THE EFFECT OF HYDROGEN ANNEALING AND SULFUR CONTENT ON THE OXIDATION RESISTANCE OF PWA 1480

JAMES L. SMIALEK
NASA Lewis Research Center

INTRODUCTION

For many decades the dramatic effect of trace amounts of reactive elements on alumina and chromia scale adhesion has been recognized and widely studied. Although various theories have been used to account for such behavior, the connection between scale adhesion and sulfur segregation was initially reported by Smeggil et al., 1986 (ref. 1). This study found strong surface segregation of sulfur from very low levels in the bulk, which could then be curtailed by the addition of reactive elements. It was assumed that the reactive elements, which are strong sulfide formers, acted by gettering sulfur in the bulk, thus precluding sulfur segregation and weakening of the oxide-metal bond. Subsequent studies confirmed that adhesion could be produced by reducing the sulfur impurity level, without reactive elements (ref. 2,3).

The understanding of this phenomenon has been applied to modern single crystal superalloys (figures 1, 2; ref. 4), where the addition of Y, although very effective, is problematic. Also problematic is definition of the level of sulfur that is acceptable and below which no further adhesion benefit is reached. Published works have indicated a broad transition defined by various materials and oxidation tests.

The present study describes the oxidation behavior of one superalloy (PWA 1480) as a function of various sulfur contents produced by hydrogen annealing for various temperatures, times, and sample thicknesses. The purpose is to define more precisely a criterion for adhesion based on total sulfur reservoir and segregation potential (figure 3).

EXPERIMENTAL PROCEDURE

Oxidation coupons were electrodischarge machined from polycrystalline bar stock of PWA 1480, to 13 x 25 mm coupons with thicknesses of 0.25, 0.5, 1.3, 2.5, or 5.1 mm and polished through 600 grit emery. The starting sulfur content was determined to be about 6.2 ppmw by GDMS (glow discharge mass spectroscopy, Shiva Technologies). Hydrogen annealing was performed in a flowing H_2/Ar mixture for 8-100 hr at 1000°C to 1300°C, as indicated in figure 5. All samples were clean and metallic, with less than ± 0.03 mg/cm^2 weight change after annealing. Cyclic oxidation was performed in air at 1100°C (2012°F) with a cycle frequency of 1-hr, for up to 500 or 1000 hr. Scales were characterized by x-ray diffraction and SEM.

RESULTS AND DISCUSSION

Gravimetric Data

The effect of annealing temperature on the 1100°C cyclic oxidation weight change curves is shown in figure 6 for a specimen thickness of 0.5 mm (20 mils) and annealing time of 20 hr. The 1000° and 1100° C anneals did little to improve the cyclic oxidation resistance over that of the

as-received control sample, resulting in more than 20 mg/cm^2 weight loss after 500 1-hr cycles. The 1200° and 1300°C annealing treatments, however, resulted in 1000 hr weight changes of only +0.10 and -3.4 mg/cm^2, respectively. This represents a very significant improvement.

The effect of annealing time on oxidation behavior is shown in figure 7 for 0.5 mm (20 mil) samples annealed at 1200°C. Here a significant improvement was noted by only an 8 hr anneal, producing a weight loss of only 6.7 mg/cm^2 after 1000 hr. The 1000 hr weight changes of the 20, 50, and 100 hr samples were all excellent (+0.10, +0.36, and +0.16 mg/cm^2, respectively). Finally the effect of specimen thickness is shown in figure 8. Here a 20 hr anneal at 1200°C produced very adherent scales for 0.25 and 0.5 mm (10 and 20 mil) samples, but substantial weight losses for 1.3 and 2.5 mm (50 and 100 mil) thicknesses.

The dependence of adherence (as exhibited by the 500 hr cyclic oxidation weight change) can be seen as a function of annealing temperature, time, and sample thickness in figures 9-11. Weight losses are reduced dramatically for temperatures over 1200°C, times over 20 hr, and samples under 0.5 mm (20 mil) thickness. Each figure also shows the improved performance of longer anneal times, higher anneal temperatures, or thinner samples between the individual curves of each family.

Scale phases were identified from X-ray diffractometer scans as primarily Al_2O_3, $Ni(Al,Cr)_2O_4$, and $CrTaO_4$. A greater relative amount of Al_2O_3 is noted for the more oxidation resistant samples, and more $NiCr_2O_4$ and $CrTaO_4$ for the samples with poor oxidation resistance. SEM/EDS analysis revealed a complex multiphase segmented scale on the control sample with clusters of high Cr or Ta oxides as compared to a relatively uniform Al_2O_3 scale on the 0.5 mm sample annealed at 1200°C for 20 hr.

Effect of Sulfur Content

The effect of hydrogen annealing on sulfur content is summarized in figure 12. The sulfur content was progressively reduced as the annealing time and temperature increased and the thickness decreased. Many values in the 0.1-0.3 ppmw range were obtained. These levels had been associated with the most oxidation resistant samples in previous studies (ref. 4). The 500 hr weight change of all the samples tested is shown in figure 13 as function of the sulfur content for the 5 sets of sample thicknesses. For each curve, the final weight change diminishes from a relatively large loss at the starting sulfur content, becoming much less severe at about 1 ppmw, and extremely small at 0.1 ppmw. Despite scatter in the sulfur data, an overall detrimental trend with sample thickness can also be discerned (figure 14).

