium should getter sulfur. It is possible that the hydrogen treatment lowers the sulfur concentration to lower levels than those produced by the hafnium gettering action. It is also possible that the gettering of sulfur by hafnium, or any other effects improving oxide scale adherence, require long times at temperatures such as 1100 and 1200°C. The results clearly show that the oxidation resistance of PWA 1487 is much better than that of PWA 1484. This condition must be due to the yttrium in PWA 1487. Yttrium may be a better sulfur getter than hafnium. If that is the case, the hydrogen anneal should not affect the oxidation resistance of PWA 1487 as substantially as it has the resistance of PWA 1484. It is also possible that a synergistic effect exists between the two reactive elements such that they are more effective when present together.

Conclusions

The results clearly show that the removal of sulfur very substantially improves the oxidation resistance of superalloys such as PWA 1480 which do not contain any oxygen

active elements. More experiments must be performed to examine the relationship between the sulfur concentration in superalloys and the effects produced by hafnium and yttrium. It is also clear that vacancy condensation occurs in superalloys after long periods of oxidation. The implications of this latter condition still must be investigated.

Acknowledgements

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Table I

Nominal Compositions of Alloys in Weight Percent

Alloys	Cr	Co	W	Mo	Ta	Ti	Al	Y	Hf	Re
PWA 1480	10	5	4	-	12	1.5	5	-	0	-
PWA 1484	5	10	6	2	8.7	1	5.6	-	0.1	3
PWA 1487	5	10	6	2	8.7	1	5.6	~0.1	0.1	3

Table II

Weight Change of Superalloy Specimens After 100 Hours at 1200°C in Flowing Hydrogen

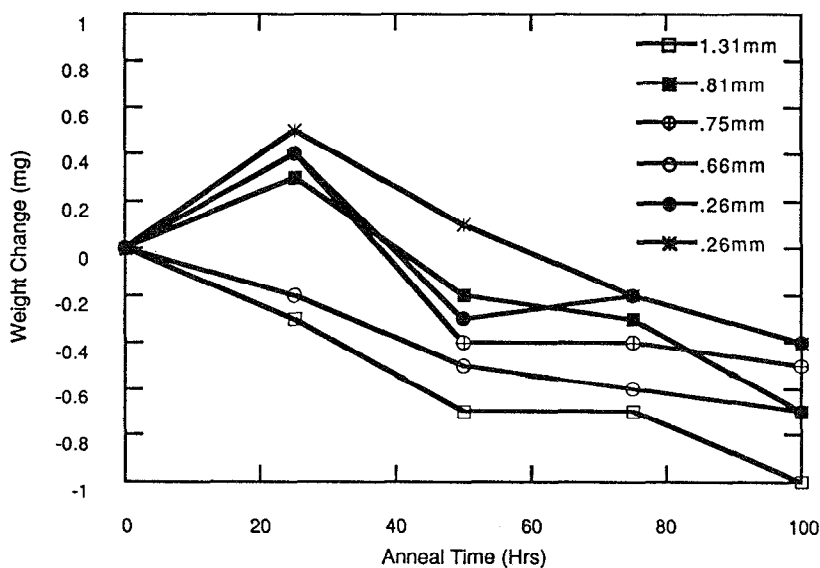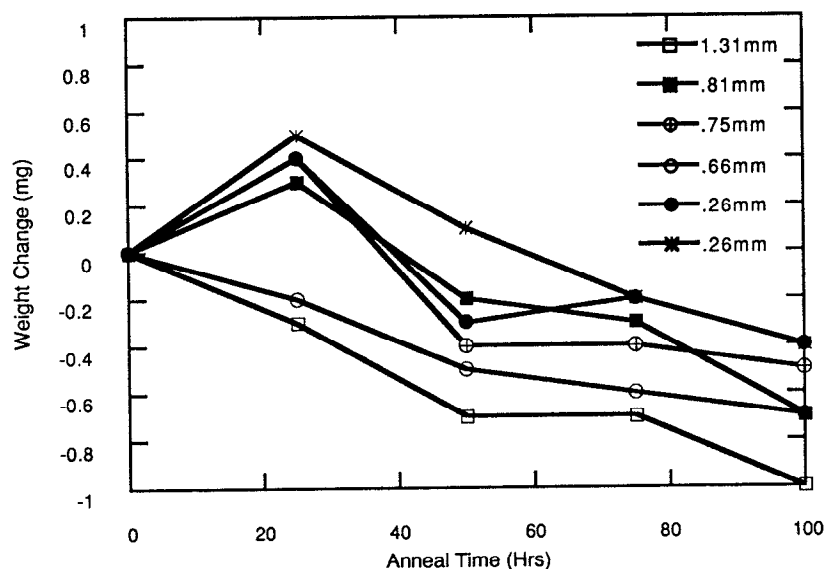|	PWA 1480			PWA 1484			PWA 1487	
	Specimen			Specimen			Specimen	
	1	2	3	1	2	3	1	2
Weight change (mg)	0.8	-0.8	-0.3	0.1	1.1	0.4	0.1	1.5

