

# The Corrosion Behavior of a New Sulfidation-Resistant Alloy in a Sulfidizing/Oxidizing/Carburizing Atmosphere

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## ABSTRACT

An investigation was carried out to study the corrosion behavior of a new sulfidation-resistant alloy in a sulfidizing/oxidizing/carburizing atmosphere. This new alloy (HAYNES® HR-160™ alloy) with Ni-29Cr-2.75Si (wt%) has been recently developed for commercial applications. Also included in the current investigation were Fe-Ni-Cr alloys, such as Type 321SS, Type 347SS and Alloy 800H, and HAYNES 556™ alloy. Corrosion tests were performed in H<sub>2</sub>-7%CO-1.5%H<sub>2</sub>O-0.6%H<sub>2</sub>S (vol%) at 700°C (1292°F) with  $P_{O_2} = 1 \times 10^{-23}$  atm,  $P_{S_2} = 1 \times 10^{-9}$  atm and  $a_c = 0.3-0.4$ . Gravimetric data were generated for periods of up to 1500 hours for both the HR-160 and 556 alloys, and up to 1000 hours for the other alloys. Analyses of corrosion products were performed using x-ray diffraction, scanning electron microscopy with energy dispersive analyzer and optical microscopy. Both kinetic and mechanistic aspects of the corrosion reactions are discussed.

A NEW HIGH TEMPERATURE ALLOY (HAYNES HR-160 alloy) which was designed to resist corrosive attack in severe sulfidizing environments was recently developed by Haynes International, Inc. for commercial applications. This alloy has been extensively tested in the field and found to perform especially well in corrosive environments contaminated with sulfur, chlorine, alkali metals and other impurities.<sup>(1-3)</sup> Since the introduction of the alloy into the marketplace about a year and a half ago, fifteen production heats of material have been melted and processed into various product forms, such as sheet, plate, bar, wire and tubulars. The applications of the alloy have, so far, included various components in waste incinerators, sulfur plants, fossil-fired boilers and chemical plants.

The present investigation was undertaken as a collaborative study between the Institute for Advanced Materials, Petten, The Netherlands, and Haynes International, Inc., Kokomo, Indiana, U.S.A., to evaluate the corrosion behavior of this new alloy in sulfidizing environments of relevance to coal gasification processes. Also included in the investigation were commercial Fe-Ni-Cr alloys, such as Type 321SS, Type 347SS and Alloy 800H, Ni-base alloys, such as HASTELLOY® alloy X, INCONEL® alloy 617 and Alloy 625, and HAYNES 556 alloy. The results comparing the performance of HR-160 alloy with those of the commercial alloys were published in an earlier paper<sup>(4)</sup>. The present paper focuses mainly on the study of the corrosion products formed on HR-160 alloy during the exposure to a sulfidizing/oxidizing/carburizing atmosphere. Formation of corrosion products on Alloy 800H and 556 alloy will be highlighted as well.

## EXPERIMENTAL PROCEDURES

The test gas mixture consisted of 7% CO, 1.5% H<sub>2</sub>O, 0.6% H<sub>2</sub>S and balance H<sub>2</sub> (vol %). This gas composition was selected such that, at the test temperature of 700°C and assuming equilibration of the gas mixture, phases of Cr<sub>2</sub>O<sub>3</sub>, CrS, FeS and Ni<sub>3</sub>S<sub>2</sub> are thermodynamically stable at the gas-metal interface. The thermodynamic potentials of the environment at the test temperature were:  $P_{O_2} = 1 \times 10^{-23}$  atm,  $P_{S_2} = 1 \times 10^{-9}$  atm, and  $a_c = 0.3-0.4$ . The environment in terms of sulfur and oxygen potentials is plotted in a M-O-S stability diagram, as shown in Figure 1.

The design of the autoclave used for these studies has been described elsewhere.<sup>(5)</sup> The reaction tube, specimen support system and thermocouple protection tubes were all made of alumina with the test coupons being the only metallic materials in contact with the gas mixture. The coupons (6 x 8 x 10mm) were loaded into the reaction chamber at room

