The Effect of Preoxidation on the Sulfidation of Ni-20Cr (2-5)Al Alloys

I. Effect of Preoxidation on Scale Characteristics and Sulfidation at 750°C

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Ni–20Cr alloys with 2, 3.5, and 5 wt.% Al have been preoxidized up to 100 hr at 1000°C in dry H_2 , in $H_2/23\%$ H_2O and in air and subsequently exposed to an $H_2/5\%$ H_2S atmosphere at 750°C. During the preoxidation treatment different types of oxide scales were formed which affect the sulfidation protection in different ways. Optimum results were obtained for alloys with 3.5 and 5 wt.% Al after 20 hr exposure to dry H_2 at 1000°C. A thin Al_2O_3 scale is formed which decreases the sulfur attack by more than one order of magnitude. Preoxidation conditions for Ni–20Cr–2Al alloys in H_2 and for Ni–20Cr–2Al and Ni–20Cr–3.5Al in H_2/H_2O were observed to be less effective. No improvement was found for preoxidation in air or for Ni–20Cr–5Al alloys preoxidized in H_2/H_2O .

KEY WORDS: nickel-base alloys; sulfidation; preoxidation; Al₂O₃ scales; Cr₂O₃ scales.

INTRODUCTION

Nickel-base alloys are exposed to corrosive gases in numerous high-temperature applications.¹⁻³ Sulfur is one of the most harmful elements, particularly in the case of nickel-base alloys due to the relatively low eutectic temperature of nickel/nickel sulfide mixtures.⁴ Degradation of nickel alloys proceeds very

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fast in sulfidizing atmospheres with a low oxygen activity and a high activity of sulfur. It is characterized by a non-uniform attack of the metal surface,^{2,3} The mechanism of sulfidation of alloys under such conditions is not completely understood as yet, due to the complexity of the observed phenomena. However, it has been reported by many authors that oxide scales can strongly affect the sulfidation resistance of the alloys.⁵⁻¹⁴

Since the characteristic features of oxide scales depend on the chemical composition of the alloy and on the composition of the oxidizing atmosphere, it can be expected that the protection of an alloy against sulfidation by an oxide scale is strongly affected by the aluminum concentration of the alloy and/or the oxygen activity in the oxidizing atmosphere.

This paper reports on investigations of the sulfidation resistance of three Ni-20Cr-Al alloys with 2, 3.5, and 5 wt.% Al preoxidized in various oxidizing atmospheres, particularly at low oxygen activities. Aluminum concentration and preoxidation time are the parameters changed in individual runs. The alloys were preoxidized in dry H₂ (where only Al₂O₃ can be formed by reaction of the samples with the residual H₂O impurity) in H₂/H₂O gas mixture (where both Al₂O₃ and Cr₂O₃ can be formed), and in air (where NiO can also exist). Subsequently the samples were sulfidized in a reducing H₂/5% H₂S gas atmosphere. At 1000°C in air Ni-20Cr-2Al is considered to be a Cr₂O₃ former, whereas Ni-20Cr-5Al alloy is an Al₂O₃ former.¹⁵

EXPERIMENTAL

Specimens

Ni-20Cr with 2, 3.5, or 5 wt.% Al alloys were prepared from elemental metals (99.95-99.99%) in a vacuum arc furnace, ground with 600 grit SiC paper, and annealed for 20 hr at 1000°C in an evacuated sealed quartz capsule. The buttons were cut into specimens $30 \times 10 \times 1$ mm and subsequently polished on 1 μ m-diamond paste, degreased and dried.

Preoxidation

High purity H_2 and $H_2/23\%$ H_2O gas mixtures or air were chosen as preoxidation atmospheres. In order to attain an extremely low oxygen activity atmosphere, high-purity hydrogen (99.999%) was passed through a tube containing P_2O_5 and a liquid N_2 condenser. The oxygen activity in H_2 was determined indirectly from the water-vapor content measured by a dewpoint hygrometer. An analysis of the H_2 gas after passing the hot furnace showed that H_2O values less than 8 ppm were attained. In order to obtain a defined H_2/H_2O gas mixture, water vapor was added to a hydrogen gas flow by bubbling hydrogen through a water bath at room temperature, which yields Sulfidation of Ni-20 Cr (2-5)Al Alloys: I



Fig. 1. Thermodynamic phase stabilities in the Ni-Cr-Al-O system at 1000°C. The length of the horizontal bars indicates which phases are stable in a specific atmosphere.

a $H_2/23\%$ H_2O atmosphere corresponding to an oxygen activity of 5×10^{-18} atm at 1000°C.