Figure 1 -   Weight changes of PWA 1480 (thicknesses are given in legend) observed after heating at 1200°C in flowing, dry hydrogen at 1 atm pressure.

12.   J.L. Smialek, "Effect of Sulfur Removal on Al$_2$O$_3$ Scale Adhesion", Met Trans., 22A (1991) 739-752.

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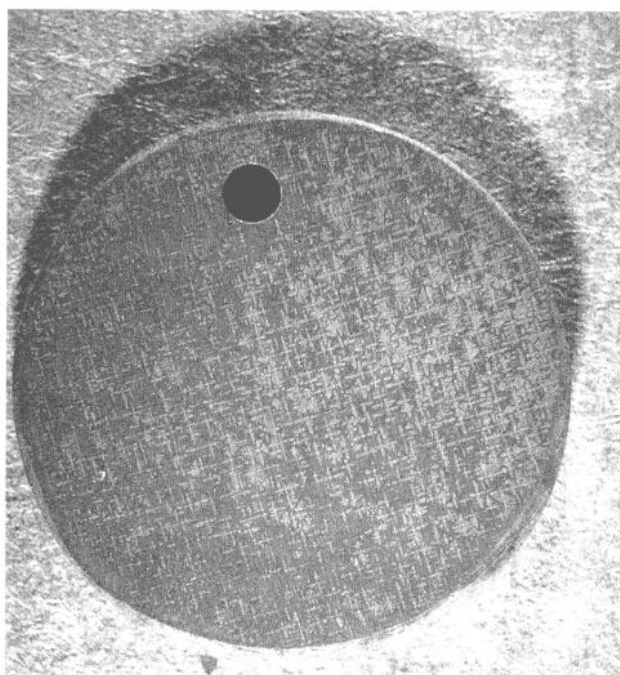
Figure 2 -   Photograph showing the surface morphology of PWA 1487 after 168
hours of oxidation in air at 1100°C. The specimen (1 cm in dia.) has
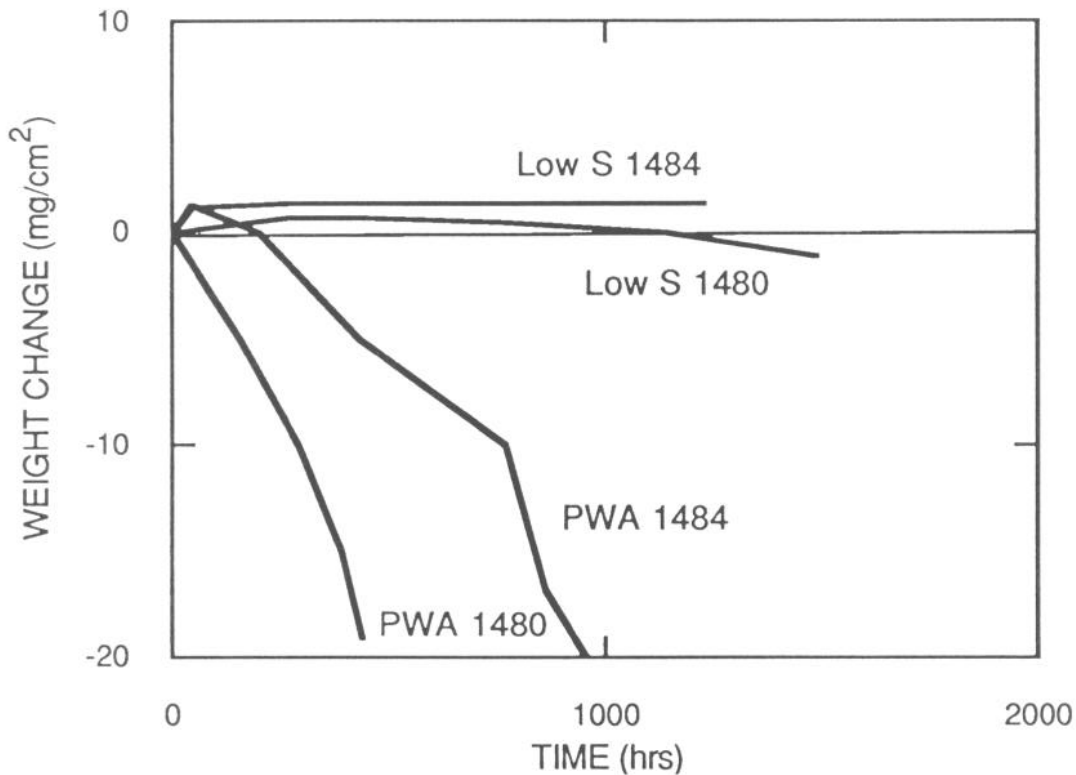formed different oxidation products at different location upon its
surface.

