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# EFFECTS OF HYDROGEN ANNEALING, SULFUR SEGREGATION, AND DIFFUSION ON THE CYCLIC OXIDATION RESISTANCE OF SUPERALLOYS: A REVIEW

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## ABSTRACT

This review is based on the phenomenon of improved oxide scale adhesion for desulfurized superalloys. The proposed adhesion mechanism involves sulfur interfacial segregation and scale-metal bond weakening. Sulfur surface segregation on superalloys is examined as a function of temperature and sulfur content and related to classical behavior predicted by the McLean isotherm. Effective desulfurization to less than 1 ppmw can be accomplished by hydrogen annealing and is governed by sulfur diffusion kinetics in nickel. Hydrogen annealing results in excellent cyclic oxidation resistance for a number of advanced superalloys. The concept of a critical sulfur content is discussed in terms of practical annealing conditions and section thicknesses.

# INTRODUCTION

Alumina scale adhesion to oxidation resistant MCrAlY-based alloys has been related to sulfur impurity gettering by reactive dopants such as Y, Zr, Hf, and rare-earth elements [1,2,3]. In support of such an argument, hot stage Auger experiments have shown strong sulfur segregation to the top 1-2 monolayers for undoped alloys with bulk sulfur contents of only 10-20 parts per million by weight (ppmw) [e.g., ref. 1,3,4,5, as summarized in 6]. Sulfur segregation is greatly reduced by either reactive element additions or by desulfurization via hydrogen annealing [7].

Scale adhesion to undoped alloys increases as the intrinsic sulfur impurity level is reduced [8-12]. These observations are consistent with a model presuming that interfacial sulfur segregation occurs during oxidation and weakens the scale-metal bond. The phenomenon is analogous to temper embrittlement caused by grain boundary segregation of sulfur in steels and superalloys. Reactive element dopants and desulfurization are both effective in preventing sulfur segregation and poor scale adhesion.

Surface segregation phenomena are typically described in terms of the Langmuir-McLean isotherm, whose principal features are bulk concentration, temperature, and heat of segregation. Classical behavior predicts a <u>reduction</u> in equilibrium saturation values at high temperature. However, reduced segregation is often observed at low temperatures upon initial heating, because equilibrium saturation is prevented by slow kinetics [13]. The situation is analogous to "C" curve precipitation kinetics on a TTT plot.

Diffusion kinetics also describe the effectiveness of desulfurization by hydrogen annealing [9]. This process has been used in a number of investigations to reduce the bulk sulfur content of superalloys to below 1 ppmw, resulting in dramatic improvements in cyclic oxidation behavior. Annealing temperature, time, sample thickness and initial sulfur content are important considerations in determining the final sulfur content. The application of this process to superalloys shows promise for increasing the oxidation resistance to a level nearly equivalent to that conferred by problematic coatings or yttrium additions.

The purpose of this paper is to review some of the key aspects of sulfur segregation, removal, and the bulk purity required for acceptable adhesion on commercial superalloys. The concept of a critical sulfur content is discussed in the context of an oxide adhesion map, summarizing cyclic oxidation data as a function of sulfur content and sample thickness. The ability to achieve these levels through hydrogen annealing can be estimated via standard diffusion equations.

## GENERAL PROCEDURES

Most of the experimental details can be found in prior publications that will be cited as discussed. The alloys studied are PWA 1480, PWA 1484, Rene'142, Rene'N5, and CMSX 4 superalloys. All are Ni-based alloys with 5-13%Co, 5-10%Cr, 5-6%Al, 0-2%Ti, and 15-20% total (Mo+Ta+W+Re) refractory element content, by weight. The conditions for experiments performed at this laboratory are as follows: Surface segregation was studied by hot stage XPS (x-ray photoelectron spectroscopy) up to 1100°C with 1-6 hr equilibration times. Sulfur compositions of the top 2-3 nm were estimated from the normalized peak areas of each element [7]. Hydrogen annealing was performed in a slowly flowing 1 atm $H_2$ or 5%$H_2$-Ar environment, in high purity alumina tubes at 1000°-1300°C. Cyclic oxidation was performed on 1.3 x 2.5 cm coupons or 0.6 x 1.3 cm strips at 1100°, 1150°, or 1200°C, with 1 hr heating cycles. Samples were polished to a 600 grit finish except for a duplicate set of strips oxidized in the as-annealed condition. Sulfur analyses were obtained by glow discharge mass spectrometry (GDMS), accurate to ±25% of the value and sensitive to parts per billion.

## SULFUR SEGREGATION STUDIES

The standard formalism for surface segregation is given by the Langmuir-McLean isotherm [13]:

$$\theta/(1-\theta) = aC_S/(1-C_S) * \exp(Q_s/RT) \qquad \text{eqn.1}$$

where: $\theta$ = surface coverage relative to saturation

$C_S$ = bulk sulfur concentration

$Q_s$ = enthalpy of segregation,

= 137 kJ/mole*K for sulfur on nickel [13]

a = constant

Miyahara et al. have measured sulfur segregation vs temperature in hot stage Auger studies of Ni doped with 200 ppma (parts per million atomic) sulfur [13]. (Atomic ppm is used in the discussion of the McLean isotherm. However ppmw is used in the remainder of the paper, enabling direct comparisons with commercial alloy chemistries by GDMS). Their data was fit to the above equation, yielding a best fit for the constant, a = 0.189 [6], using their assumed saturation value of 0.5 atom fraction.

Predicted segregation curves for bulk sulfur contents of 0.1, 1.0, 10, 100, and 1000 ppma are shown in figure 1. An important feature of the predictions is the decrease in equilibrium segregation level with increasing temperature. Thus if surface segregation studies are performed at 1100°C for alloys with bulk sulfur contents of 16 ppma (10 ppmw), the predicted level would be only 1/5 the maximum at saturation.

Bulk sulfur content also plays an important role. For alloys with lower sulfur contents, low equilibrium values are predicted down to lower temperatures. For example, at 0.1 ppma sulfur (0.063 ppmw), these low surface concentrations persist down to temperatures where slow kinetics prevent sulfur from diffusing to the surface (700°C).

The actual data of Miyahara for Ni-200 ppma S was described as three regions: I) below 775°C, where slow diffusion kinetics prevent equilibrium segregation (not shown); II) where saturation is achieved, i.e., 0.5 monolayer; and, III) above 975°C where equilibium segregation decreases with temperature [13]. Thus, if surface segregation studies are performed below 700°C, the measured sulfur levels are expected to be much lower than saturation.

Data obtained for Ni and NiCrAl in nine other investigations was also summarized in [6] and are listed in Table I. Precise agreement with the predicted curves was not obtained. However, strong surface segregation was nonetheless indicated, as alloys with 1-16 ppma (0.6-10 ppmw) bulk sulfur exhibited surface segregation ~10-50 at.%. of the top monolayer. Thus, enrichment ratios (surface-to-bulk sulfur content) of $10^4$-$10^5$ were typical.

Recent hot stage XPS data obtained on PWA 1480 is shown in figure 2 (solid circles) [7]. The temperature was varied in 50°C increments up to 1100°C and held for at least one hour while sulfur intensity was recorded. Slow kinetics resulted in low values below 800°C. At 850°C, a large increase in sulfur content occurred, as enabled by higher diffusivity. A further increase occurred with removal of the native (room temperature) oxide. Above 900°C the surface concentration decreased until, at 1100°C and above, the amount was minimal. Thus, regions I, II, and III described by Miyahara [13] appear to be followed.