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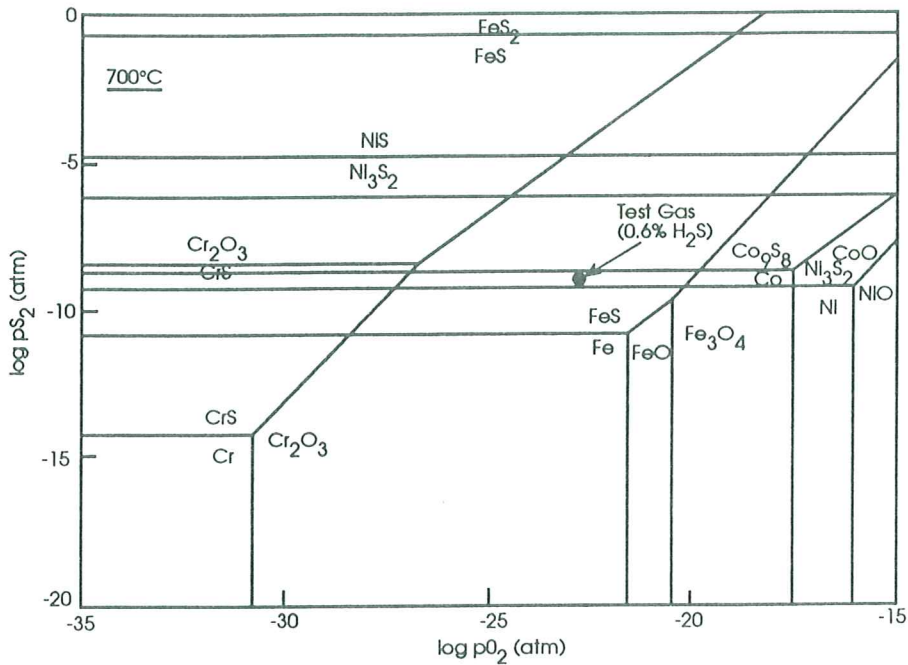


Fig. 1 - M-O-S thermodynamic phase stability diagram at 700°C (1292°F).

temperature and after the desired gas composition and flow rate had been established, the furnace was heated up to the test temperature. Testing was interrupted at pre-determined intervals of 50, 100, 250, 500, 750, 1000 and 1500 hours for weight change measurements. Following the exposure, analyses were carried out on selected coupons using x-ray diffraction, scanning electron microscopy with energy dispersive analyzer (SEM/EDX) and optical microscopy.

#### TEST RESULTS

HR-160 ALLOY - Gravimetric data for HR-160 alloy exposed to the test gas at 700°C (1292°F) for times up

to 1500 hours are summarized in Figure 2. Duplicate tests showed good reproducibility. The corrosion kinetics obeyed a parabolic law with no evidence of breakaway corrosion.

Examination of the cross-section of the sample exposed for 100 hours revealed a thin oxide scale (Fig. 3b). There were nodules, in some areas, overlying the oxide scale (Fig. 3c). These nodules were found by EDX analysis to be Cr-rich sulfides (Fig. 4). X-ray diffraction analysis of the sample surface confirmed the presence of  $Cr_2S_4$ . No evidence of  $Cr_2O_3$  was detected by x-ray diffraction, presumably the oxide scale was too thin. EDX analysis on the surface area not covered by sulfide nodules revealed high Cr along with Si, Ni, Co and Fe (Fig. 4a).

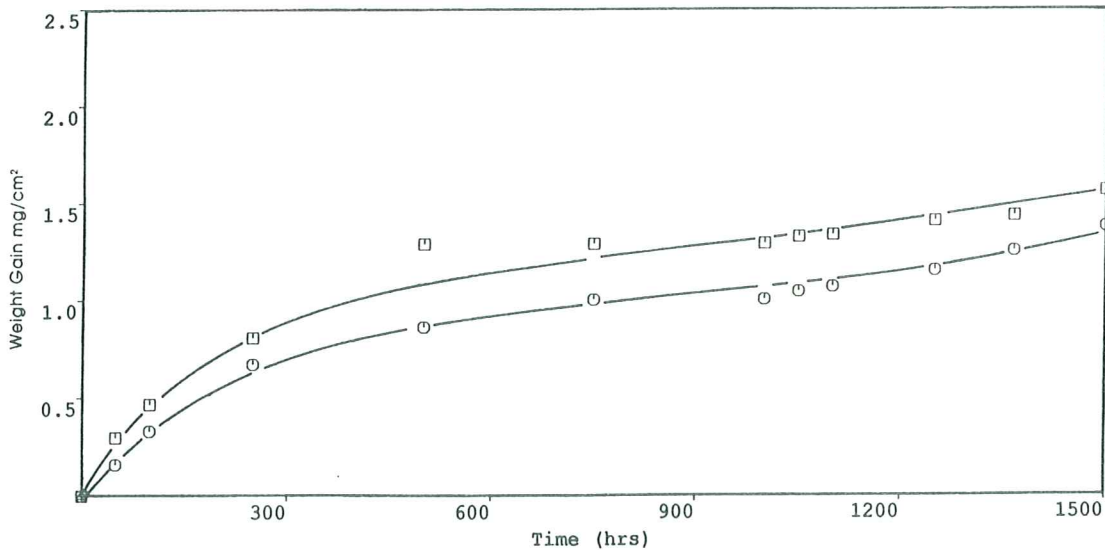


Fig. 2 - Gravimetric data for HR-160 alloy tested at 700°C (1292°F) in  $H_2-7CO-1.5H_2O-0.6H_2S$ .