Figure 3 -   Weight change versus time measurements obtained for the cyclic
oxidation at 1100°C in air of untreated and pretreated specimens of
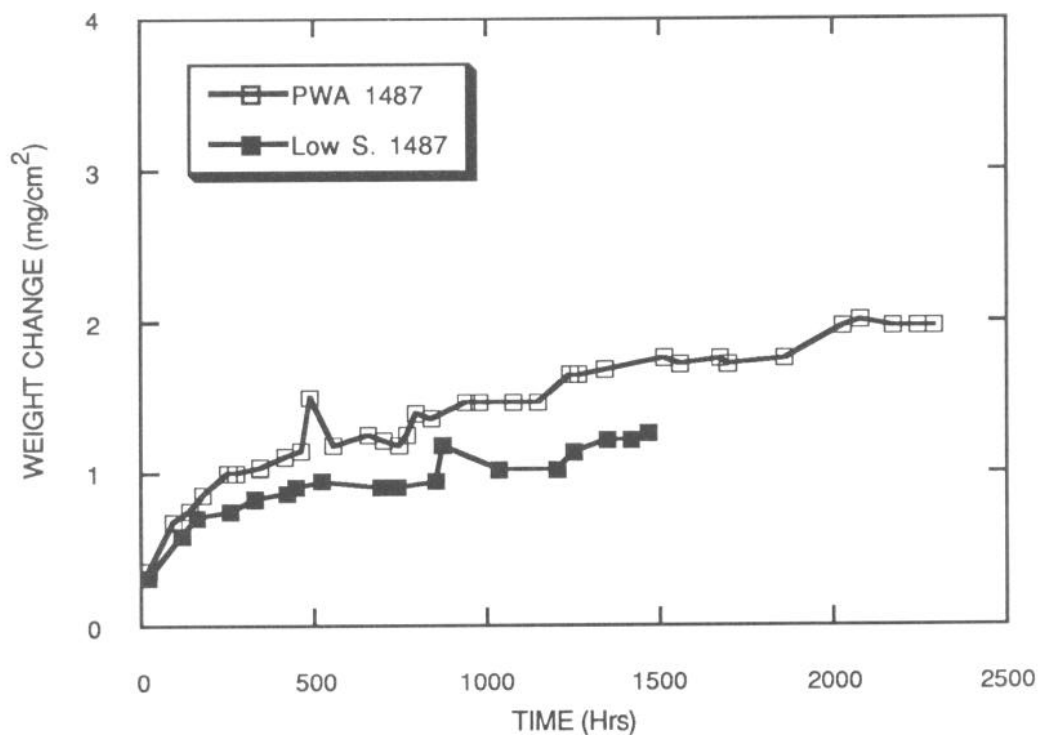PWA 1480 and PWA 1484.

