SULFIDATION RESISTANCE OF VARIOUS HIGH-TEMPERATURE ALLOYS

IN LOW OXYGEN POTENTIAL ATMOSPHERES

by

G. Y. LAI

# High Temperature Corrosion
## in
# Energy Systems

CONFERENCE ℙ PROCEEDINGS

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# LOW OXYGEN POTENTIAL ATMOSPHERES

G. Y. Lai

Cabot Corporation
1020 W. Park Avenue
Kokomo, IN 46901

## ABSTRACT

The sulfidation behavior of various commercial iron-, nickel- and cobalt-base alloys was investigated by performing laboratory tests in low oxygen potential atmospheres. Test coupons were exposed isothermally at 760°, 871° and 982°C (1400°, 1600° and 1800°F) in a gas mixture containing $H_2$, CO, $CO_2$, $H_2O$ and $H_2S$. Following exposure, the specimens were cathodically descaled for determination of metal wastage resulting from sulfidation attack. Internal attack was later evaluated by examining the descaled specimen's cross section. Relative performance ranking for the alloys tested is presented. The possible correlation between performance and alloy composition is discussed.

# I. Introduction

Sulfur is one of the most common contaminants present in the combustion products generated by various high-temperature industrial processes. Sulfur generally comes from fuels, feedstocks, fluxes, or chemical additives. Depending upon the process or combustion conditions, sulfur can be present in the gas stream as either $SO_2$ and $SO_3$ or $H_2S$. In general, sulfur converts to $SO_2$ and $SO_3$ when the combustion involves excess air or oxygen. An atmosphere of this type is generally highly oxidizing. However, oxygen-poor conditions can be established locally under certain conditions. The deposits on the metal surface, for example, can lower the oxygen potential significantly at the deposit-metal interface.

When stoichiometric combustion prevails, sulfur is generally present in the flue or process gas stream as $H_2S$. The atmosphere in this case is generally reducing and is characterized by low oxygen potentials. Gas streams generated by many high-temperature industrial process systems are of this type.

When exposed to a sulfur-contaminated gas stream, metallic components can suffer premature failure due to sulfidation attack if the alloy of construction is not properly selected. The industries that have frequently experienced sulfidation-related materials problems include chemical and petrochemical processing, waste incineration, metallurgical processing, glass manufacturing, fossil-fired power generation, and advanced energy-conversion technologies.

Sulfidation of metals or alloys has been the subject of numerous investigations. However, few have generated the engineering data that is needed to allow materials engineers or designers to make an informed materials selection. In the past several years, investigations have been actively pursued elsewhere to evaluate commercial alloys for coal gasification applications.[1-4] The present paper reports the test results generated from a reducing, sulfidizing environment that is relevant to many industrial processes including coal gasification.

## II. Experimental Procedures

The alloys investigated included a variety of commercial, wrought, iron-, nickel-, and cobalt-base alloys. The nominal chemical compostions of these alloys are listed in Table 1. Test coupons (approximately 0.10 to 0.15 cm x 2.2 cm x 2.2 cm) obtained from annealed sheet stock were ground to a 120-grit surface finish. Tests were performed in a reducing, sulfidizing environment with the inlet test gas composition being 5% $H_2$, 5% CO, 1% $CO_2$, 0.15% $H_2S$, 0.1% $H_2O$, and balance Ar (by volume percent). This gas mixture was introduced into the test retort (a 7-cm I.D. alumina tube) with a flow rate of about 150 cc/min and a pressure of about 1.5 atm. Test coupons (four coupons per test run) were suspended by an alumina rod which was, in turn, supported by an alumina boat. No metallic materials except the test coupons were exposed to the test gas. Test coupons were isothermally exposed to the environment for 215 hours at 760°, 871° and 982°C (1400°, 1600° and 1800°F).

The test environment was characterized by low oxygen and high sulfur potentials. The calculated equilibrium gas compositions at the test temperatures are given in Table 2. The test environment plotted in a M-S-O stability diagram is shown in Figure 1.