Figure 1 shows the thermodynamic phase stability diagram for the Ni– Cr–Al–O system at 1000°C. It indicates that both Cr_2O_3 and Al_2O_3 can be formed in H_2/H_2O , but only Al_2O_3 is stable in dried H_2 .

The preoxidation treatment was carried out by inserting the specimen into the cold furnace under a flow of helium. After sealing the reaction tube, helium was replaced by the oxidizing atmospheres. At the end of the oxidation treatment the specimen was cooled down to room temperature.

Sulfidation

The preoxidized specimens were exposed to a $H_2/5\%$ H_2S gas mixture, where further oxidation is impossible. These sulfidation experiments were carried out in a separate furnace in order to avoid contamination during preoxidation with sulfur and other impurities. In order to accelerate the degradation reaction, the sulfidation tests were performed at 750°C which is above the Ni/Ni₂S eutectic (645°C) but below ordinary operating temperatures of high-temperature Ni alloys.

Morphology

Composition and morphological features of the scales were investigated by AES depth profiles, x-ray diffraction, and SEM/EDX (Table I). EDX results have been obtained from standardless data corrected by ZAF-factors and checked in critical cases by WDS.

	Air	H_2/H_2O	H ₂	H_2/H_2S
NiO	XRD			
NiCr ₂ O ₄	XRD			
NiAl ₂ O ₄				
Cr_2O_3	XRD	XRD		
Al_2O_3	EDX	EDX	AES, TEM	
Ni_3S_2				EDX, XRD
Ni_7S_6				EDX, XRD
Cr_3S_4				EDX, XRD
(CrNi)₃S₄				EDX, XRD
$(CrAl)_3S_4$				EDX, XRD

 Table I. Phases Identified by Various Methods in Scales after Annealing in Different Atmospheres

RESULTS

Preoxidation in H₂

Oxide-Scale Formation

After oxidation in H₂, very thin aluminum oxide scales were detected on the alloys by AES regardless of the aluminum concentration. Figure 2 shows AES depth profiles of the surface of Ni-20Cr-2, 3.5, and 5Al alloys, oxidized for 50 hr at 1000°C in H₂. The oxide scale formed on the alloys is essentially aluminum oxide, although the formation of NiAl₂O₄ would be possible according to thermochemical data. These oxide scales showed reasonable adhesion to the alloys and did not crack or spall during cooling to room temperature. The oxide-layer thickness varied from about 0.2–0.5 μ m depending on the location of AES depth profiles. Any effect of the Al bulk concentration must have been smaller than this scatter margin.

However, the morphologies of the aluminum oxide scales were influenced remarkably by the bulk aluminum concentration. The 2 wt.% Al alloy exhibited a scale on which small oxide particles are visible. The density of these particles seems to depend on the grain orientation at the interface (see Fig. 3). When the aluminum concentration was increased above 2%, the formation of fine subgrains in the oxide scale was observed, and the grain boundaries of the alloy could no longer be distinguished from the surface structure of the oxide layer (see Figs. 4 and 5).

Sulfidation Resistance of Preoxidized Alloys

The sulfidation resistance of the alloys preoxidized in H_2 varied with the aluminum concentration as demonstrated in Fig. 6. The x-axis indicates



Fig. 2. AES-depth profiles across oxide scales formed on Ni–20Cr–Al alloys preoxidized for 50 hr at 1000°C in H_2 : (a) Ni–20Cr–2Al, (b) Ni–20Cr–3.5Al, and (c) Ni–20Cr–5Al.

the preoxidation time and the y-axis the weight gain after exposure of 4 hr to the H_2/H_2S environment at 750°C. Increasing aluminum concentration improves the sulfidation resistance of preoxidized alloys. Even the thin aluminum oxide film formed on the Ni-20Cr-5Al alloy after exposure of about 2 hr to H_2 acted as a protective barrier for the sulfidation reaction. In the case of Ni-20Cr-2Al, the beneficial effect of a thin aluminum oxide scale was also detected, but the protective barrier effect was less pronounced when compared to Ni-20Cr-5Al. Longtime exposures in O₂ also did not reduce the sulfur attack of this 2% Al alloy after exposure of 4 hr to H_2/H_2S at 750°C. Figure 7a shows Ni₃S₂ islands on the oxide scale of the Ni-20Cr-2Al alloy preoxidized for 70 hr in H_2 at 1000°C and then sulfidized 4 hr in $H_2/$ H_2S at 750°C. Fine chromium-sulfide particles (CrS) were found mainly along grain-boundary-like structures of the oxide scale (see Fig. 7b). Whether or not this structure is affected by alloy grain boundaries cannot be decided, but it is too wide to be considered as scale grain boundaries.