Adhesion Criteria

A fundamental approach has been suggested to define a critical sulfur content (ref. 5). This concept claims that a limit to an adhesion benefit is reached when the sample contains a total amount of sulfur less than that required to produce ~1 monolayer of segregation. The implication is that about one monolayer will produce significant spallation events, but, with no replenishment, it is unable to sustain repetitive degradation. The equivalence between bulk sulfur content and segregated monolayers has been approximated:

$$C_s \text{ (ppmw)} = (8.27 \times 10^{-2} \text{ gm/cm}^2) * N_m A/W \qquad \text{(ref. 5)}$$

where: C_s = bulk sulfur content in ppmw; N_m = number of segregated monolayers; A = sample surface area in cm^2; and W = sample weight in gm. The 1 monolayer criterion is shown on the "adhesion map"

of figure 16 for PWA 1480 samples of density = 8.42 gm/cm^3. The weight change data are represented by symbols, where the degree of shading corresponds to a weight change interval. The 0 and -10 mg/cm^2 contour lines obtained from figures 13 and 14 mark the transition from excellent adherence (solid symbols) to poorly performing (lightly shaded symbols). Excellent behavior is thus indicated for samples having a total sulfur content less than about one monolayer equivalent. This appears to be as good a criterion that can be made at this time, given the scatter in the sulfur data. It should also be noted that the thermodyanmic equilibrium surface concentration of sulfur at 0.1 ppmw bulk is predicted to be vastly reduced from the 30 % saturation value (ref. 4). Thus low bulk levels also produce low equilibrium segregation levels, which can then benefit scale adhesion regardless of specimen thickness.

CONCLUDING REMARKS

This study has shown the strong dependence of superalloy oxidation resistance on low levels of sulfur impurity contents. Extraordinary improvements are possible from desulfurization by hydrogen annealing. Typical sample thickness ~1 mm may be easily desulfurized to <1ppmw by annealing at 1200°C. Sulfur segregation is reduced which in turn produces excellent cyclic oxidation behavior at 1100°C (very small weight changes of only 0.5 to 1 mg/cm^2 after 1000 hours). A basic criteria of scale adhesion was developed which suggests that a critical sulfur content of 0.1-1 ppmw is required to obtain the maximum adhesion for alloys without Y. The benefit of low sulfur superalloys may be taken by reducing the amount of Y required, by operating without a coating, or by extending oxidative lives with coatings.

ACKNOWLEDGEMENTS

The author is grateful to D. Humphrey for performing the hydrogen annealing treatments.

REFERENCES

1) Smeggil, J.G., Funkenbusch, A.W., and Bornstein,N.S., "A Relationship between Indigenous Impurity Elements and Protective Oxide Scale Adherence Characteristics," Metall. Trans., Vol 17A, 1986, pp. 923-932.

2) Smeggil, J.G., "Some Comments on the Role of Yttrium in Protective Oxide Scale Adherence," Mater. Sci. and Engineer., Vol. 87, 1987, pp. 261-265.

3) Smialek, J.L., "Adherent Al_2O_3 Scales Produced on Undoped NiCrAl Alloys," Metall. Trans., Vol 18 A, 1987, pp. 164-167.

4) Smialek, J.L., "Oxidation Resistance and Critical Sulfur Content of Single Crystal Superalloys," Presented at IGTI, Birmingham, U.K., June 10-13, 1996; Paper 96-GT-519, ASME, 1996, pp. 1-7.

5) Smialek, J.L., "Effect of Sulfur Removal on Al_2O_3 Scale Adhesion," Metall. Trans., Vol. 22A, 1991, pp. 739-752.

Previous Studies Have Shown:

- Conventional SX superalloys contain ~3-10 ppmw sulfur impurity
- Unacceptable cyclic oxidation resistance (w/o Y)
- Sulfur segregation saturates at about 30 at.%
- Desulfurization improves scale adhesion (in melt or hydrogen annealing)
- 0.1 ppmw appears to be lower limit needed
- Acceptable upper limit still needs to be defined

Fig. 1

Correlation of Weight Change With Sulfur Content for the Oxidation of Superalloys