Table I

Nominal Chemical Composition of Alloys Under Investigation

| Alloy | | Nominal Chemical Composition (Wt. Pct.) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Fe | Ni | Co | Cr | Mo | W | Si | Mn | Others |
| Type 310 | .25+ | Bal | 20 | - | 25 | - | - | 1.5+ | 2.0+ | - |
| CABOT[c] alloy No. 800H | .08 | Bal | 33 | - | 21 | - | - | 1.0+ | 1.5+ | Al=.38, Ti=.38, Cu=.75+ |
| HAYNES[c] alloy No. 556 | .10 | Bal | 20 | 18 | 22 | 3 | 2.5 | .4 | 1.0 | Al=.2, Ta=0.8, La=.02, N=.2, Zr=.02 |
| CABOT alloy No. 600 | .08+ | 8 | Bal | - | 16 | - | - | .5+ | 1.0+ | Al=.35+, Ti=.3+, Cu=.5+ |
| CABOT alloy No. 214 | .04 | 4 | Bal | - | 16 | - | - | - | - | Al=4.5, Y=.01 |
| INCONEL[c] alloy 601 | .10+ | 14.1 | Bal | - | 23 | - | - | .5+ | 1.0+ | Al=1.35, Cu=1.0+ |
| INCONEL alloy 617 | .07 | 1.5 | Bal | 12.5 | 22 | 9 | - | .5 | .5 | Al=1.2, Ti=.3, Cu=.20 |
| CABOT alloy No. 263 | .06 | .7+ | Bal | 20 | 20 | 6 | - | .4+ | .6+ | Al=.5, Ti=2, Cu=.20+ |
| HASTELLOY alloy X | .10 | 18.5 | Bal | 1.5 | 22 | 9 | .6 | 1.0+ | 1.0+ | - |
| RA[c] alloy 333 | .05 | 18 | Bal | 3 | 25 | 3 | 3 | 1.25 | 1.5 | - |
| CABOT alloy No. R-41 | .08 | 5+ | Bal | 11 | 19 | 10 | - | .5+ | .1+ | Al=1.5, Ti=3.0, B = .006 |
| WASPALOY[c] alloy | .08 | 2+ | Bal | 14 | 19 | 4 | - | - | - | Al=1.5, Ti=3.0, B = .006, Zr = .05, Cu = .1+ |
| HAYNES alloy No. 188 | .10 | 3+ | 22 | Bal | 22 | - | 14 | .35 | 1.25+ | La=.04 |
| HAYNES alloy No. 25 | .10 | 3+ | 10 | Bal | 20 | - | 15 | 1.0+ | 1.5 | - |
| HAYNES STELLITE[c] alloy No. 6B | 1.2 | 3+ | 3+ | Bal | 30 | 1.5+ | 4.5 | 2.0+ | 2.0+ | - |

+ Maximum

c CABOT, HAYNES, HASTELLOY, and HAYNES STELLITE are registered trademarks of Cabot Corporation.

INCONEL is a registered trademark of The Inco Family of Companies.

RA is a registered trademark of Rolled Alloys.

WASPALOY is a registered trademark of United Technologies Corporation.

Following the exposure, the test coupons were weighed, descaled cathodically in a salt bath, and weighed again in order to calculate average metal loss (or metal wastage). The descaled samples were then sectioned for metallographic examination to determine internal penetration of sulfides. The total depth of attack is a sum of metal loss (or metal wastage) and internal penetration. For those specimens which suffered severe pitting or localized attack, a different method was used to determine the depth of metal wastage (or metal loss). In this case, the depth of metal wastage and internal penetration were determined by the measurements from metallographic mounts of the descaled specimens. The depth of attack, in this case, was obtained by subtracting the unaffected metal thickness (measured from the mount) from the original coupon thickness and then dividing it by two.
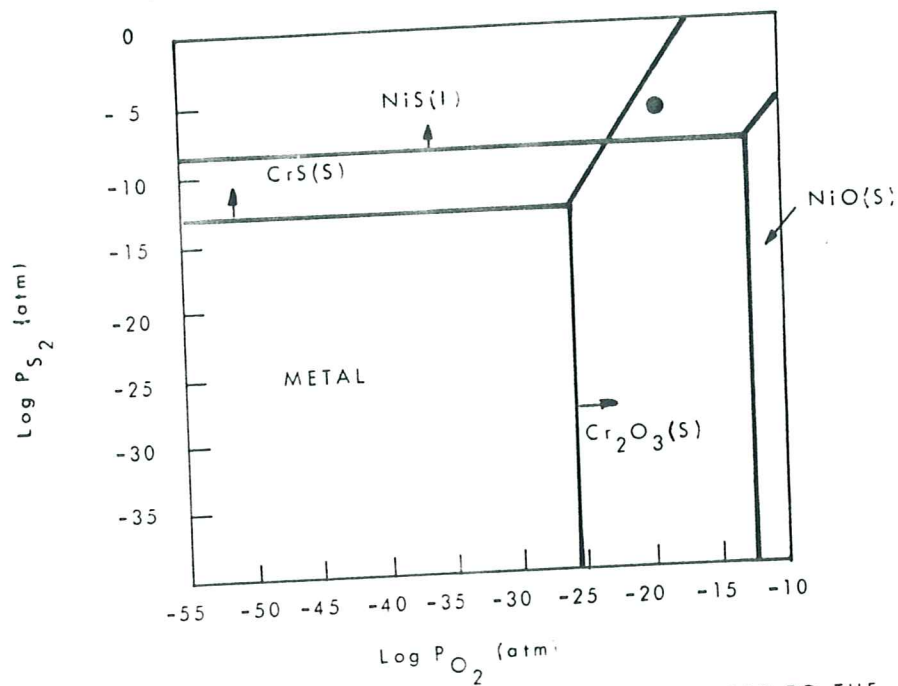
FIGURE 1: THE TEST ENVIRONMENT WITH RESPECT TO THE M-S-O SYSTEM AT 871°C (1600°F).