A maximum sulfur concentration of only 9.6 at.% was reached at 900°C. But since XPS samples about three times deeper than Auger, the surface composition may be underestimated compared to those in figure 1. However, glancing angle measurements (70° off-normal electron take-off angles) gave approximately a factor of 3 increase in sulfur level by reducing the sampling depth a factor of 3 [7]. This correction factor was used to modify XPS data obtained at various temperatures [from Table III in ref.7] and compared to a curve calculated for Ni according to equation 1, (figure 3). The bulk sulfur content was 12 ppma (7.5 ppmw) on duplicate samples (Shiva Technologies). Here reasonable conformation to the McLean isotherm is seen. A maximum of 24 at. % sulfur is now indicated for the top 1-2 monolayers.

Figure 2 also presents sulfur segregation data for a Ni-15Cr-13Al coating alloy, with a bulk sulfur content of 15.7 ppma (9.8 ppmw, Charles Evans). Auger studies have previously documented sulfur segregation to 30-37% of the top monolayer after heating to 700°-750°C [4,5]. The NiCrAl XPS segregation profile in figure 2 was remarkably close to that of PWA 1480, indicating that sulfur segregation behavior for NiCrAl coating alloys and advanced superalloys are similar. However, the native oxide did not disappear until 1100°C, resulting in a temporary spike in the sulfur level and a somewhat depressed level up to 1100°C.

A final important point in figure 2 is the effect of hydrogen annealing. A 0.18 mm (7 mil) thick PWA 1480 sample was annealed in 5%$H_2$-Ar at 1200°C for 100 hr, resulting in a sulfur level of only 0.02 ppma (0.01 ppmw, Shiva). Essentially no segregation took place up to 850°C, where the sulfur level remained below 0.5 at.%. A maximum of only 1.2% occurred at 1000°C (equivalent to 3.6%, angle resolved). This is actually higher than expected from equation 1, where less than 1% is calculated for 800°C and above.

## DESULFURIZATION KINETICS

Strong sulfur segregation can thus be expected above 800°C for Ni-base alloys. Surface segregation follows a trend predicted by the Langmuir-McLean relationship, namely, a strong dependence on bulk sulfur content, with little segregation for levels below 0.1 ppma. In this section the kinetics of desulfurization required to obtain the requisite low levels are discussed.

The basis for desulfurization by hydrogen annealing is diffusion from the bulk to the free surface and removal by volatilization or reaction with hydrogen. Another critical role of hydrogen is to prevent any scale formation, which would block sulfur removal. The kinetics have been described by the thin slab diffusion solution [14] in an earlier study of PWA 1480 [9]:

$$C_S/C_{S,i} = 8/\pi^2 \sum_{n=0}^{n=\infty} (2n+1)^{-2} * \exp[-(2n+1)^2(\pi^2 D_{S,Ni} t/L^2)] \qquad \text{eqn. 2a}$$

where $C_S$ = residual sulfur content (average)

$C_{S,i}$ = initial sulfur content

$D_{S,Ni}$ = diffusion coefficient for sulfur in nickel

= $1.4 \exp[-218.6 kJ/RT]\ cm^2/sec$ [15]

t = time (sec)

L = thickness (cm)

and for $D_{S,Ni}t/L^2 > 0.05$:

$$C_S/C_{S,i} = 8/\pi^2 * \exp(-\pi^2 D_{S,Ni} t/L^2) \qquad \text{eqn. 2b}$$

Figure 4 illustrates the agreement found between predicted and measured sulfur contents for 1.6 mm PWA 1480 coupons annealed for 100 hr in 1 atm $H_2$ with an initial sulfur content of 11 ppmw [9]. For these conditions, annealing above 1150°C is required to reach levels below 1 ppmw. (The actual 1200°C sample, however, produced a thin scale on the underside and was desulfurized to only 2.0 ppmw). The thin slab equation can thus be used to estimate residual sulfur levels for various initial contents, thicknesses, annealing time and temperature. Table II summarizes a number of desulfurization results for various T, t, and L.

## CYCLIC OXIDATION BEHAVIOR

The effect of sulfur content on cyclic oxidation resistance can be seen in the standard weight change vs time gravimetric plots, where poor adherence results in large weight losses and protective behavior enables small weight gains. Results from a number of studies are summarized in Table II. The original study on PWA 1480, (a), showed a strong dependence of cyclic oxidation behavior on hydrogen annealing temperature [9]. High annealing temperatures reduced sulfur to <0.1 ppmw, producing very adherent behavior. The final 200 hr weight change and a visual measure of spalling to bare metal strongly correlated with residual sulfur content.

Similar behavior was observed for long term oxidation of PWA 1480 and PWA 1484, annealed at 1200°C for 100 hr in 1 atm. hydrogen, (c), [16]. Annealed PWA 1480 sustained a loss of only 1 mg/cm$^2$ after 1500 hr of cyclic oxidation at 1100°C, compared to 20 mg/cm$^2$ after 400 hr without annealing. Annealed PWA 1484 produced a 2.0 mg/cm$^2$ weight gain after 1200 hours, compared to a 20 mg/cm$^2$ loss after 1000 hr for the control. PWA 1487 contains yttrium and exhibited adherent behavior with or without annealing.

The present authors examined hydrogen annealing effects on Rene' 142 and Rene'N5, both with yttrium (N5+) and without (N5-). Annealing was performed at 1280°C for 100 hr in 1 atm. $H_2$ on 3 x 8 mm strips that were 1, 2, or 3 mm thick. The sulfur levels for Rene'142, (d, in Table II), were 6.3 ppmw (Shiva) for as-received 1 mm, 0.3 ppmw for annealed 1 mm, and 0.6 ppmw for annealed 2 mm strips. Cyclic oxidation was performed at 1150°C with 1 hr cycles. Both annealed strips showed adherent behavior and 1000 hr weight changes of 1.0 mg/cm$^2$, figure 5. The control sample without annealing lost 19.9 mg/cm$^2$ and exhibited spalling to bare metal.

The N5+ samples did not show any effect of hydrogen annealing, (e). The sulfur levels were 3.2 ppmw for 1 mm as-received, 3.3 for 1 mm annealed, and 5.9 for 2 mm annealed samples. The 1000 hr weight changes were 0.72, 0.52 and -0.40 mg/cm$^2$, respectively, as shown in figure 6. The weight loss for the 2 mm sample occurred after final cooldown, when a water immersion test for adhesion produced a substantial amount of bare metal spalling. This phenomenon has been observed for undoped NiCrAl with marginal amounts of residual sulfur [10].

Samples of N5- were also annealed and tested as above (0.5 x 13 x 25 mm, f), and the results are presented in figure 7. Here, in the absence of yttrium, the positive effects of hydrogen annealing are readily demonstrated. The 500 hr weight change for the as-received sample was -23.3 mg/cm$^2$, compared to +0.85 mg/cm$^2$ for the annealed sample after 1000 hr. Again, bare metal spalling was widespread on the as-received sample, but nonexistent on the annealed sample.

Similar results have been reported for sections of an actual N5- turbine airfoil, (g), where hydrogen annealing at 1280°C for 100 hr reduced the sulfur content from 3.0 to 0.2 ppmw. The unannealed sections lost 4.0 mg/cm$^2$ after 250 hr of cyclic oxidation at 1150° C, while the annealed sections gained 1.25 mg/cm$^2$ in the same test [17]. Other pertanent studies have shown similar results for CMSX-4, hydrogen annealed to 0.1-0.3 ppmw S, tested at 1200°C for 690 hr, (h) [18] and for FeCrAl, annealed to 0.05-0.10 ppmw S, tested at 1100°C for 1800 hr, (k) [19].