1100-1200 °C, 200-1500 hr

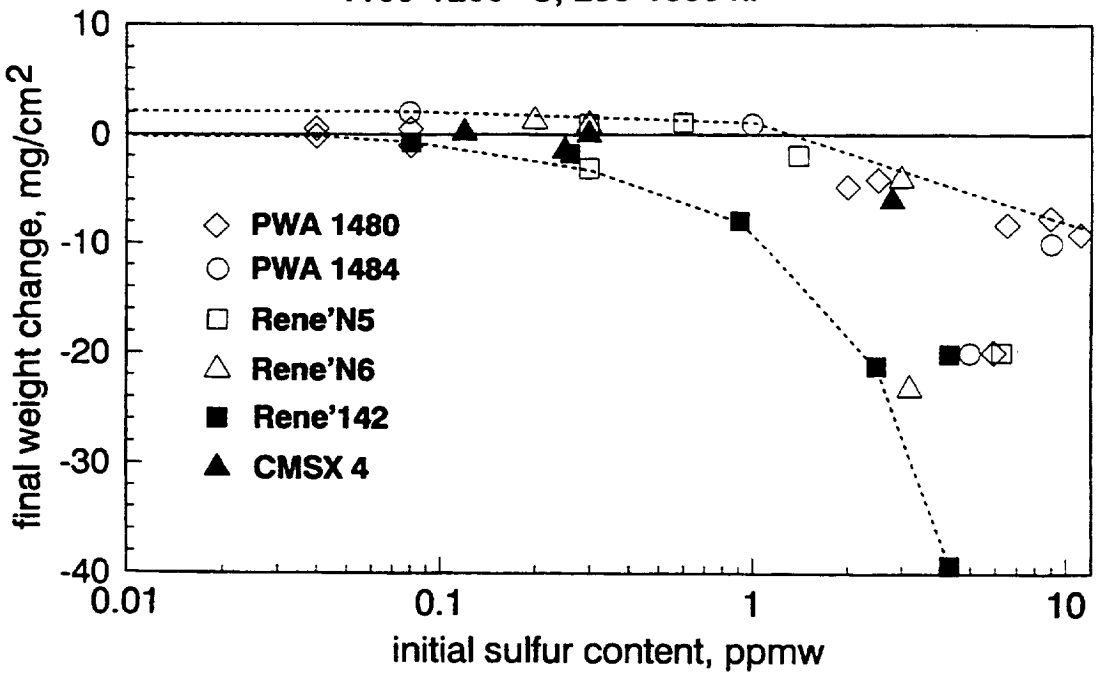

Fig. 2

Motivations

(Tubbs and Smialek, 1989; 1995)

- Hydrogen annealing effects on sulfur content (T, t, L)
- Sulfur diffusivity vs temperature
- Optimum annealing conditions

- Quantified sulfur effect on cyclic oxidation
- Critical sulfur content vs thickness:
  (adhesion map)
- Internally consistent data base:
  (one ingot, one anneal process, one oxidation test)

Fig. 3

Experimental Strategy

- Partial hydrogen annealing matrix: Dt/L^2
  - L: 10, 20, 50, 100, 200 mils (0.25 - 5 mm)
  - t: 8, 20, 50, 100 hr
  - D=A*exp(-Q/RT)
  - T: 1000°, 1100°, 1200°, 1300°C (1830-2370°F)
- GDMS measurement of ppm levels of sulfur
- Cyclic oxidation: 1100°C, 1-hr cycles, 500-1000 hr
- Weight change, XRD, SEM/EDS

Fig. 4

Selection of Hydrogen Annealing Parameters

(sample thickness, temperature, time)

	control	1000 °C	1100 °C	1200 °C	1300 °C
control	b,c				
8 hr		a		b,c	
20 hr		a,b	b	a,b,c,d	b,c, e
50 hr				b	
100 hr		a	d	a,b,c,d,e	d