## RESULTS

The test results generated at 760°, 871° and 982°C (1400°, 1600° and 1800°F) are summarized in Figures 2, 3 and 4, respectively. The data are presented in the order of performance ranking. In general, three cobalt-base alloys (i.e., alloys 6B, 25 and 188) were found to be most resistant to sulfidation attack. Nickel-base alloys exhibited a wide range of resistance, ranging from very poor for alloys such as alloys 600, 601 and X to very good for alloy R-41 and WASPALOY® alloy. In these short-time tests, both alloy R-41 and WASPALOY alloy exhibited a sulfidation resistance approaching to that of cobalt-base alloys. These two nickel-base alloys, however, suffered some localized attack particularly at the sample's edges and corners. Cobalt-base alloys, on the other hand, exhibited excellent surface conditions. The degree of sulfidation attack upon various alloys was clearly revealed after the specimens were descaled. Figure 5 illustrates the conditions of several test samples after descaling.

## Table 2

### Inlet Test Gas Composition and Calculated Equilibrium Gas Compositions

| | Inlet Gas Composition (Vol. %) | Calculated Equilibrium Composition (Vol. %) at 1 Atm. | | |
| | | 760°C (1400°F) | 871°C (1600°F) | 982°C (1800°F) |
|---|---|---|---|---|
| $H_2$ | 5.0 | 4.6 | 4.6 | 4.5 |
| CO | 5.0 | 5.3 | 5.4 | 5.5 |
| $CO_2$ | 1.0 | 0.65 | 0.58 | 0.5 |
| $H_2S$ | 0.15 | 0.15 | 0.15 | 0.15 |
| $H_2O$ | 0.1 | 0.45 | 0.52 | 0.6 |
| $CH_4$ | – | $0.2 \times 10^{-4}$ | $0.1 \times 10^{-5}$ | $0.2 \times 10^{-6}$ |
| Ar | Bal | Bal | Bal | Bal |
| $P_{O_2}$ | | $5 \times 10^{-22}$ atm | $3 \times 10^{-19}$ atm | $3 \times 10^{-17}$ atm |
| $P_{S_2}$ | | $1 \times 10^{-7}$ atm | $0.9 \times 10^{-6}$ atm | $4 \times 10^{-6}$ atm |
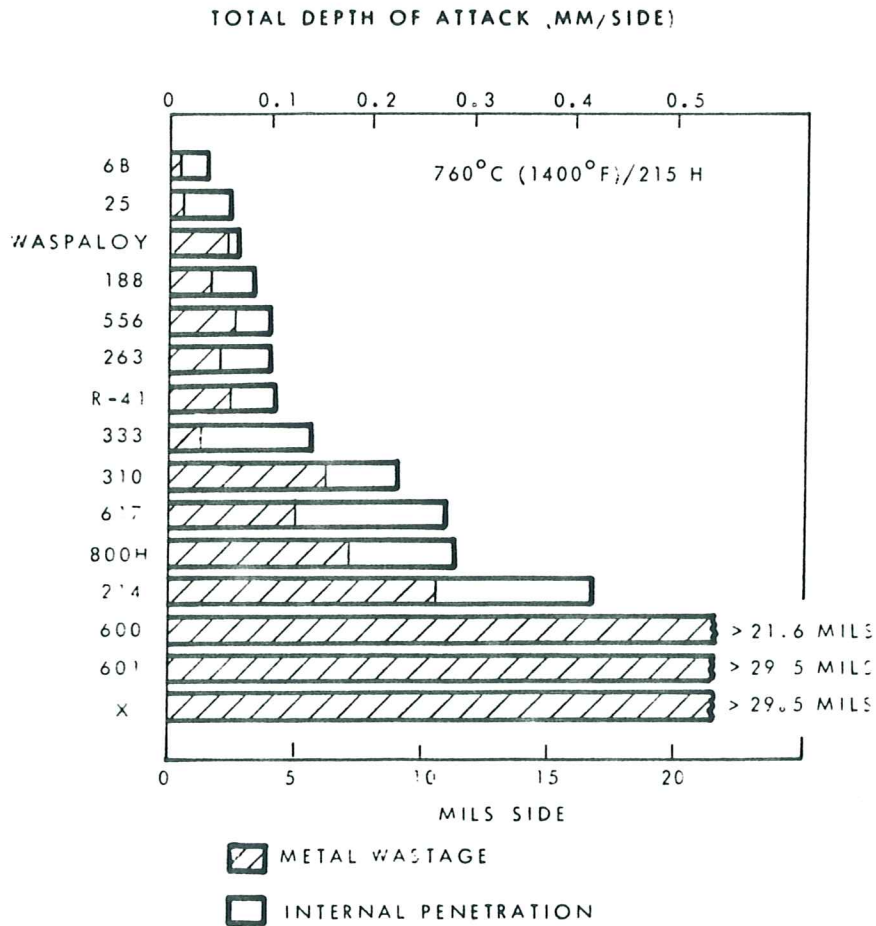