# CRITICAL SULFUR CONTENT

The general conclusion of these studies on hydrogen annealed superalloys is that desulfurization to less than 1 ppmw produces substantial improvements in cyclic oxidation resistance. In determining the critical sulfur level required for adhesion, the following factors warrant consideration: a) the segregation level that causes spallation, b) self-purging caused by spalling to bare metal and re-oxidation, c) the potential number of monolayers of segregation for a given bulk sulfur content and sample geometry.

The first factor is difficult to determine, but a useful preliminary assumption is that spalling results when full saturation occurs (at 1/2 monolayer). The second factor is also indeterminant because of the random patterns of spalling to bare metal. On average, 1/2 monolayer can be assummed to be lost after the entire surface area spalls at least once. The third factor **can** be precisely described by a mass balance of the amount of bulk sulfur required to achieve monolayer coverage for a specific sample geometry. This has been done for coupon-type samples [10]:

$$C_S = (8.27\times10^{-2}\mathrm{gm/cm^2})*N_m A/W \qquad \text{eqn. 3}$$

where: $C_S$ = bulk sulfur content in ppmw

$N_m$ = number of monolayers

$A$ = sample surface area in $\mathrm{cm}^2$

$W$ = sample weight in gm

The relationship between bulk sulfur content and sample thickness at 1 monolayer of coverage for a thin infinite plate (where $A/W = 2/(\text{density}*L)$ is shown in figure 8 (modified from the adherence map in [10]). The allowable bulk sulfur content for 1 monolayer total segregation decreases linearly with thickness: from 19 ppmw allowable at 10 $\mu$m, to .019 ppmw allowable at 10 mm.

Also shown are filled symbols for adherent behavior and open symbols for non-adherent behavior from the oxidation tests described above for as-received and hydrogen annealed superalloys (Table II). The majority of the filled symbols, corresponding to adherence, fall below the line for one monolayer of segregation. While this is not a strict boundary, it is a useful target sulfur concentration for a specific sample thickness.

These targets can then be used to specify a given annealing treatment according to eqn. 2. From figure 8 (eqn. 3), a 1 mm sample would have to be annealed to 0.2 ppmw sulfur to fall under the $N_m$ = 1 total segregation critera. For an initial sulfur content of 10 ppmw, an annealing treatment at 1200°C would have to be 43 hr (using a density of PWA 1480 = 8.715 gm/cm$^3$). The required annealing times for annealing temperatures of 1000° to 1300°C and thicknesses of 0.1 to 2.5 mm (4 to 100 mils) are shown in Table III. For 100 hr or less, only the 0.1 mm sample would qualify at 1000°C, 0.1 and 0.5 mm thicknesses at 1100°, those thinner than 1 mm at 1200°C, and all four at 1300°C.

The general solution for obtaining the critical sulfur content by hydrogen annealing is obtained by solving equations 2b and 3 for $C_S$, and equating them to yield:

$$C_{S,i} = (8.27\times10^{-2}\text{gm/cm}^2)*(N_mA/W)*(\pi^2/8)*\exp(-\pi^2D_{S,Ni}t/L^2) \qquad \text{eqn. 4}$$

where $C_{S,i}$ is in ppmw, L in cm, A in cm$^2$, and W in gm.

This relationship can be used to estimate the proper diffusion treatment for various initial sulfur contents ($C_{S,i}$), adhesion criteria ($N_m$), and thicknesses (L).

## CONCLUDING REMARKS

This review has summarized high temperature sulfur segregation studies, desulfurization by hydrogen annealing, and cyclic oxidation behavior of low sulfur nickel base superalloys. Surface segregation of sulfur appears to follow the Langmuir-McLean relation, with substantial concentrations occurring above 800°C for ppm levels of bulk sulfur. Hydrogen annealing at 1200°C or above results in bulk sulfur levels <1 ppmw, greatly reduced surface segregation, if any, and marked improvements in cyclic oxidation behavior. The degree of desulfurization can be described by a thin slab diffusion equation using $D_{S,Ni}$; the critical sulfur level can be described by means of an adhesion map relating bulk sulfur content to the potential number of segregated monolayers. By combining these two concepts, an appropriate hydrogen annealing treatment can be formulated for excellent high temperature cyclic oxidation resistance of advanced nickel base superalloys without yttrium.

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TABLE I. Sulfur surface segregation on nickel alloys (from [6]).

| Investigation | Alloy | Temp. | Heating | Bulk Sulfur ppma | Bulk Sulfur (ppmw) | Surface Sulfur, a/o | $H_s/H_m$ |
|---|---|---|---|---|---|---|---|
| A. Briant, Luthra | HP Ni-20Cr-12.5Al | 800°C | 30 hr. | 2-13 | (1-8) | 3.9 | |
| | | 900°C | 6 hr. | 2-13 | (1-8) | 13.0 | |
| | | 1000°C | 2 hr. | 2-13 | (1-8) | 10.5 | |
| | | 1100°C | 0.1-2 hr. | 2-13 | (1-8) | 9.7 | |
| B. Briant, Luthra | VHP Ni-20Cr-12.5Al | 1100°C | 0.1-2 hr. | 2-13 | (1-8) | 0-1.1 | |
| C. Smeggil, et. al | Ni-20Cr-12.5Al | 800-1000°C | 0.1 hr. | 50-60 | (30-40) | 15-21.5 | |
| D. Browning, et. al | Ni-15Cr-13Al | 750-850°C | 10°/min. | 15.7-16.5 | (9.8-10.3) | 30(a) | 0.43 |
| E. Walker, El Gomati | Ni-15Cr-13Al | 700°C | 10-20 hr. | 15.7-16.5 | (9.8-10.3) | 37.3(a) | |
| F. Perdereau, Oudar | Ni | | | | | 50 | |
| G. Ferhat, et. al | Ni 270 | 700° | 5 hr. | 0.9* | (0.5) | 25(c) | 0.97 |
| H. Ladna, Birnbaum | Ni | 900-1200°C | 2 hr. | 2* | (1.1) | 19 | 0.75 |
| I. Miyhara, et. al | Ni | 700-1000°C | 1°/min. | 200 | (110) | 50(b) | |

*Low sulfur alloys showing high saturation.
(a) Measured after cooldown. (b) Assumed saturation value. (c) Inferred from $H_s/H_m$ H = peak heights

TABLE II.—SUMMARY OF DESULFURIZATION AND CYCLIC OXIDATION STUDIES OF SUPERALLOYS [7-10, 16-20]

| Material | Sample thickness, mm | $H_2$ anneal, °C/h/%$H_2$ | Residual sulfur, ppmw | Cyclic oxidation, °C/h | Final weight change, mg/cm$^2$ |
|---|---|---|---|---|---|
| PWA 1480, P.C.[a] | 0.74 | No anneal | 11 (7.5) | 1100/200 | –9.05 |
| | 1.55 | 1000/100/100 | 6.5 | | –8.09 |
| | 1.40 | 1100/100/100 | 2.5 | | –4.07 |
| | 1.58 | 1200/100/100 | 2.0 | | –4.70 |
| | 1.00 | 1300/100/100 | 0.04 | | –0.17 |
| PWA 1480, S.C.[a′] | 2.20 | No anneal | 8.8 | 1100/200 | –7.58 |
| | 0.74 | 1000/100/100 | --- | | –7.68 |
| | 0.75 | 1100/100/100 | --- | | –2.03 |
| | 0.74 | 1200/100/100 | <0.08 | | 0.34 |
| | 0.55 | 1300/100/100 | <0.04 | | 0.33 |
| PWA 1480, P.C.[b] | 0.18 | 1200/100/005 | (0.01) | --- | --- |
| | 1.07 | 1200/100/005 | (0.08) | --- | --- |
| PWA 1480, S.C.[c] | 1 | No anneal | 6 | 1100/400 | –20.00 |
| | 1 | 1200/100/100 | --- | 1100/1500 | –1.00 |
| | 3 | 1200/100/100 | --- | 1100/1200 | –3.28 |
| PWA 1484, S.C.[c′] | 1 | No anneal | 5 | 1100/1000 | –20.00 |
| | 1 | 1200/100/100 | --- | 1100/1200 | 2.00 |
| PWA 1487, S.C.[c″] | 1 | No anneal | --- | 1100/2700 | 1.00 |
| | 1 | 1200/100/100 | --- | 1100/1200 | 1.50 |
| René 142[d] | 1.32 | No anneal | (6.3) | 1150/1000 | –19.94 |
| | 0.85 | 1280/100/100 | (0.3) | | 0.96 |
| | 1.82 | 1280/100/100 | (0.6) | | 1.08 |
| | 1.17 | No anneal | (6.3) | | –96.19 |
| No polish[d′] | 0.99 | 1280/100/100 | (0.3) | | –3.09 |
| | 2.80 | 1280/100/100 | (1.4) | | –1.89 |