a	b	c	d	e	
10	20	50	100	200	mils
0.25	0.5	1.3	2.5	5.1	mm

Fig. 5

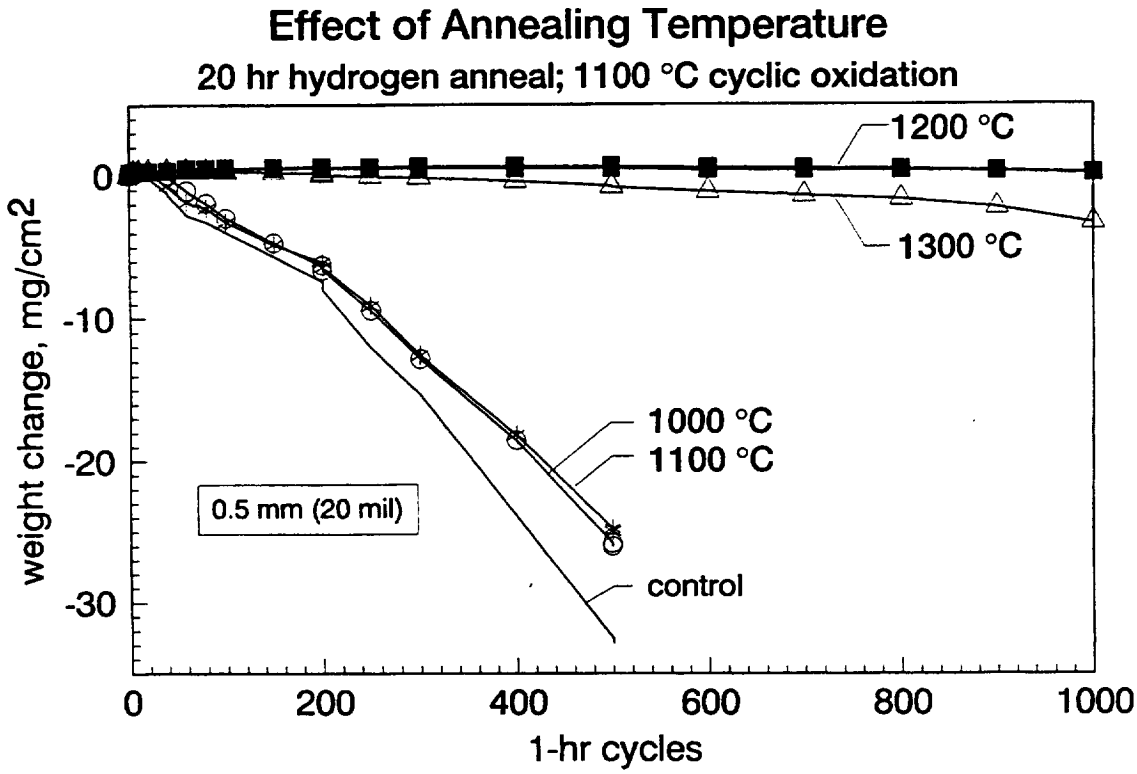

Fig. 6

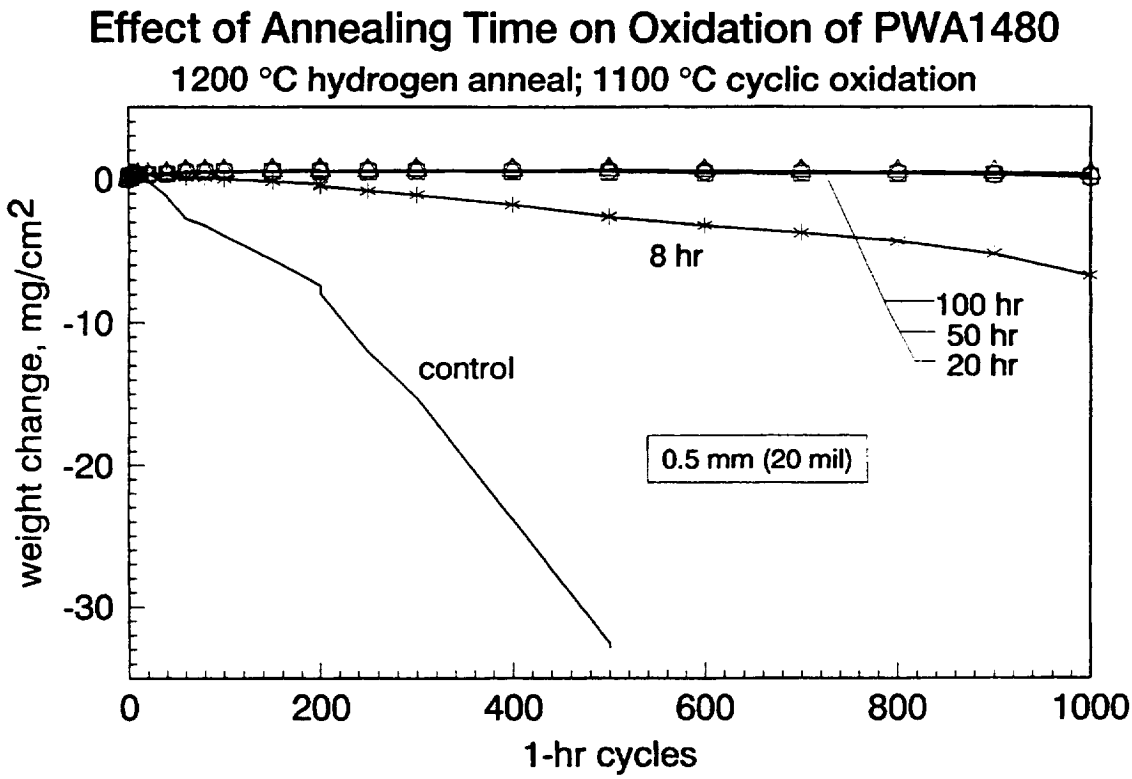
Effect of Annealing Time on Oxidation of PWA1480
1200 °C hydrogen anneal; 1100 °C cyclic oxidation
weight change, mg/cm2
0
-10
-20
-30
8 hr
100 hr
50 hr
20 hr
control
0.5 mm (20 mil)
0
200
400
600
800
1000
1-hr cycles