FIGURE 2: RESULTS OF SULFIDATION TESTS PERFORMED AT 760°C 1400°F; FOR 215 HOURS

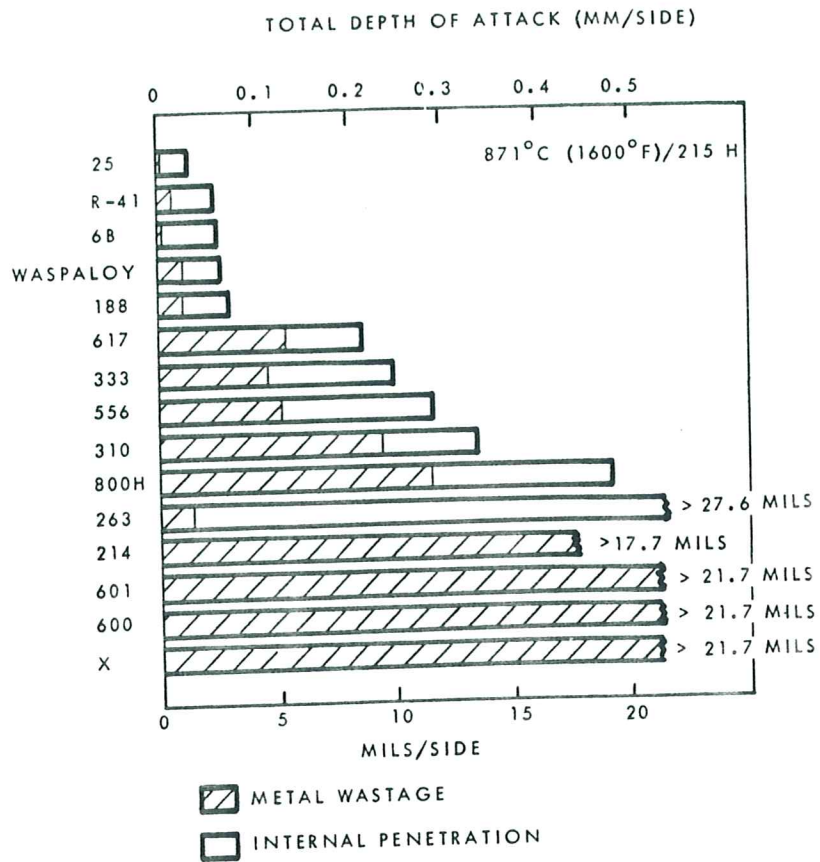TOTAL DEPTH OF ATTACK (MM/SIDE)



FIGURE 3: RESULTS OF SULFIDATION TESTS PERFORMED
AT 871°C (1600°F) FOR 215 HOURS

TOTAL DEPTH OF ATTACK (MM/SIDE)