[a]Ref. [9]. [b]Ref. [7]. [c]Refs. [16,20]. [d-f]This study. [g]Ref. [17]. [h]Ref. [18]. [i]This study. [j]Ref. [10]. [k]Ref. [19].

For residual sulfur, values in parentheses are for Shiva and those without are for C. Evans.

TABLE II.—Concluded.

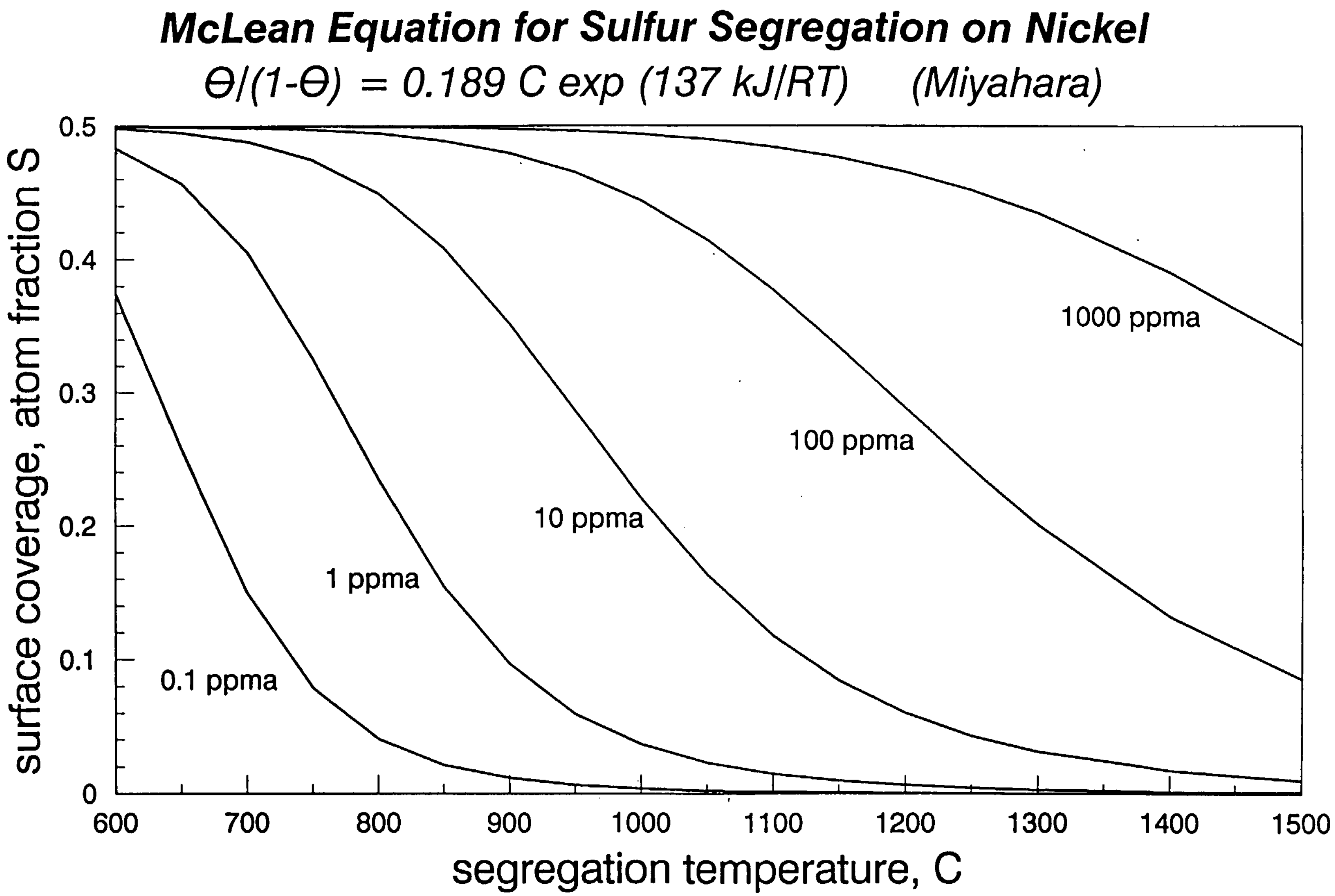
| Material | Sample thickness, mm | $H_2$ anneal, °C/h/%$H_2$ | Residual sulfur, ppmw | Cyclic oxidation, °C/h | Final weight change, mg/cm$^2$ |
|---|---|---|---|---|---|
| René N5 (+Y)[e] | 1.40 | No anneal | (3.2) | 1150/1000 | 0.72 |
| | 0.91 | 1280/100/100 | (3.3) | | 0.52 |
| No polish[e′] | 1.86 | 1280/100/100 | (5.9) | | –0.40 |
| | 1.32 | No anneal | (3.2) | | 0.53 |
| René N5 (–Y)[f] | 1.04 | 1280/100/100 | (3.3) | 1150/500 | 0.53 |
| | 2.97 | 1280/100/100 | (3.7) | 1150/1000 | –0.82 |
| Blade N5 (–Y)[g] | 0.72 | No anneal | (≈3) | 1150/250 | -23.28 |
| Blade N5 (–Y)[g] | 0.50 | 1280/100/005 | (<0.3) | | 0.86 |
| Blade N5 (+Y)[g] | | | | | |
| | 1.2-2.2 | No anneal | (3.0) | | –4.06 |
| CMSX 4[h] | 1.2-2.2 | 1280/100/100 | (0.2) | 1200/240 | 1.22 |
| | 1.2-2.2 | No anneal | (3.0) | 1200/690 | -1.18 |
| | | | | 1200/690 | |
| | 0.38 | No anneal | 2.8 | 1200/530 | –6.00 |
| | 0.38 | 1200/005/100 | 0.3 | | 0.00 |
| NiCrAl[i] | 0.38 | 1200/010/100 | 0.12 | 1100/200 | 0.18 |
| | 0.38 | 1200/005/005 | 0.25 | 1100/500 | -1.46 |
| | | | | 1100/200 | |
| | 0.95 | No anneal | 24.8 | | -21.91 |
| NiCrAl, M.S.[j] | 0.95 | 1200/100/100 | (0.02) | 1100/080 | –6.09 |
| | 0.61 | 1200/024/005 | --- | 1100/500 | -2.71 |
| | | | | 1100/500 | |
| | 0.06 | No anneal | 2.5 | 1100/500 | –0.17 |
| | 0.08 | 1000/100/100 | 0.62 | | 0.54 |
| FeCrAl[k] | 0.07 | 1100/100/100 | 0.19 | 1100/210 | 0.67 |
| | 0.04 | 1200/100/100 | <0.12 | 1100/1800 | 0.69 |
| | | | | 1100/1800 | |
| | 1.00 | No anneal | (12.5) | 1100/1400 | 4.75 |
| | 0.29 | 1200/100/005 | (0.05) | | 1.30 |
| | 0.59 | 1200/100/005 | --- | | 1.30 |
| | 1.50 | 1200/100/005 | (0.10) | | 2.80 |

[a]Ref. [9]. [b]Ref. [7]. [c]Refs. [16,20]. [d-f]This study. [g]Ref. [17]. [h]Ref. [18]. [i]This study. [j]Ref. [10]. [k]Ref. [19].