Fig. 7

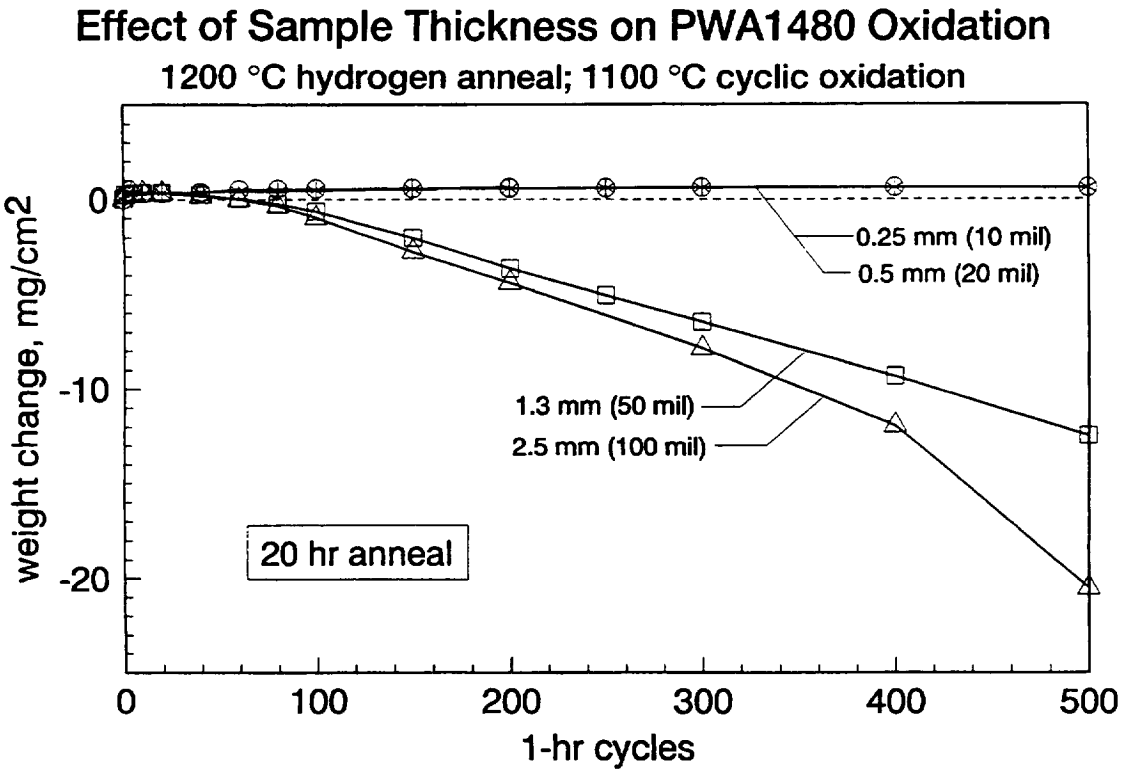
Effect of Sample Thickness on PWA1480 Oxidation
1200 °C hydrogen anneal; 1100 °C cyclic oxidation
weight change, mg/cm2
0
-10
-20
0.25 mm (10 mil)
0.5 mm (20 mil)
1.3 mm (50 mil)
2.5 mm (100 mil)
20 hr anneal
0
100
200
300
400
500
1-hr cycles

Fig. 8

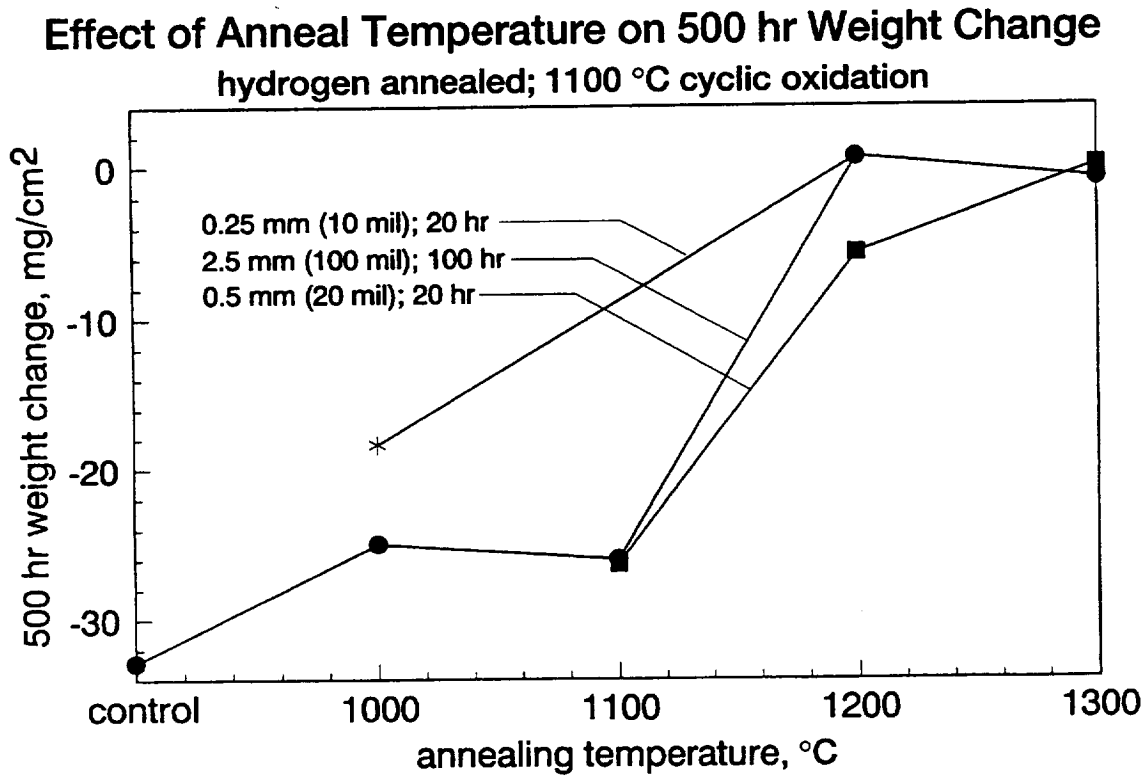
Effect of Anneal Temperature on 500 hr Weight Change
hydrogen annealed; 1100 °C cyclic oxidation
500 hr weight change, mg/cm2
0
-10
-20
-30
0.25 mm (10 mil); 20 hr
2.5 mm (100 mil); 100 hr
0.5 mm (20 mil); 20 hr
control
1000
1100
1200
1300
annealing temperature, °C