FIGURE 4: RESULTS OF SULFIDATION TESTS PERFORMED
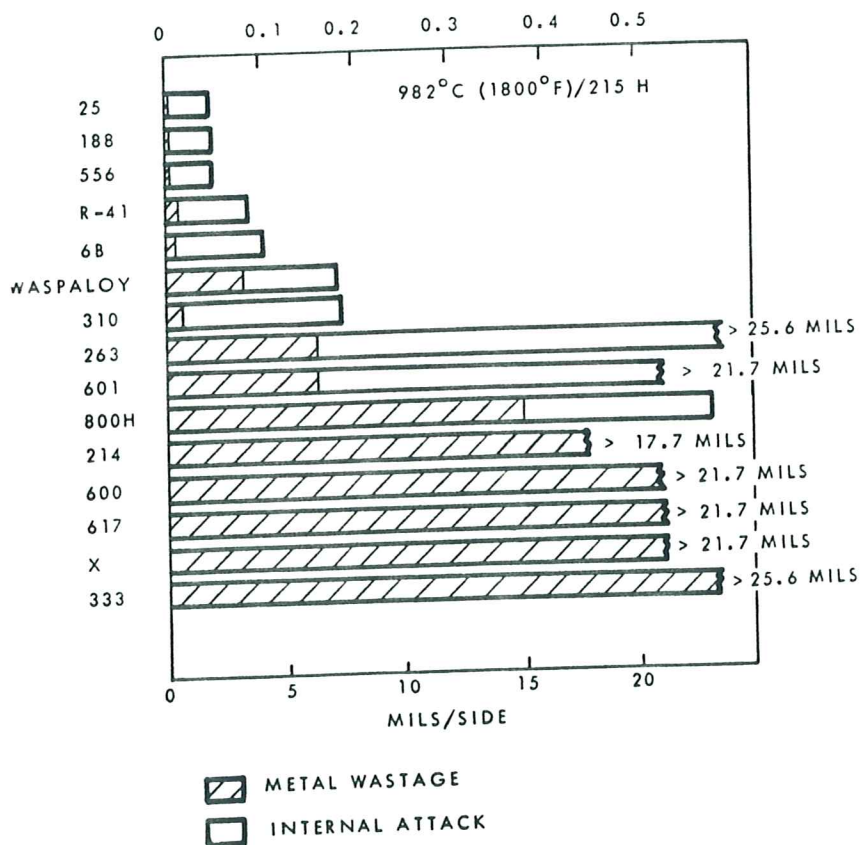AT 982°C (1800°F) FOR 215 HOURS.

|__ 1 cm __|

(a)  Alloy 25          (b)  Alloy R-41          (c)  Alloy 333
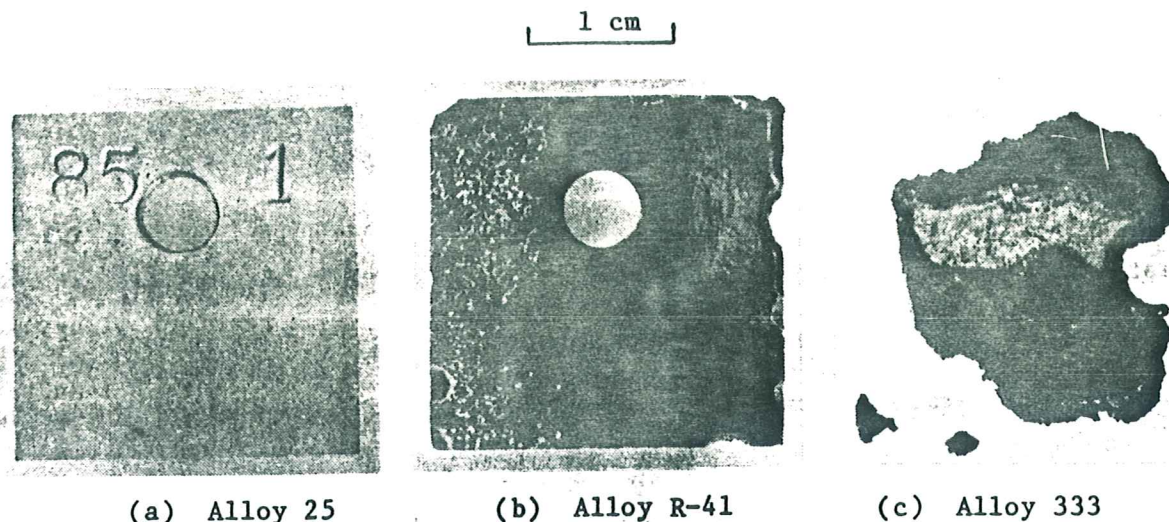
Figure 5:  Optical photomicrographs showing the condition of the
           samples of alloys 25, R-41 and 333 tested at 982°C (1800°F)
           for 215 hours and cathodically descaled.