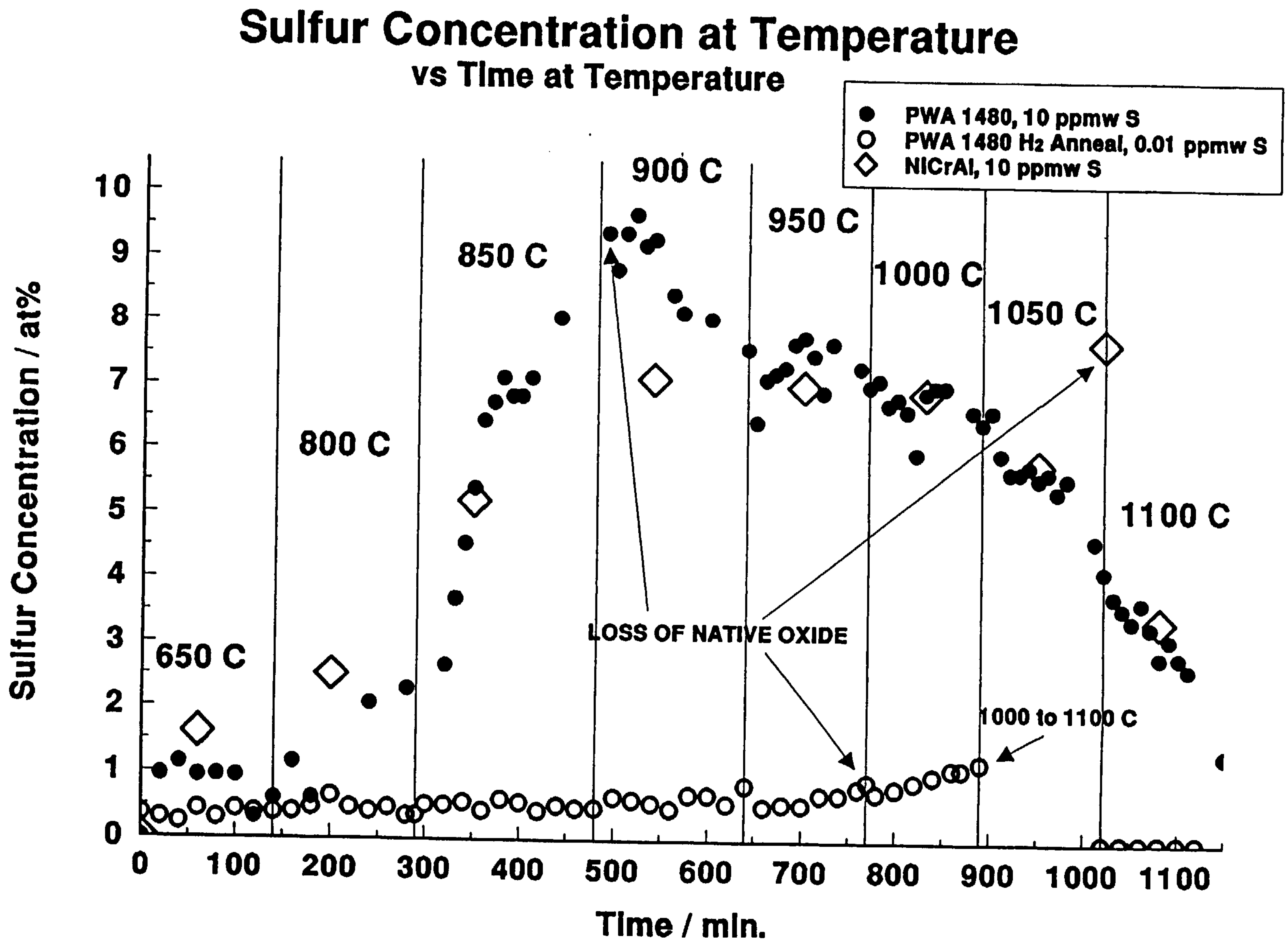
For residual sulfur, values in parentheses are for Shiva and those without are for C. Evans.

TABLE III. Annealing times (HOURS) predicted by eqn. 4 to achieve a critical sulfur content for adhesion for various temperatures and thicknesses at $C_i/N_m = 10$.

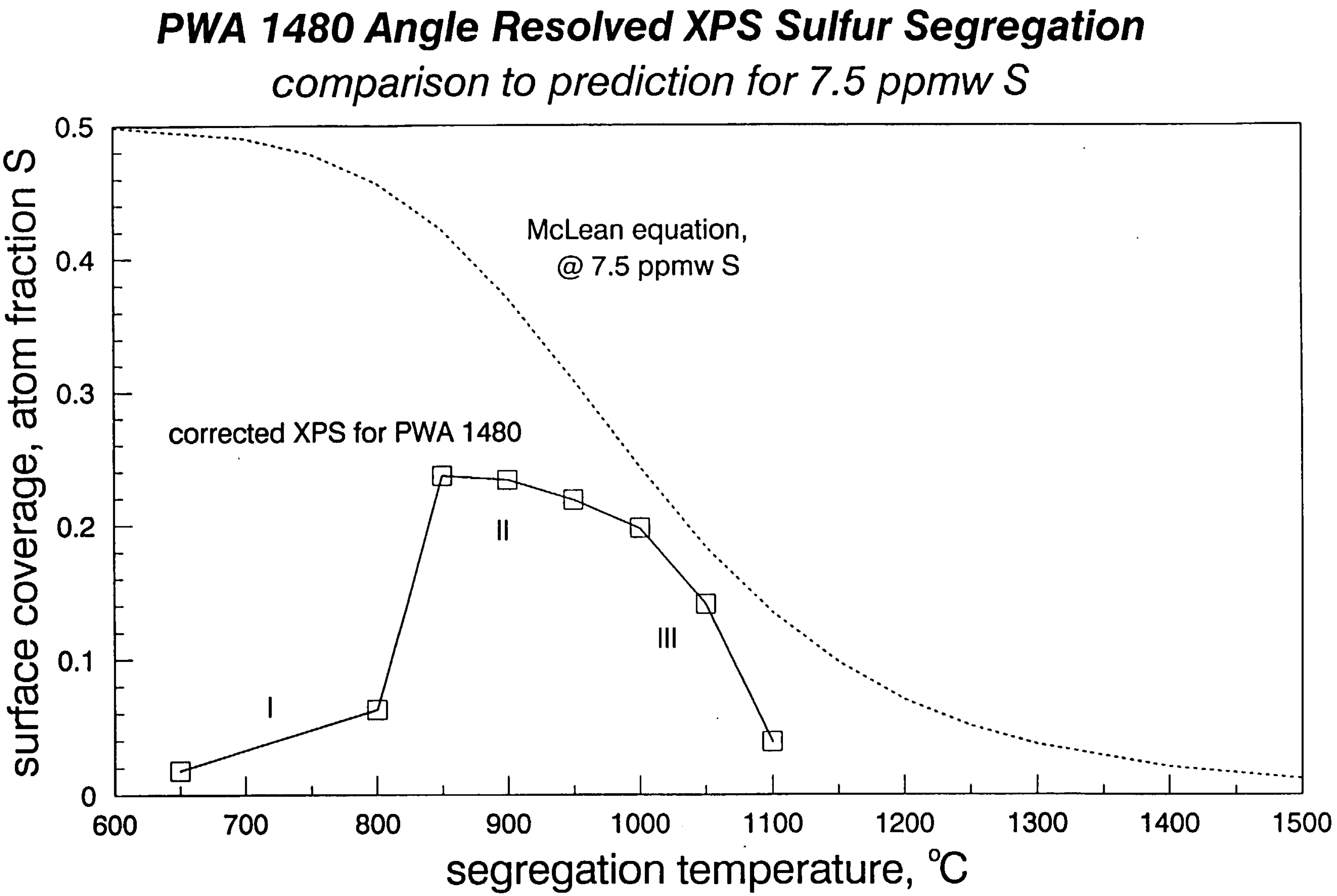
| L<br>T | 0.1 mm (4 mils) | 0.5 mm (20 mils) | 1.0 mm (40 mils) | 2.5 mm (100 mils) |
|---|---|---|---|---|
| 1000 C | 2.72 | 143.64 | 704.61 | 5478.28 |
| 1100 C | 0.61 | 31.92 | 156.58 | 1217.40 |
| 1200 C | 0.16 | 8.69 | 42.62 | 331.35 |
| 1300 C | 0.05 | 2.80 | 13.73 | 106.72 |