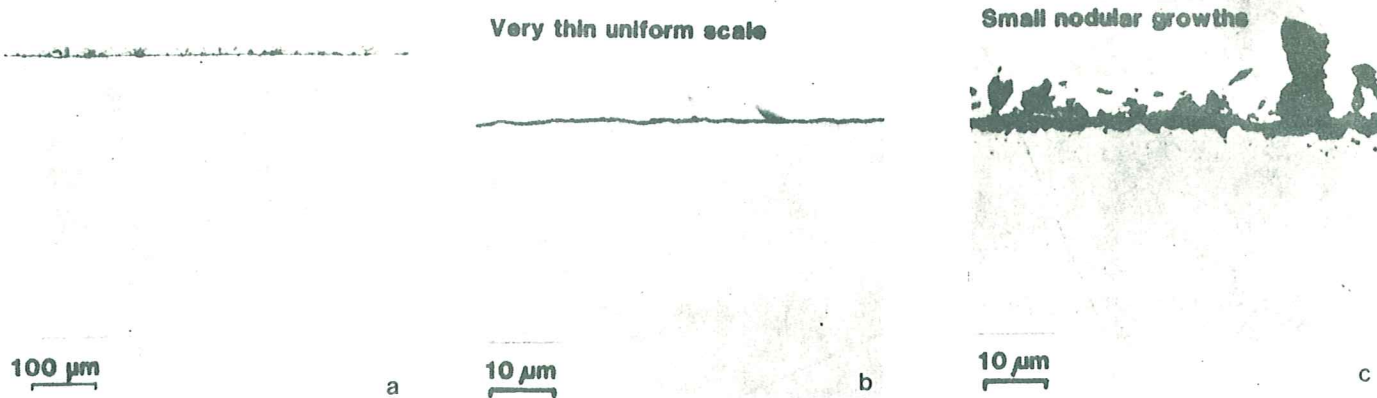


Fig. 3 - Optical photomicrographs showing an oxide scale with sulfide nodules over the oxide scale for HR-160 alloy exposed at 700°C (1292°F) for 100h. The specimen was nickel-plated prior to mounting.