Fig. 9

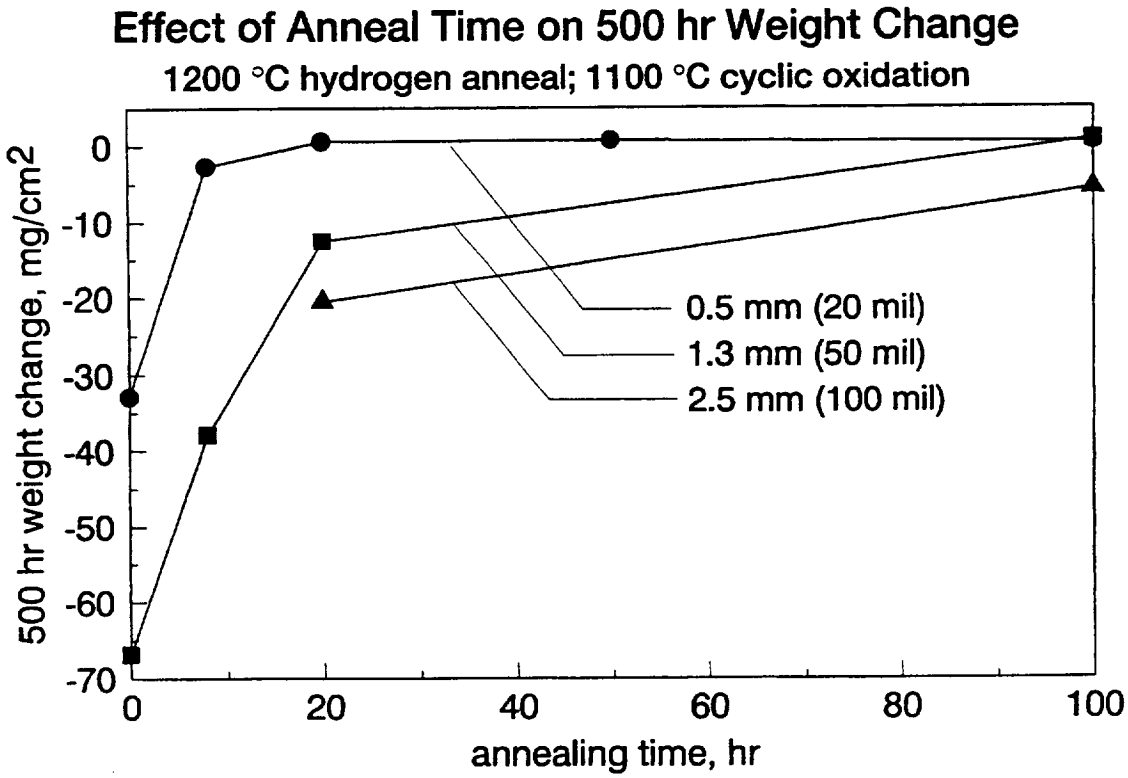
Effect of Anneal Time on 500 hr Weight Change
1200 °C hydrogen anneal; 1100 °C cyclic oxidation
500 hr weight change, mg/cm2
0
-10
-20
-30
-40
-50
-60
-70
0.5 mm (20 mil)
1.3 mm (50 mil)
2.5 mm (100 mil)
0
20
40
60
80
100
annealing time, hr