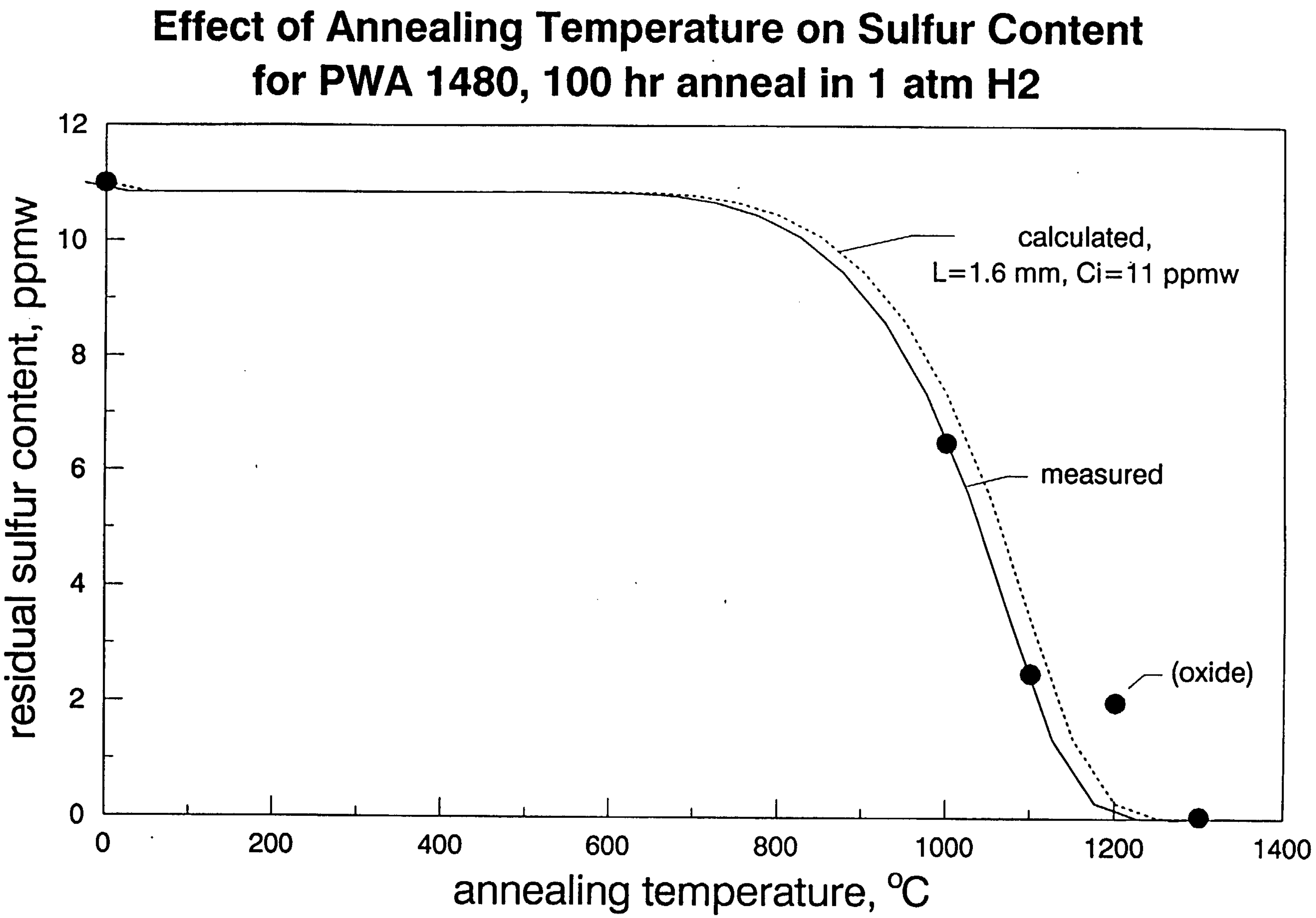
1) Temperature dependence of sulfur segregation in nickel alloys. (curves from the Langmuir-McLean isotherm, eqn. 1, after [6,13]).