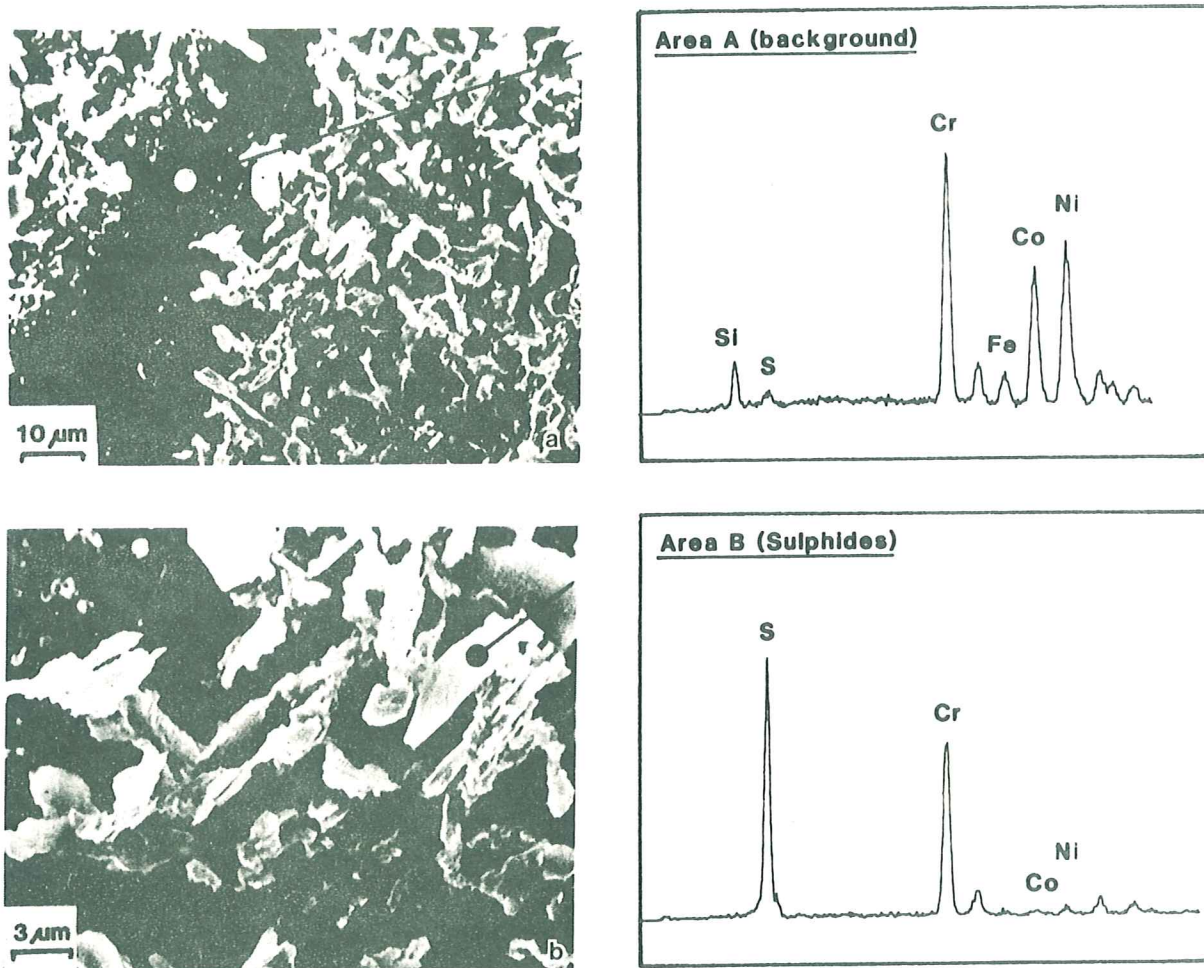


Fig. 4 - SEM/EDX analysis of the surface of the HR-160 specimen tested at 700°C (1292°F) for 100h

The x-ray peaks for Ni, Co and Fe were most likely related to the alloy matrix. The surface is believed to be covered by a chromium oxide scale with Si enrichment.

After 500 hours of exposure, the sample surface

was completely covered by Cr sulfide nodules. These nodules were relatively fine, as shown in Figs. 5 and 6. They were again identified as  $\text{Cr}_3\text{S}_4$ . In addition, a  $\text{Cr}_2\text{O}_3$  scale was detected by x-ray diffraction.



Fig. 5 - Optical photomicrographs showing the chromium oxide scale with chromium sulfides formed on top of the oxide scale for HR-160 alloy tested at 700°C (1292°F) for 500h. The specimen was nickel-plated prior to mounting.

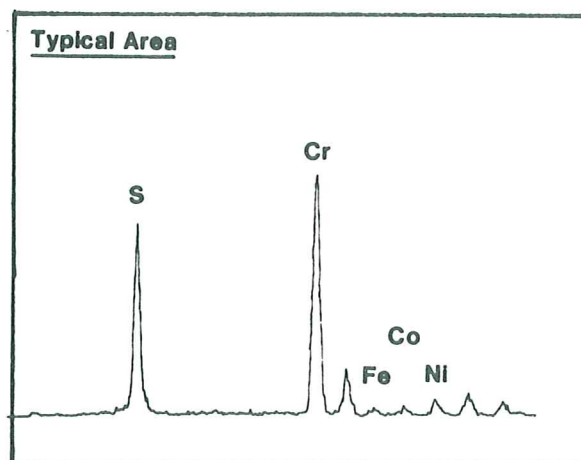
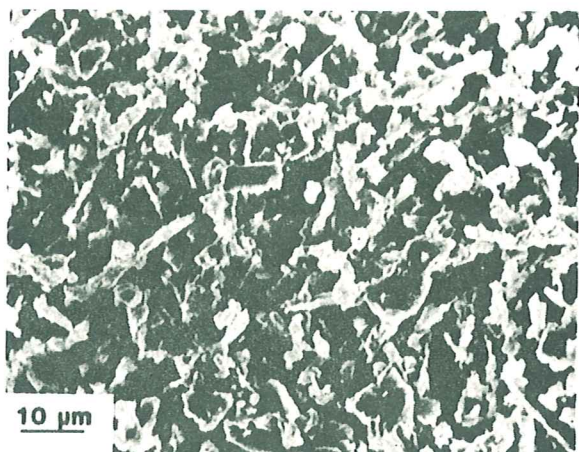


Fig. 6 - SEM/EDX analysis of the surface of the HR-160 specimen tested at 700°C (1292°F) for 500 h.

Continued exposure to 1000 and 1500 hours resulted in little change of the scales. The oxide scale was still very thin (Fig. 7). Phases detected by x-ray diffraction were again  $\text{Cr}_2\text{O}_3$  and  $\text{Cr}_3\text{S}_4$ . The thickness of the chromium sulfides after 1500 hours varied from 5 to 20  $\mu\text{m}$ . Very little internal sulfide precipitation was evident underneath the continuous chromium oxide scale. The specimen exposed for 1500 hours still appeared to be in excellent shape, as shown in Fig. 7a.