Fig. 10

Effect of Sample Thickness on 500 hr Weight Change

hydrogen annealed; 1100 °C cyclic oxidation

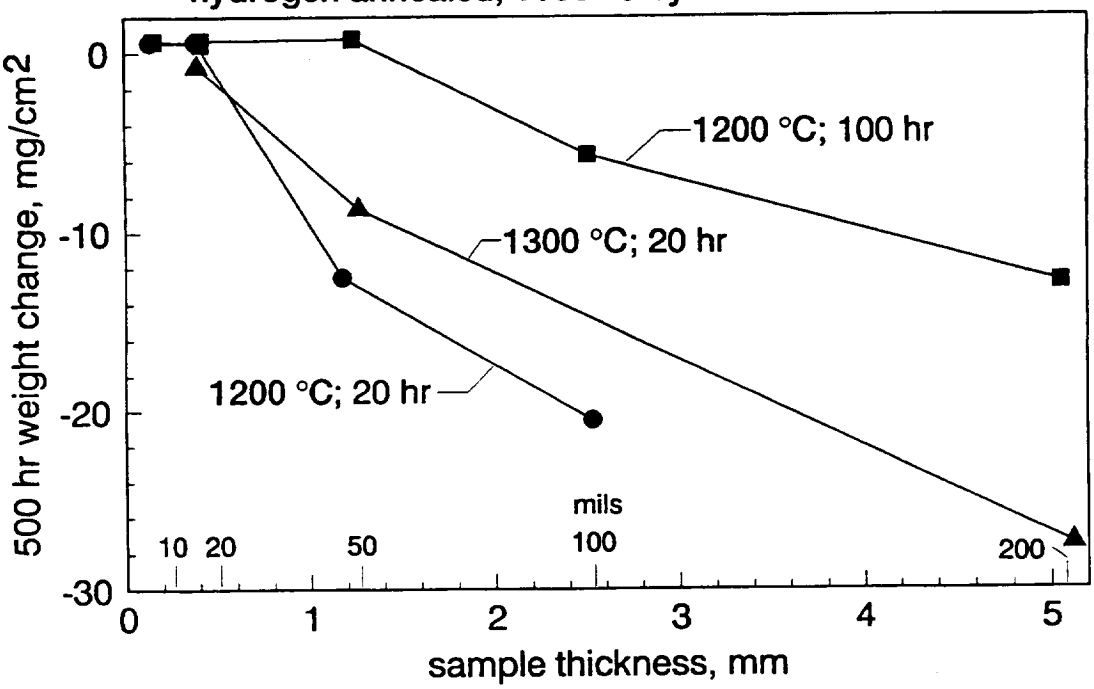

Fig. 11

Sulfur Content after Hydrogen Annealing

(vs sample thickness, temperature, time)

	control	1000°C	1100°C	1200°C	1300°C
control	6.2, 6.2 b, c				
8 hr		4.9 a		.8, 2.0 (b) c	
20 hr		4.6, 3.9 a, b	2.1, 2.6 b, c	.15 .28 1.5 1.5 (a) (b) c, d	.06 .34 3.3 (b) (c) e
50 hr				0.05 (b)	
100 hr		4.3 a	2.1 d	.12 .14 .12 .4 1.4 (a) (b) (c) (d) e	.01 (d)

key: (X) <1 ppmw S

a	b	c	d	e	
10	20	50	100	200	mils
0.25	0.5	1.3	2.5	5.1	mm

Fig. 12

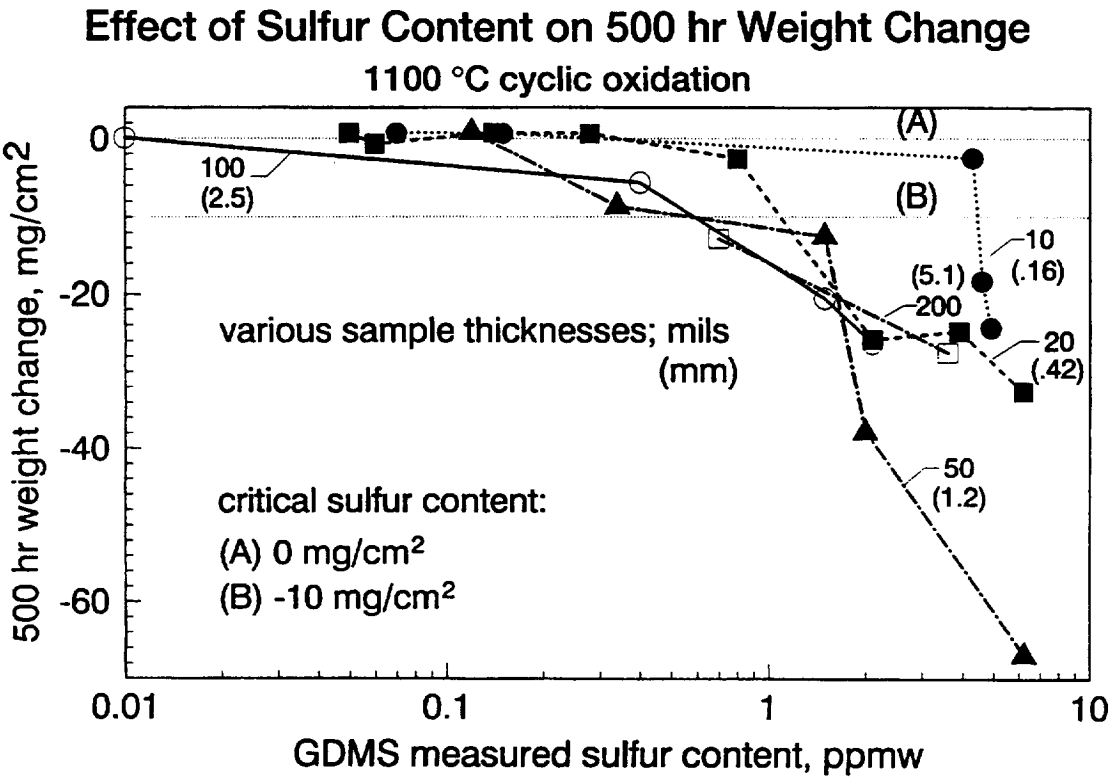

Fig. 13

Critical Sulfur Contents (ppmw) for PWA 1480
(1100 °C cyclic oxidation)