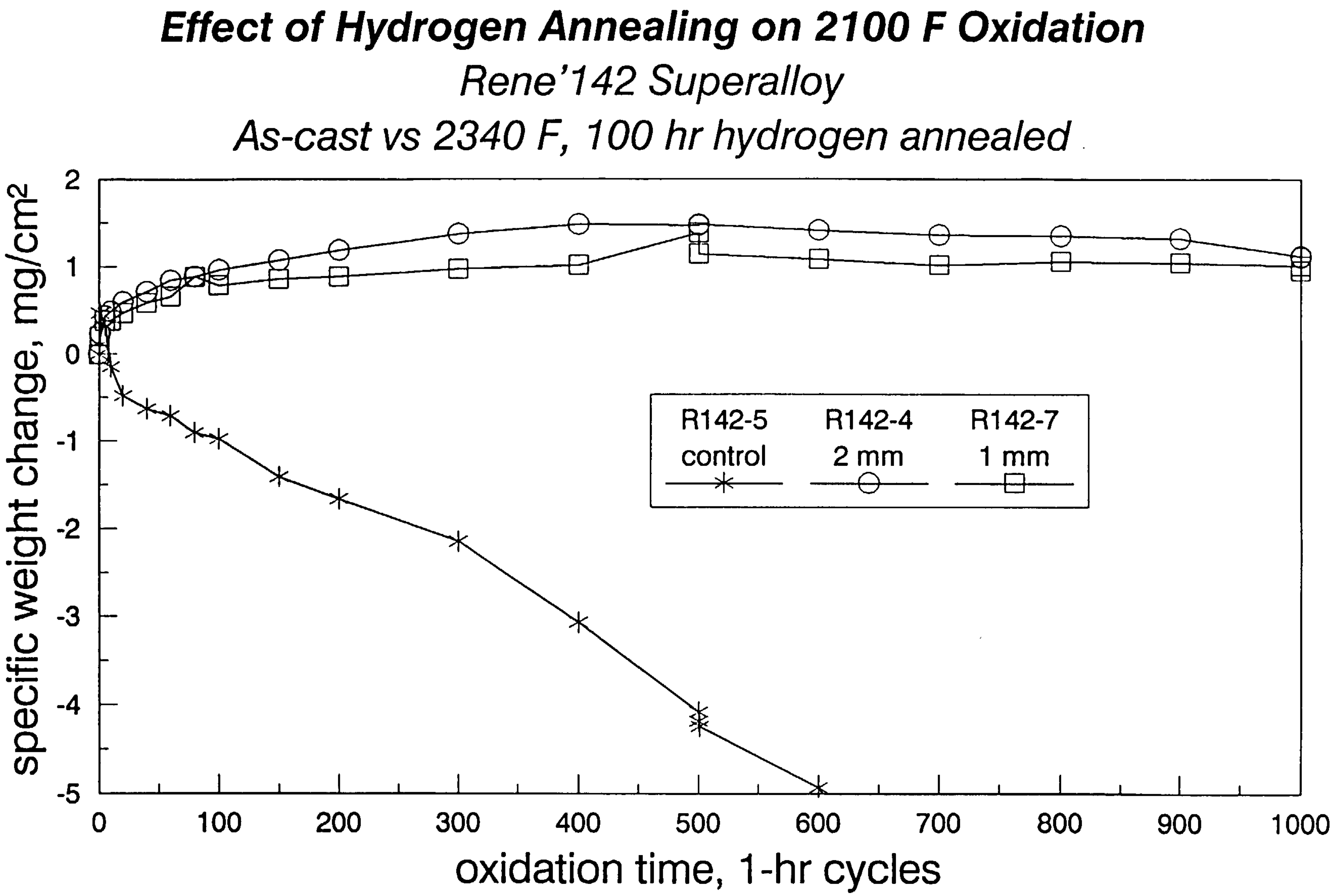
2) Hot stage XPS sulfur segregation for as-cast NiCrAl and PWA 1480, and for desulfurized (0.01 ppmw S) PWA 1480 [7].



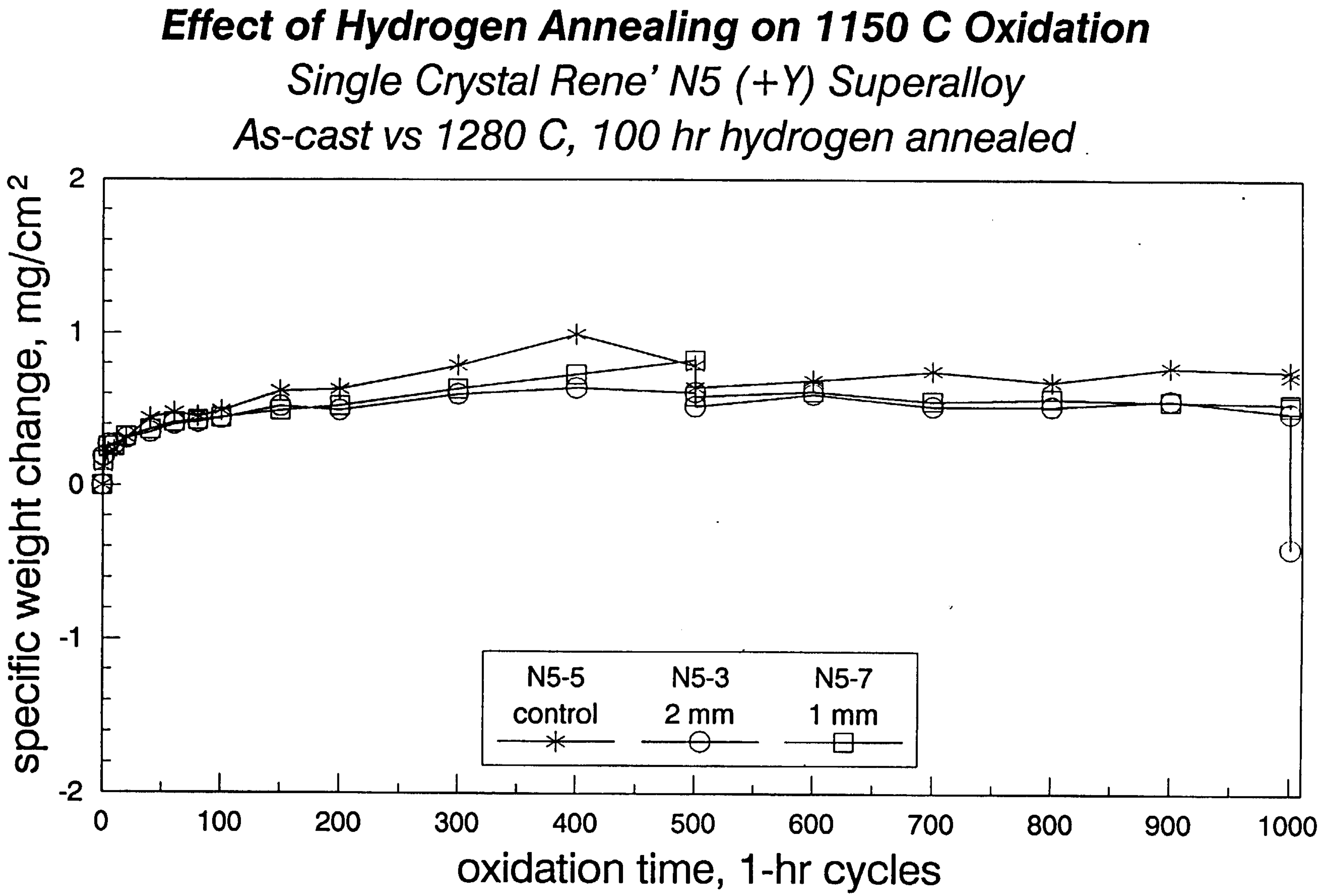
3) Angle resolved corrected XPS sulfur content for PWA 1480 [7] compared to values predicted from the Langmuir-McLean isotherm, eqn. 1.