556 ALLOY - Gravimetric data of duplicate tests for 556 alloy are summarized in Fig. 8. Reproducibility was, again, quite good. The alloy corroded according to a parabolic law for times up to about 900 hours. Further exposure resulted in breakaway corrosion.

During the "protective" stage, the majority of the specimen surface was covered by external Cr-rich sulfides over the Cr-rich oxide scale. However, significant areas around corners and edges were covered by much thicker crystalline Fe-rich sulfides. These external Fe-rich sulfides became thicker as they

approached the corner or the edge. This is illustrated in Fig. 9. It is also noted that, in general, more severe subscale (or internal) attack was observed underneath heavy external sulfide scale. This is generally observed for other alloy systems as well. It implies that, as the oxide scale is losing its protectiveness, the external sulfide scale is beginning to thicken, while at the same time the underlying matrix suffers increased internal attack.

The phases formed during the protective stage were analyzed by x-ray diffraction, indicating  $\text{Cr}_2\text{O}_3$ ,  $\text{M}_3\text{O}_4$  and  $\text{M}_3\text{S}_4$  after 100 and 500 hours. EDX analysis showed the external sulfide scale to consist of mainly Cr-rich sulfides containing Fe. However, the level of Fe in the Cr-rich sulfide was higher after 1500 hours than that measured after 500 hours. After 1500 hours of exposure, thick sulfide scales near and at corners and edges of the specimen remained Fe-rich.

FE-NI-CR ALLOYS - Type 321SS, Type 347SS and Alloy 800H suffered severe corrosive attack in this environment. Gravimetric data for these three alloys are summarized in Fig. 10.



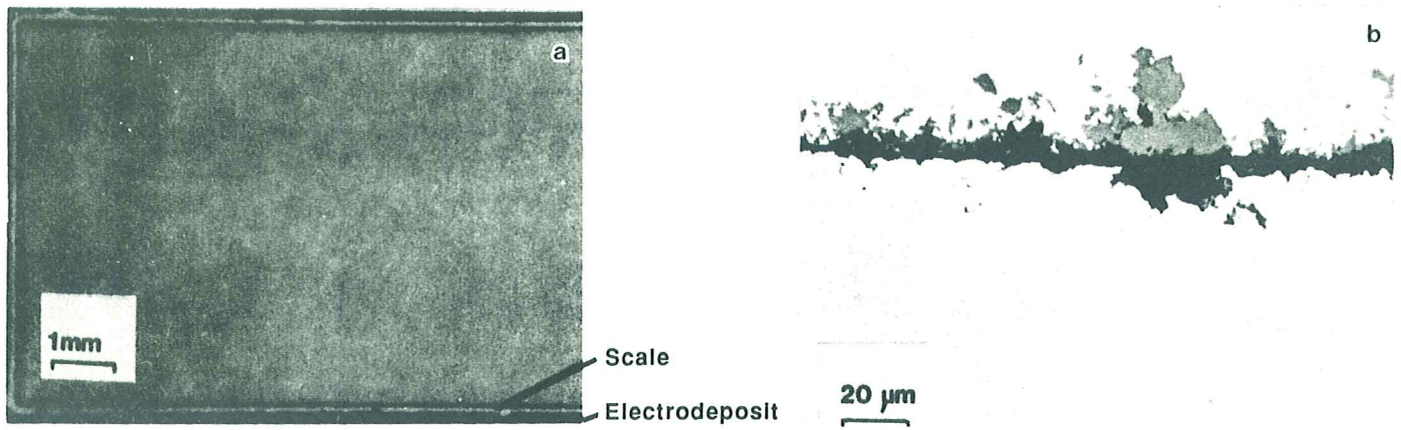


Fig. 7 - Optical photomicrographs showing (a) the cross section of the specimen and (b) chromium sulfides over the chromium oxide scale for HR-160 alloy tested at 700°C (1292°F) for 1500 hours. The specimen was nickel-plated prior to mounting.