For some nickel-base alloys, samples were either perforated or nearly
consumed, such as the alloy 333 sample shown in Figure 5 (c).  Figure 6
shows the cross section of a descaled alloy 600 sample which was essen-
tially consumed after testing at 982°C (1800°F) for 215 hours.  For
comparison, the cross section of a descaled alloy 188 sample is shown in
Figure 6, illustrating little sulfidation attack after exposure to the
same test conditions.

Original Sample Thickness



(a)  Alloy 188                    (b)  Alloy 600
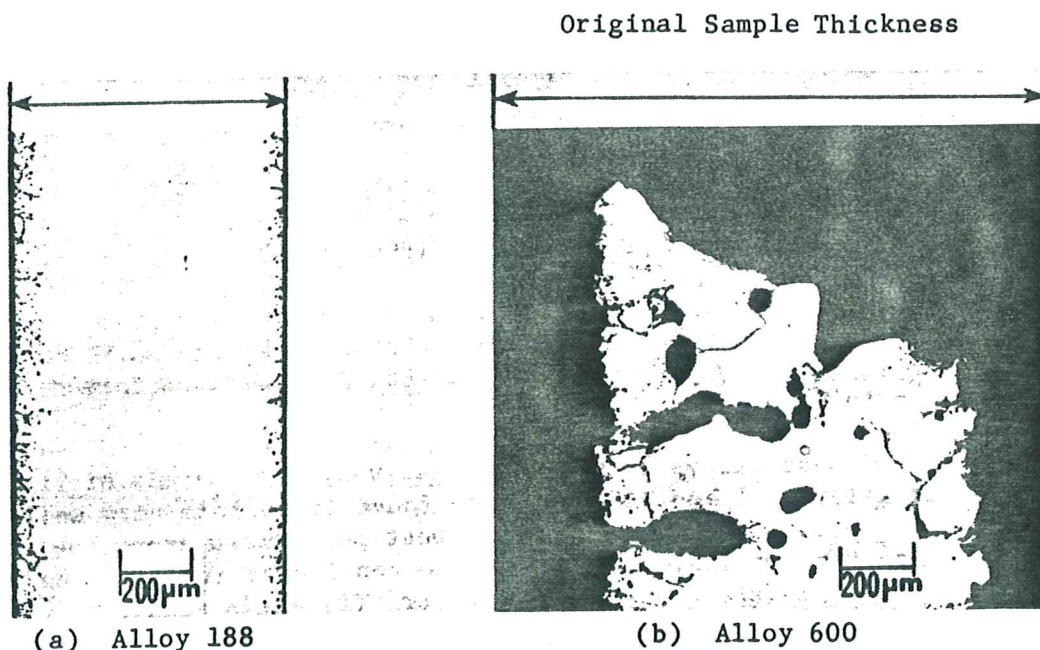
Figure 6:  Optical photomicrographs showing cross sections of the
           descaled alloy 188 and alloy 600 samples tested at 982°C
           (1800°F) for 215 hours.

Among the three iron-base alloys tested, alloy 556 was found to be the
best performer followed by Type 310 stainless steel and alloy 800H
(worst).  For both alloy 556 and Type 310 stainless steel, the attack was
found to increase as the temperature was increased from 760°C (1400°F) to
871°C (1600°F), and to decrease when the temperature was raised further to

982°C (1800°F). Alloy 800H similar to nickel-base alloys, on the other hand, suffered increased attack with increasing temperatures from 760°C (1400°F) to 982°C (1800°F).

## Discussion

It is well known that high nickel alloys are prone to rapid sulfidation attack because of the formation of molten nickel-rich sulfides. This was clearly indicated by the present results. Some Fe-Ni-Cr alloys such as alloy 800H, were also shown to suffer severe sulfidation attack due to the formation of molten sulfides. Test samples of alloys 601 and 800H with numerous molten sulfide nodules are shown in Figure 7.