Fig. 3. Aluminum oxide scale on Ni–20Cr–2Al preoxidized for 50 hr at 1000°C in H₂: (a) 200×, and (b) 3000×.



Fig. 4. Aluminum oxide scale on Ni-20Cr-3.5Al preoxidized for 50 hr at 1000°C in $\rm H_2:$ (a) 200×, and (b) 3000×.



Fig. 5. Aluminum oxide scale on Ni–20Cr–5Al preoxidized for 50 hr at 1000°C in H₂: (a) 200×, and (b) 3000×.



Fig. 6. Sulfidation resistance of alloys preoxidized in H_2 , after exposure of 4 hr to H_2/H_2S at 750°C.

Preoxidation in H₂/H₂O

Oxide-Scale Formation

During preoxidation treatments of the alloys in H_2/H_2O at 1000°C, basically two different types of oxide scales were observed. The oxide scale developed on Ni-20Cr-2Al or Ni-20Cr-3.5Al consisted of an external Cr₂O₃ layer with stringer-shaped internal oxide pecipitates of Al₂O₃ aligned perpendicular to the alloy/oxide interface (see Figs. 8 and 9). The oxide phases were separated by a chromium-depleted alloy region. The external Cr₂O₃ scales were relatively thin (3 μ m) and maintained good contact with the alloy substrate. On the other hand, oxide scales formed on Ni-20Cr-5Al after oxidation for 50 hr in H₂/H₂O were composed mainly of external and internal aluminum oxides (see Fig. 10). The external Al₂O₃ scales with a thickness of about 1 μ m were severely cracked and spalled, as it is shown in Fig. 10b.

Sulfidation Resistance of Preoxidized Alloys

Figure 11 shows the influence of aluminum concentration and exposure time on the sulfidation resistance of alloys preoxidized at 1000°C in H_2/H_2O . The curves demonstrate that the oxide scale formed on Ni-20Cr-5Al does not affect the sulfidation resistance, whereas the preoxidized Ni-20Cr-2 or 3.5Al alloys show a pronounced improvement of sulfidation resistance.

Furthermore, not only the aluminum concentration but also the preoxidation time improves the sulfidation resistance of alloys with 2 and 3.5 wt.%



Fig. 7. Sulfides formed on the oxide scale of Ni-20Cr-2Al alloy preoxidized 70 hr in H₂ at 1000°C and then sulfidized 4 hr in H₂/H₂S at 750°C: (a) large Ni₃S₂ islands, and (b) fine chromium sulfides, formed mainly along a grain-boundary-like structure visible on the scale.



Fig. 8. Cross-section of Ni-20Cr-2Al oxidized for 50 hr at 1000°C in H_2/H_2O .



Fig. 9. Cross-section of Ni-20Cr-3.5Al oxidized for 50 hr at 1000°C in H_2/H_2O .



Fig. 10. Ni-20Cr-5Al oxidized for 50 hr at 1000°C in H_2/H_2O : (a) cross-section, and (b) morphology of external Al_2O_3 scales.



Fig. 11. Sulfidation resistance of alloys preoxidized in H_2/H_2O after exposure of 4 hr to H_2/H_2S at 750°C.

Al. The preoxidation time to achieve a resonable sulfidation resistance shows an obvious dependence on the aluminum concentration. Whereas for 3.5 wt.% Al alloys a preoxidation time of 20 hr at 1000°C in H_2/H_2O is sufficient to form an oxide film protective against sulfidation, a 2 wt.% Al alloy needs 45 hr preoxidation to reach similarly low corrosion rates in H_2/H_2S .

Preoxidation in Air

The oxide scales formed on Ni-20Cr-2 or 5Al alloys oxidized at 1000°C in air consist of Al_2O_3 , Cr_2O_3 and a small amount of NiO found by XRD (Table I). In contrast to the oxide scales developed during oxidation in H_2 or H_2/H_2O , no uniform oxide scale was formed, and the morphology of the oxide scale depended on oxidation time. The sulfidation resistance of the two alloys is not improved remarkably by these oxide scales, as can be seen in Fig. 12. Both alloys presumably spalled after preoxidation.

DISCUSSION

Aluminum Concentration

Sulfidation of Ni-20Cr-Al alloys show a different dependence on the aluminum concentration after preoxidation treatments in dried H_2 and



Fig. 12. Sulfidation of alloys preoxidized in air after exposure of 4 hr to H_2/H_2S at 750°C.