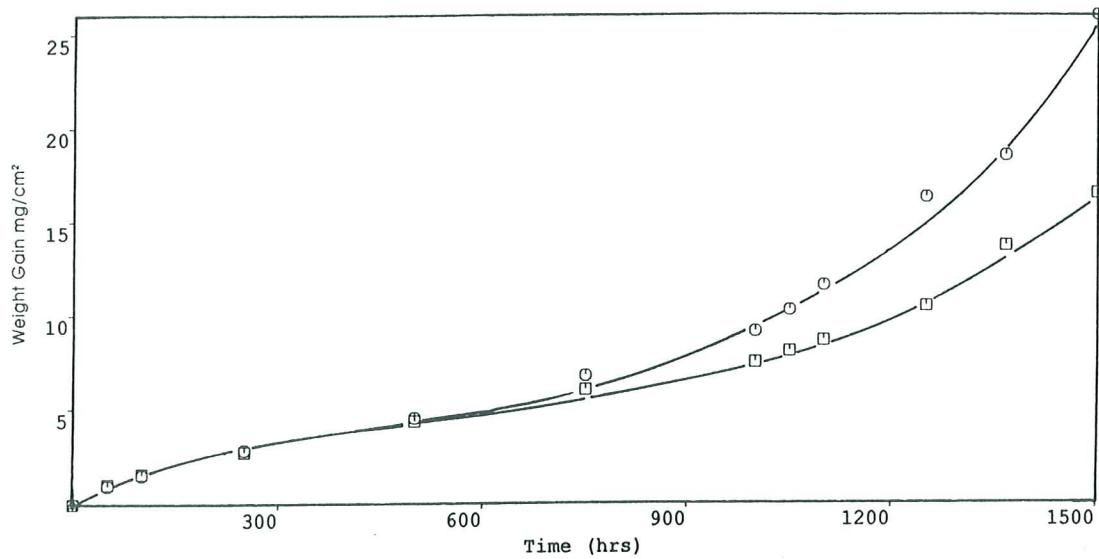


Fig. 8 - Gravimetric data for 556 alloy tested at 700°C (1292°F) in  $H_2-7CO-1.5H_2O-0.6H_2S$

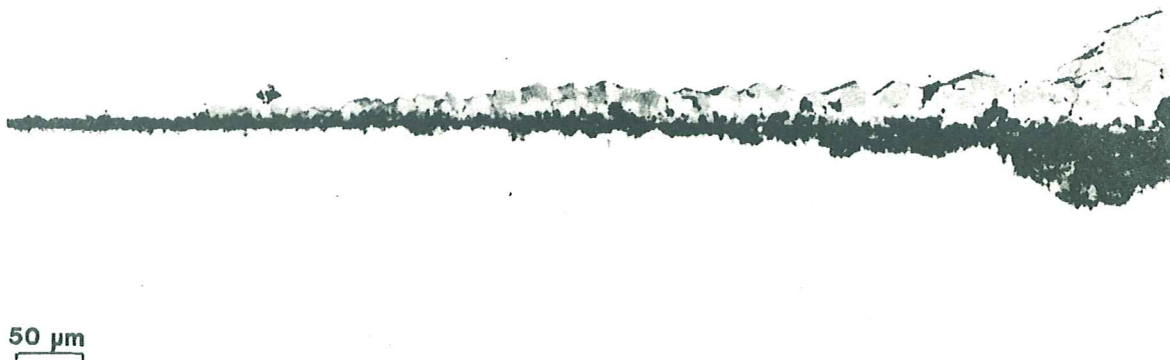


Fig. 9 - Optical photomicrograph showing that the severity of internal (subscale) attack increases with the increasing thickness of the external sulfide scale for 556 alloy tested at 700°C (1292°F) for 500h. The specimen was nickel-plated prior to mounting.

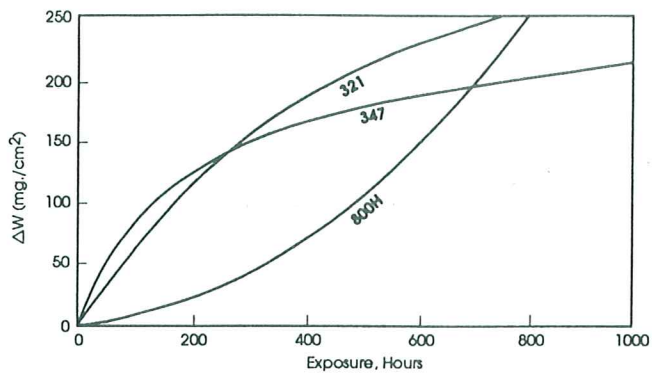


Fig. 10 - Gravimetric data for Type 321SS, Type 347SS and alloy 800H tested at 700°C (1292°F) in H<sub>2</sub>-7CO-1.5H<sub>2</sub>O-0.6H<sub>2</sub>S.

Both Type 321SS and Alloy 800H exhibited about 300 mg/cm<sup>2</sup> of weight gain after 1000 hours, and Type 347SS about 200 mg/cm<sup>2</sup> after 1000 hours. All three alloys suffered tremendous scaling, with significant spallation of the scales. This is illustrated in Fig. 11, which shows low magnification photomicrographs of the specimen cross sections of Alloy 800H after 100 and 1000 hours of exposure. EDX analysis of the scales indicated that these alloys formed mainly Fe-rich sulfides. For example, after 1000 hours, Fe-rich sulfides were observed for Type 347SS and Fe-rich sulfides and Fe-Ni sulfides were observed for Alloy 800H.