mg/cm²	10 (0.16)	20 (0.42)	50 (1.21)	100 (2.54)	200 mils (5.09) mm	(nom.) (avg.)
0.0	1.6	0.4	0.20	0.20	0.15	
-10.0	3.8	1.2	0.65	0.65	0.49	

Fig. 14

Equivalence Between Bulk and Surface Sulfur Content

(N_m= 1; one sulfur atom per one (001) Ni atom)

- C_s (ppmw) = 8.27 x 10^{-2} gm/cm^2 x $N_m A / \rho V$
- C_s x L ~ 8.27 x 10^{-2} cm x N_m

Fig. 15

Oxide Adherence Map for Desulfurized PWA1480

1100 °C, 1-hr cycles, 500 hours

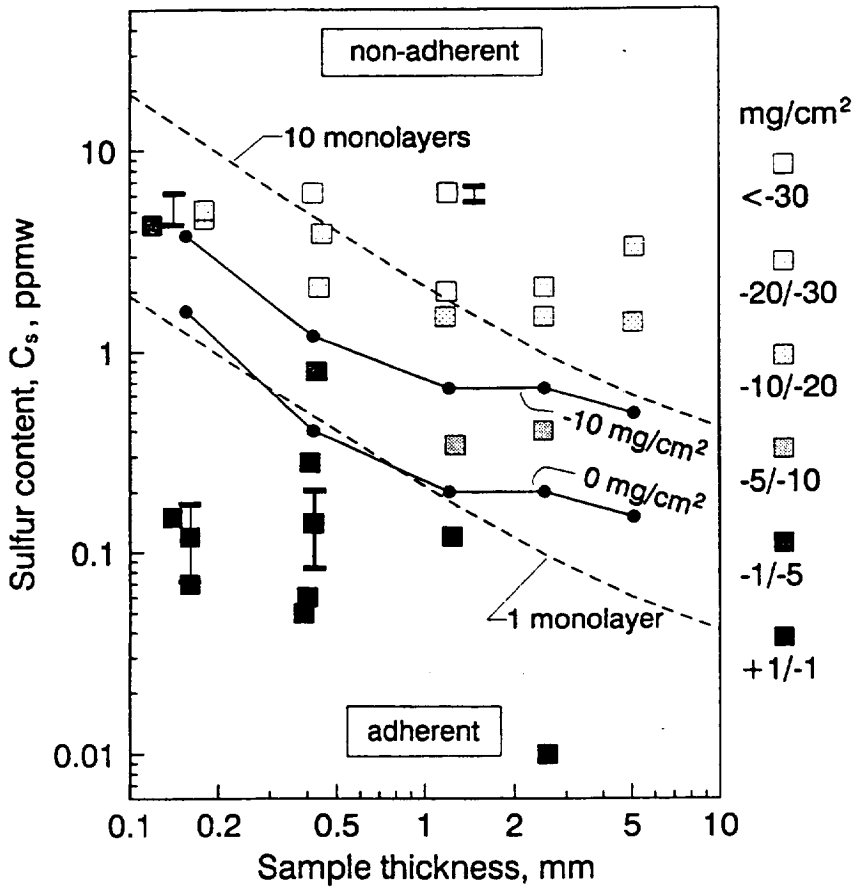

Fig. 16

Why Is ~1 Monolayer Equivalent Critical ?

- Saturation at 0.3 monolayers; sufficient for massive Al_2O_3 spallation
  - Repeated spallation events cause depletion zones, trigger Ni,Cr,Ta-rich oxides; conversely,
  - Limited sulfur reservoir limits spallation events
- Low bulk sulfur reduces equilibrium saturation level (~0.01 monolayer @ 0.2 ppmw sulfur)

Fig. 17

Summary and Conclusions

- Hydrogen annealing very effective in sulfur reduction

  Strong T, t, L dependence, e.g., $\exp(-Dt/L^2)$
- Strong effects of hydrogen annealing and sulfur content on 1100°C cyclic oxidation:

  <20 mils, >1200°C, >20 hr, <0.3 ppmw S:
  (+1 mg/cm^2 vs -30 mg/cm^2)
- Adhesion criteria suggested by mapping:
  Critical sulfur • thickness parameter equivalent to ~ 1 monolayer of total segregation

Fig. 18

Future Considerations

- Complete D_s, critical anneal evaluations
- Evaluate critical S/Y ratios
- Evaluate melt desulfurized PWA1484
- Coatings and TBC's
- HT-XPS segregation vs C_s

Fig. 19