 H_2/H_2O at 1000°C and on exposure time since different types of oxide scales were formed. Thin aluminum oxide scales, formed on the alloys in H_2 atmospheres with extremely low oxygen activity, improved the sulfidation resistance of the Ni–20Cr–Al alloys (see Fig. 6). The effect of these thin oxide scales on protection against a sulfidizing atmosphere is a function of the aluminum concentration of the alloy. With increasing aluminum concentration the sulfidation reaction decreased strongly. This marked difference of the extent of protection afforded is considered to be a result of different morphological features of the oxide scales. The alloys with 3.5 and 5 wt.% Al were covered with thicker Al₂O₃ layers and exhibited a similar ridge structure as observed with β -NiAl samples oxidized at temperatures higher than 1000°C in air.^{16,17} The oxide scale on Ni–20Cr–2Al seemed to be thinner and obviously provided preferential sites for the formation of sulfides on areas visible on the surface which resemble grain boundaries.

As expected from thermochemical considerations, oxide scales consisting of Cr₂O₃ and Al₂O₃ formed on Ni-20Cr-Al alloys after exposure to H₂/ H₂O at 1000°C. The formation of two different types of oxide scales was observed. Oxide scales with a Cr₂O₃ overlayer on the surface formed on alloys containing 2 and 3.5 wt.% Al. Such layers remarkably improved the sulfidation resistance in H₂/H₂S. The external scale on alloys containing 5 wt.% Al consisted of Al₂O₃ after preoxidation in H₂/H₂O. These oxide scales were not protective due to the high degree of cracking and spalling. Since the thin aluminum oxide scale, which develops in H₂ to a thickness of 0.2-0.5 μ m, showed reasonable adhesion to the substrate, the tendency to spall seems to depend on the thickness of the aluminum oxide scale or other oxides formed. The low residual H_2O content in dry H_2 permitted the formation of only very thin Al_2O_3 oxide layers during the course of the preoxidation treatment.

Spalling of oxide layers on Ni–Cr–Al alloys seems to depend strongly on sulfur segregation at the metal/oxide interface.^{16,17} Since annealing in hydrogen also removes sulfur from the surface, it cannot be decided from the results of this study whether the change in the morphology of the oxide layers or removal of sulfur, or both effects, are the main reason for the improvement of sulfidation resistance. Further improvement of the adherence of Al₂O₃ scales on Ni–Cr–Al alloys is achieved by additions of Y, Zr, Hf, and other elements.^{18–22} However, Ni–20Cr–3.5Al alloys with additions of 0.5 wt.% of Hf, Ti, and Si showed no improved sulfidation resistance in a 4-hr sulfidation test in H_2/H_2S after preoxidation in H_2 up to 100 hr.²²

Preoxidation Time

The sulfidation resistance of Cr_2O_3 scales formed on Ni-20Cr-2 or 3.5Al alloys in H₂/H₂O depends on the preoxidation time, i.e., on the oxidelayer thickness (see Fig. 11). The effect of oxide thickness on the sulfidation resistance can be explained in terms of a diffusion barrier.¹⁰⁻¹³ However, if alloys containing 2 wt.% Al are preoxidized in H₂, the influence of preoxidation time on the sulfidation resistance was found to have no effect after 20 hr. This result indicates that the sulfidation resistance of preoxidized alloys clearly depends on structural features of the oxide scale as well, i.e., the scales may be discontinuous or at least very non-uniform.

Conclusions

- Thin aluminum-oxide scales formed on Ni-20Cr-2, 3.5 or 5Al alloys during oxidation at 1000°C in dry H₂. The oxide scales formed after 20 hr, improved the sulfidation resistance of the alloys remarkably. Increasing aluminum concentration from 2-5 wt.% Al resulted in higher sulfidation resistance of the preoxidized alloys.
- 2. Two different types of oxide scales formed on Ni-20Cr-Al alloys during preoxidation at 1000°C in H₂/H₂O. The external Cr₂O₃ scale formed on Ni-20Cr-2 and Ni-20Cr-3.5Al showed reasonably good sulfidation resistance. The sulfidation resistance of Cr₂O₃ scales was improved with increasing preoxidation time. The external Al₂O₃ scale formed on Ni-20Cr-5Al alloys does not afford protection due to the high degreee of cracking and spalling.
- 3. The oxide scales formed on Ni-20Cr-2 and Ni-20Cr-5Al during preoxidation at 1000°C in air showed no improvement in sulfidation resistance.

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