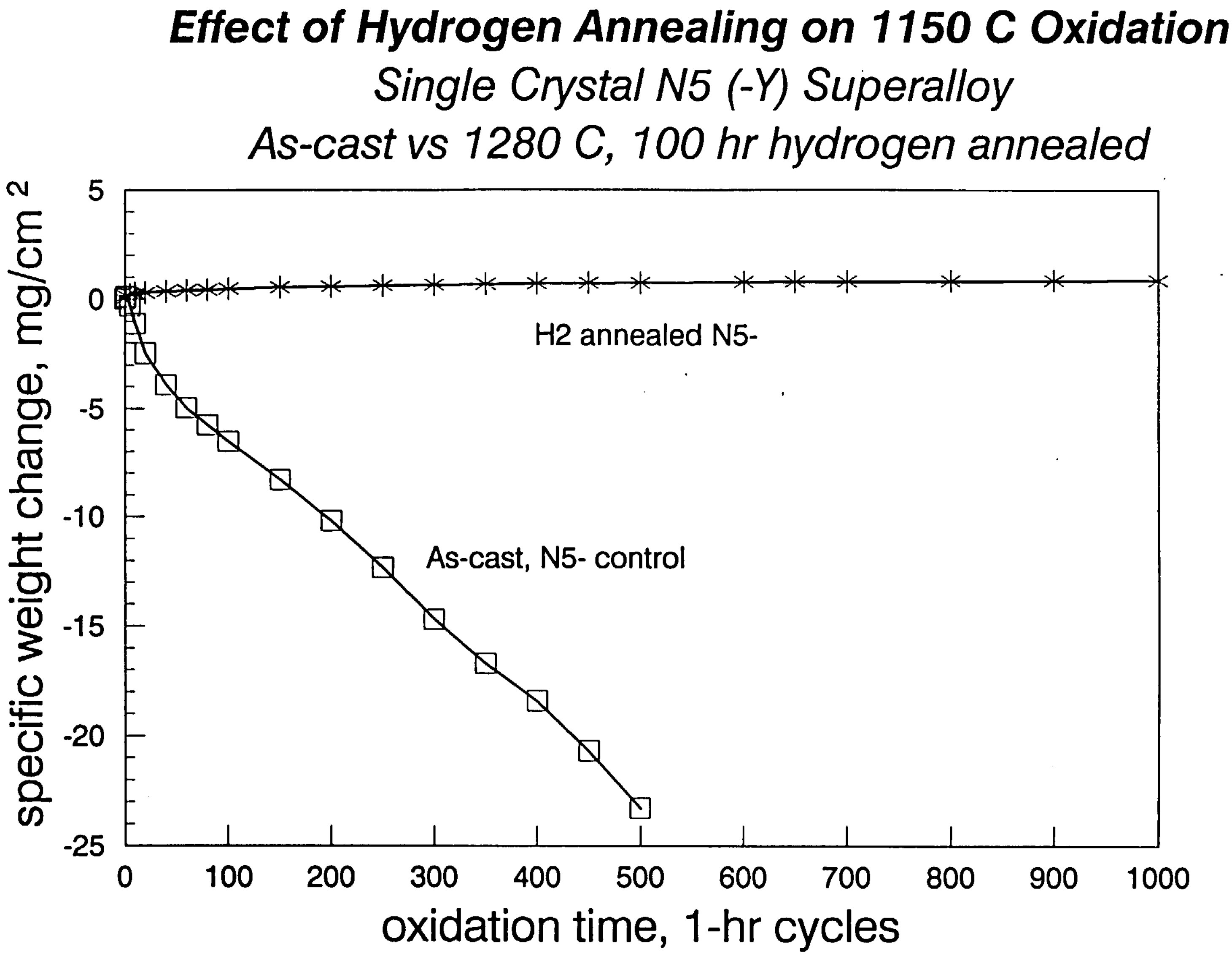
4) Residual bulk sulfur content after hydrogen annealing compared to that predicted from diffusion kinetics, eqn. 2. (1.6 mm coupons of PWA 1480, annealed at 1000-1300°C) [9].



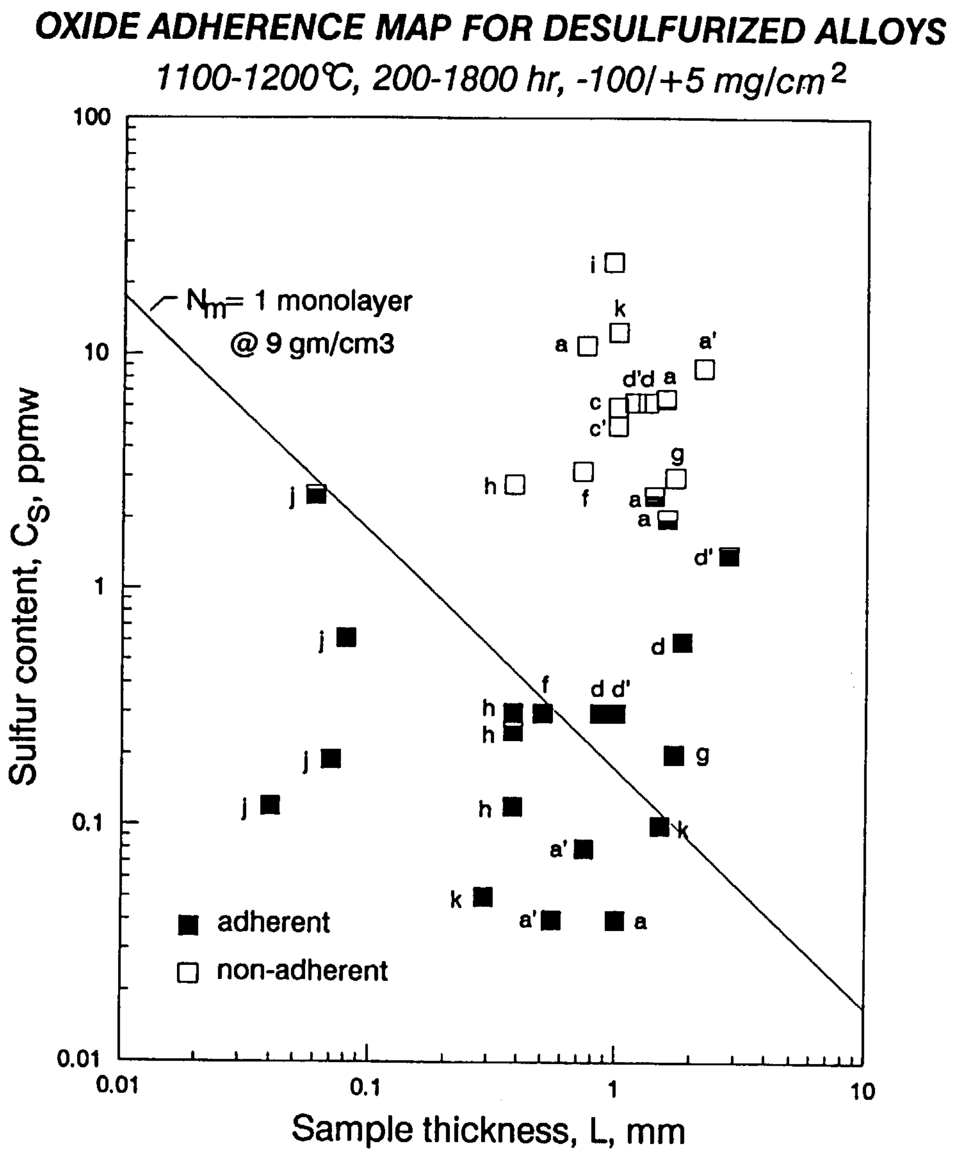
5. Effect of hydrogen annealing on the 1150°C cyclic oxidation of Rene'142 strips. (annealed at 1280°C for 100 hr in 100% $H_2$ vs unannealed control).



6. Effect of hydrogen annealing on the 1150°C cyclic oxidation of Rene'N5 (with Y) strips. (annealed at 1280°C for 100 hr in 100% $H_2$ vs unannealed control).



7. Effect of hydrogen annealing on the 1150°C cyclic oxidation of Rene'N5 (without Y) coupons. (annealed at 1280°C for 100 hr in 5% $H_2$ vs unannealed control).



8. Oxide adherence map for hydrogen annealed samples, modified from [10]. (Line is for 1 monolayer of total segregation possible, eqn. 3; unfilled symbols represent non-adherent behavior; filled symbols represent adherent behavior; see Table II for sample code).

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**13. ABSTRACT** ***(Maximum 200 words)***

This review is based on the phenomenon of improved oxide scale adhesion for desulfurized superalloys. The proposed adhesion mechanism involves sulfur interfacial segregation and scale-metal bond weakening. Sulfur surface segregation on superalloys is examined as a function of temperature and sulfur content and related to classical behavior predicted by the McLean isotherm. Effective desulfurization to less than 1 ppmw can be accomplished by hydrogen annealing and is governed by sulfur diffusion kinetics in nickel. Hydrogen annealing results in excellent cyclic oxidation resistance for a number of advanced superalloys. The concept of a critical sulfur content is discussed in terms of practical annealing conditions and section thicknesses.

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