#### DISCUSSION

HR-160 alloy was found to be significantly more resistant to sulfidation attack than Fe-Ni-Co-Cr 556 alloy

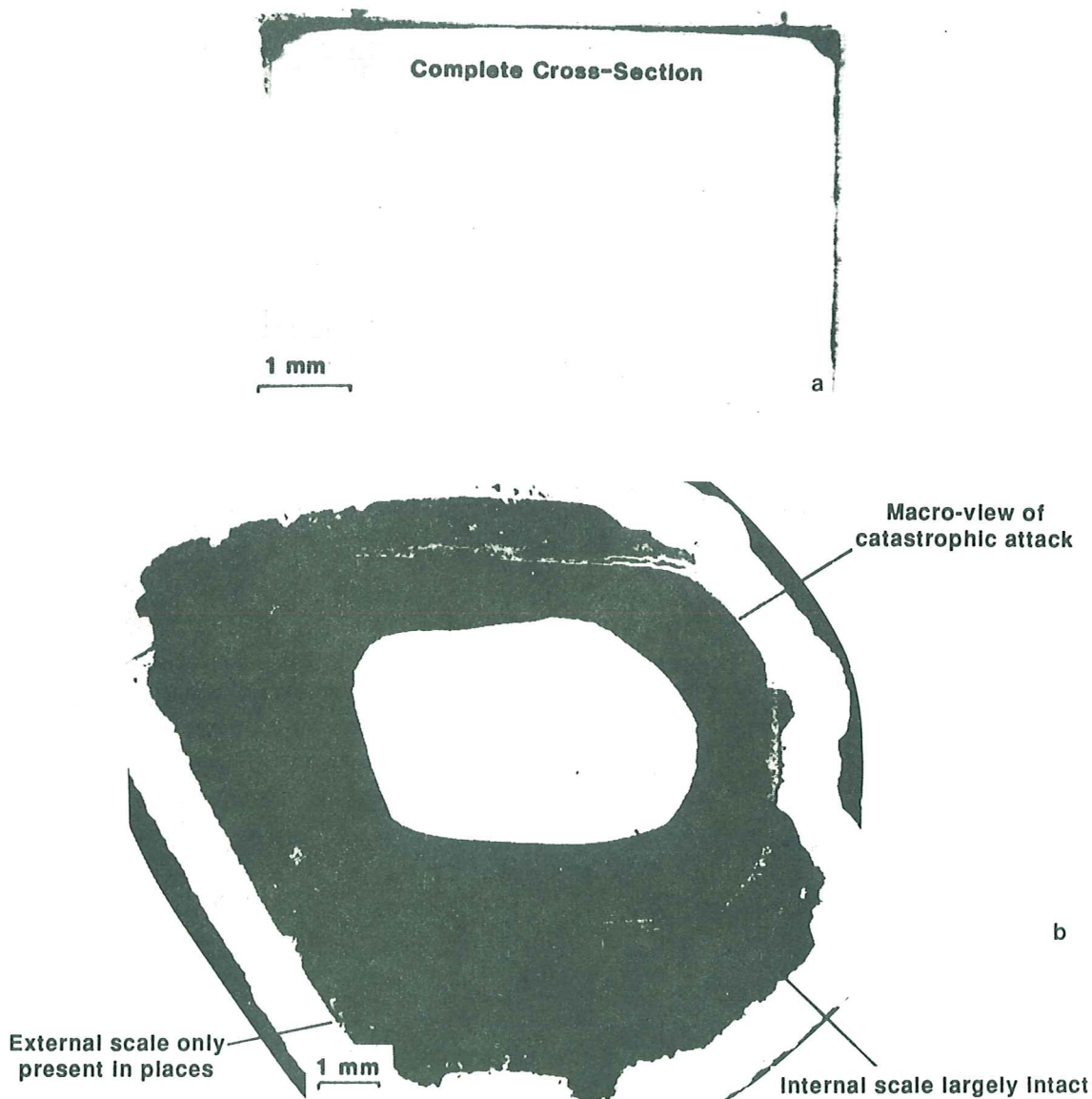


Fig. 11 - Cross-sections of alloy 800H after testing at 700°C (1292°F) for (a) 100h, and (b) 1000hr.



and Fe-Ni-Cr alloys, such as Type 321SS, Type 347SS and Alloy 800H. All these alloys are chromia formers (i.e., they form chromium oxide scales when heated to elevated temperatures), and are thermodynamically capable of forming  $\text{Cr}_2\text{O}_3$  under the present test conditions. The Fe-Ni-Cr alloys tested suffered rapid sulfidation attack by forming Fe-rich sulfides. No chromium-rich oxide scales were observed even after relatively short exposures (i.e., 100 hours).