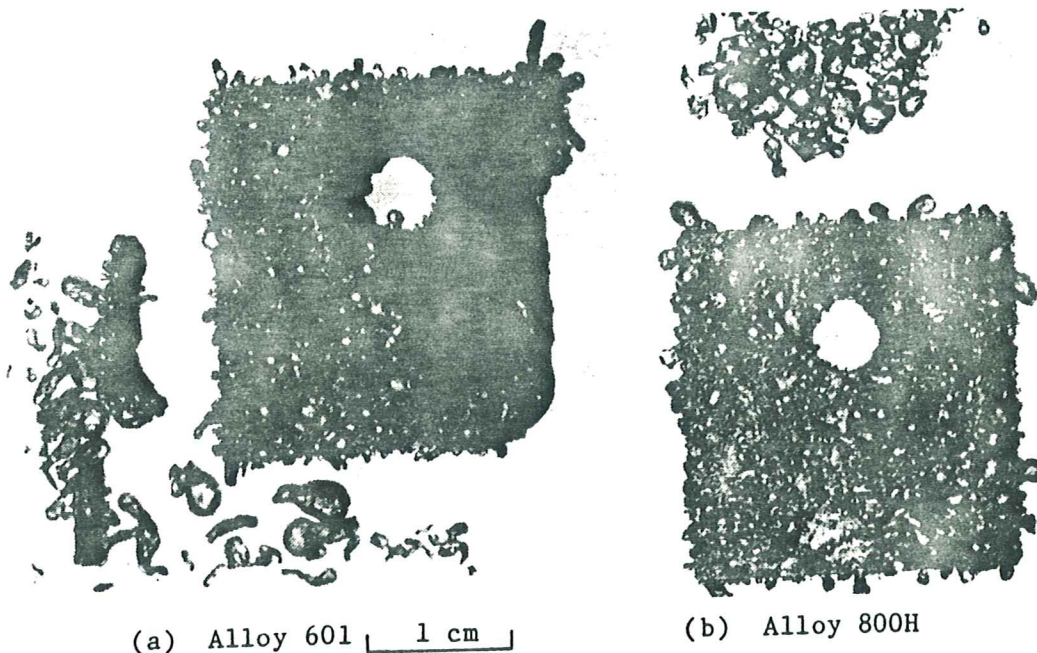(a)  Alloy 601 |  1 cm  |          (b)  Alloy 800H

Figure 7:  Optical photographs showing samples of alloy 601 and alloy 800H tested at 871°C (1600°F) for 215 hours.

An SEM/EDX analysis of the molten sulfides was performed on selected samples. These molten phases were either nickel-rich sulfides or (Ni, Fe) sulfides. An analysis of the molten (Ni, Fe) sulfides formed on alloy 601 is shown in Figure 8.

Nickel-base alloys containing relatively high levels of Ti and Al, such as alloy R-41 and WASPALOY were found to perform very well. As discussed previously, they were the best performers among the nickel-base alloys tested. Titanium appears to be beneficial in improving the alloy's sulfidation resistance by forming a (Cr, Ti) oxide scale.

Rapid sulfidation could take place if this oxide scale was disrupted. As previously discussed, alloy R-41 and WASPALOY alloy suffered localized attack on the sample's edges or corners. Figure 9 illustrates the accelerated internal sulfidation underneath the disrupted (Cr, Ti) oxide scale (marked as No. 2). The disrupted oxide scale was found to contain some sulfur. Little attack was observed under the protective (Cr, Ti) oxide scale (marked as No. 1). The beneficial effect of titanium in sulfidation resistance of Fe-Ni-Cr alloys was also reported by Bradshaw and Stoltz (3).
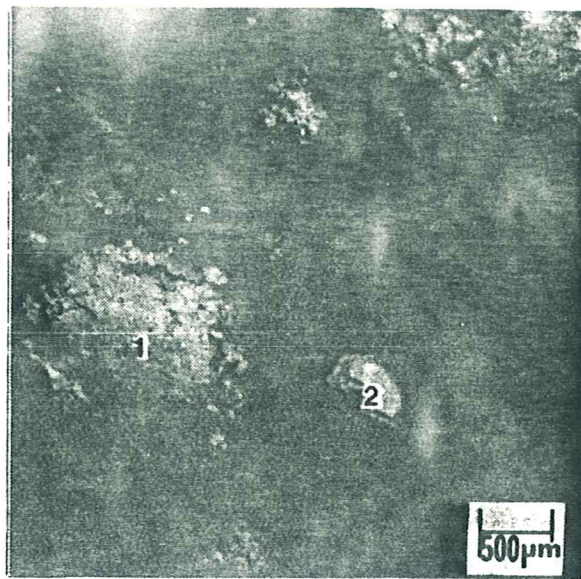
| Semi-Quantitative Analysis* | | | | |
|---|---|---|---|---|
| Phase | Ni | Fe | Cr | S |
| 1 | 53.7 | 11.3 | – | 35.0 |
| 2 | 38.6 | 27.5 | – | 33.9 |
| 3 | 1.5 | 2.8 | 92.5 | 3.2 |