Figure 4 - Weight-change versus time measurements obtained for the cyclic oxidation of PWA 1487 and low sulfur PWA 1487 at 1100°C in air.
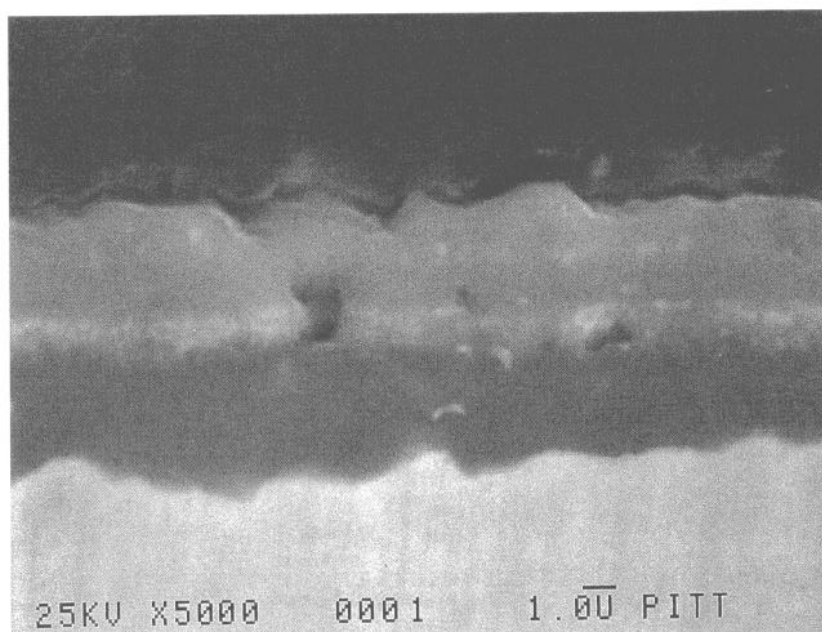