Alloy 556 was more resistant to sulfidation than Fe-Ni-Cr alloys. The alloy initially developed a chromium oxide scale, which was covered mainly by Cr-rich sulfides. At this stage the kinetics still obeyed a parabolic law. The observation that Cr-rich sulfides had formed on the outer surface of the oxide scale on 556 alloy tends to support the model proposed by Perkins<sup>(6)</sup> that alloying elements, such as Mn, Fe, Co, Cr, Ni, etc. may diffuse through the chromium oxide scale and react with the environment to form external sulfides. These were thought to cause breakaway corrosion. The Cr-rich sulfide scale formed over the chromium oxide scale was generally thin. The growth rate appeared to be slow. After breakaway corrosion took place, significant surface areas, particularly near or at corners and edges, were found to be covered by thick Fe-rich sulfides. Once the thick Fe-rich sulfides had formed, significant subscale (or internal) attack was observed. Under the current test conditions, it is clear that 556 alloy was capable of developing a protective  $\text{Cr}_2\text{O}_3$  scale which initially resisted sulfidation attack, but with time, this scale eventually broke down, resulting in breakaway corrosion.

HR-160 alloy, on the other hand, developed a protective  $\text{Cr}_2\text{O}_3$  scale which remained protective for the total duration of the test for times up to 1500 hours. The oxide scale had remained thin during the exposure, even though with Cr-rich sulfides formed on top of the oxide scale. The sulfide scales had undergone little change during this exposure period. Little internal attack was observed underneath the oxide scale. Apparently, the chromium oxide scale formed on HR-160 alloy was extremely resistant to sulfidation attack. The alloy derives its unique resistance to sulfidation from a critical control of Cr, Si and Co.<sup>(2)</sup> The chromium oxide scale formed on the alloy appears to have Si enrichment. The exact mechanism by which silicon improves the corrosion resistance of this alloy is not clear at the present time. Based on the current studies, it appears that it is possible to develop a chromia forming alloy that can form an oxide scale extremely resistant to sulfidation attack in environments with low oxygen potentials and high sulfur potentials. It is generally considered that an aluminum oxide scale offers better protection than a chromium oxide scale. One major problem with alumina formers is that the kinetics of aluminum oxide formation are relatively slow at lower temperatures (e.g., less than 1000°C). Santorelli, et al.<sup>(7)</sup> studied the sulfidation behavior of two alumina formers, FeCrAlloy and MA956 at 600°C (1112°F) in a simulated coal gasification atmosphere, using the same gas mixture as the present investigation. Both alloys failed to develop an aluminum oxide scale during the exposure, even though FeCrAlloy and MA956 contained 5.2% and 4.5%Al, respectively.

Formation of Fe sulfides and Cr-Fe sulfides was observed for both alloys exposed to the test gas at 600°C (1112°F) for 1000 hours.

## SUMMARY

The corrosion behavior of a new high temperature alloy (HR-160 alloy) along with commercial Fe-Ni-Cr alloys, such as Type 321SS, Type 347SS and Alloy 800H, and Fe-Ni-Co-Cr 556 alloy was investigated in  $\text{H}_2$ -7%CO-1.5% $\text{H}_2\text{O}$ -0.6% $\text{H}_2\text{S}$  at 700°C (1292°F). HR-160 alloy corroded in a parabolic manner with about 1.5 mg/cm<sup>2</sup> of weight gain after 1500 hours of exposure. The alloy developed a protective chromium oxide scale with evidence of Si enrichment. The scale remained thin and protective even after 1500 hours of exposure. The present study indicates that HR-160 alloy is capable of developing a protective chromium oxide scale extremely resistant to sulfidation in environments having low oxygen potentials and high sulfur potentials.

Type 321SS, Type 347SS and Alloy 800H were found to suffer rapid sulfidation attack. These alloys failed to develop a chromium oxide scale under the current test conditions. The corrosion reactions were dominated by the rapid growth of Fe-rich sulfides. With regard to 556 alloy, a protective chromium oxide scale was formed initially. However, the alloy later suffered breakaway corrosion with the formation of external Fe-rich sulfides.

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**Figures:**

Figures 1-6, Figures 8-9, and Figure 10 were taken from a report by J.F. Norton, titled "ASSESSMENT OF THE HIGH TEMPERATURE CORROSION BEHAVIOUR OF ALLOYS IN COMPLEX SULPHUR-CONTAINING GASEOUS ENVIRONMENTS". These photographs were halftone prints, they were reproduced by sending those halftone prints to the print shop and line negatives were made and then exposed on Versalite QCP film and run through the processor to furnish a contact print..

Figure 7 are copy negatives with metlab #'s 64078 and 64079.

Figure 10 was taken from Steve Ernst 91 ASM publication paper for Lake Geneva.