Figure 5 - Scanning electron micrograph of the oxide scale observed on low sulfur PWA 1487 after 1460 hours of cyclic oxidation in air at 1100°C. The inner zone is α-Al$_2$O$_3$ whereas the outer is Al$_2$O$_3$ containing chromium and nickel.
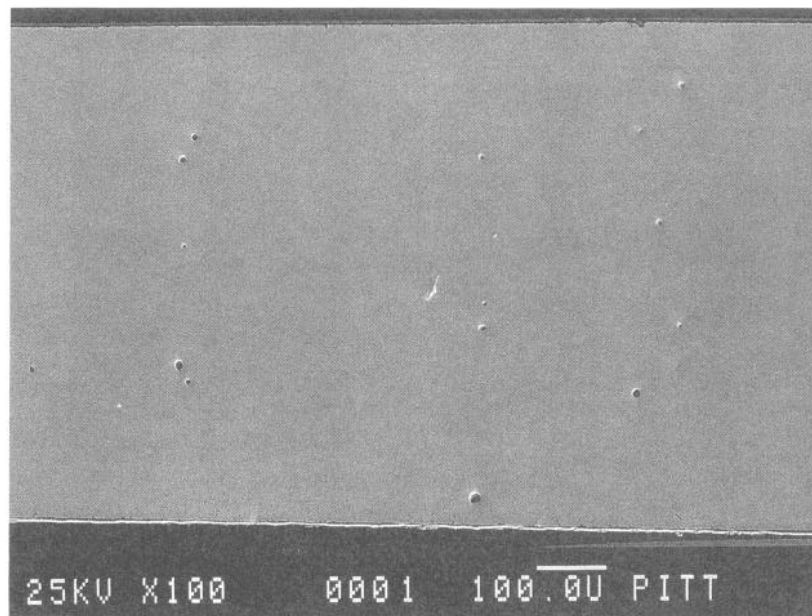
Figure 6 - Cross sectional micrograph of low sulfur PWA 1487 after 1460 hours of cyclic oxidation showing voids in the alloy substrate.
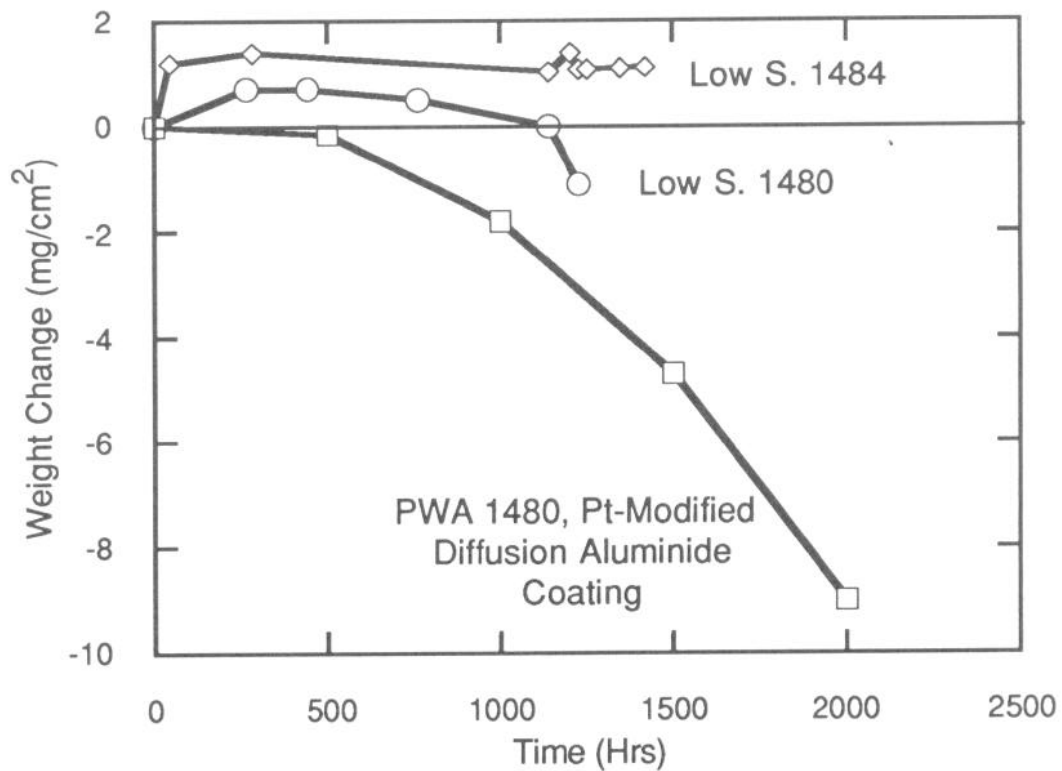

Figure 7 - Weight-change versus time measurements obtained for the cyclic oxidation (1100°C, air) of some low sulfur alloys and PWA 1480 with a diffusion aluminide coating.