\* relative intensity

Figure 8:  SEM photomicrograph of the sulfide nodules formed on the alloy 601 sample (tested at 871°C for 215 hours) and a semi-quantitative analysis of these phases.
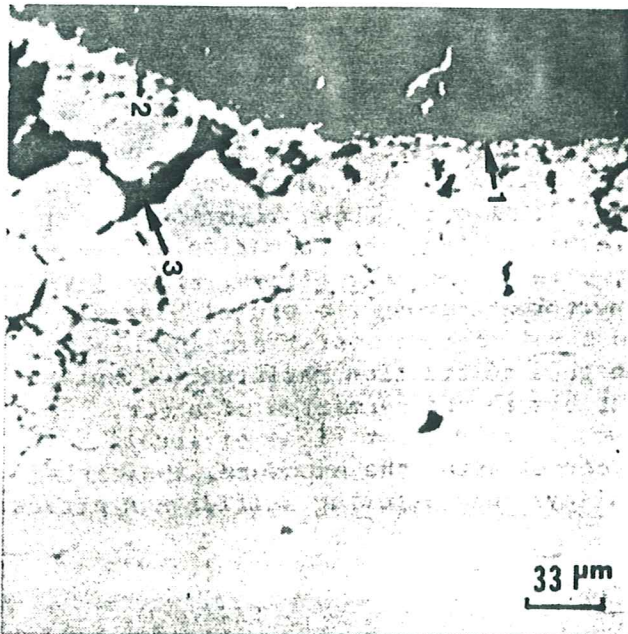


| Semi-Quantitative Analysis* | | | | |
|---|---|---|---|---|
| Phase | Cr | Ti | Ni | S |
| 1 | 71.8 | 28.2 | – | – |
| 2 | 85.4 | 5.4 | 2.3 | 6.9 |
| 3 | 36.2 | 2.2 | 3.5 | 58.1 |

\* relative intensity

Figure 9:  SEM/EDX analysis of a WASPALOY alloy sample tested at 871°C (1600°F) for 215 hours.

Both Type 310 stainless steel and alloy 556 showed significantly less attack at 982°C (1800°F) than at 871°C (1600°F). An SEM/EDX analysis of these samples indicated that the surface scales formed at 982°C (1800°F) consisted of chromium oxides and chromium-rich sulfides. Unlike the 760°C and 871°C tests, which involved mainly sulfidation, the 982°C tests involved both oxidation and sulfidation for these low-nickel, iron-base alloys. Alloy 800H containing a higher nickel content, on the other hand, exhibited increased sulfidation attack with increasing temperature. Most nickel-base alloys behaved in a similar fashion.

For cobalt-base alloys, no molten sulfides were observed at the three test temperatures. The corrosion products formed at 760° and 871°C (1400° and 1600°F) consisted mainly of sulfides. The sulfides formed were essentially chromium sulfides and/or (Cr, Co) sulfides. Small amounts of chromium oxides were also detected in some cases. It appears that slightly more oxides were detected at 871°C (1600°F) than at 760°C (1400°F). At 982°C (1800°F), these cobalt-base alloys exhibited only oxide scales.

Apparently under the present test conditions in which oxidation is competing with sulfidation, the alloy composition appears to be important in determining the development of oxides, sulfides or mixtures of both. Oxidation was found to take place more readily on cobalt-base alloys than on nickel- and iron-base alloys. Lowering the nickel content in Fe-base alloys may favor the formation of oxides kinetically, particularly at high temperatures, as in the case of alloy 556 and Type 310 stainless steel tested at 982°C (1800°F).

## Summary

The sulfidation resistance of a wide variety of commercial iron-, nickel- and cobalt-base alloys was investigated by performing laboratory tests in a reducing, severely sulfidizing environment at 760°, 871° and 982°C (1400°, 1600° and 1800°F). The relative performance ranking for these alloys was presented. The data and information would be useful to materials engineers or designers for making an informed materials selection for applications in reducing, sulfidizng environments.

Cobalt-base alloys as a class suffer the least attack among the three classes of alloys. In general, the alloys suffering the worst attack were nickel-base alloys, followed by Fe-Ni-Cr alloys. These alloys suffered severe metal wastage and pitting, resulting from the formation of nickel-rich sulfides or (Fe, Ni) sulfides. Two nickel-base alloys, alloy R-41 and WASPALOY alloy, were the best performers among the nickel-base alloys tested. These two alloys exhibited a sulfidation resistance approaching to that of cobalt-base alloys. The good sulfidation resistance displayed by these alloys is probably attributable to the formation of a (Cr, Ti) oxide scale. These two alloys, however, have shown signs of localized attack on the specimens' edges and corner after the exposure, indicating the propensity of the nickel-base alloys for suffering sulfidation attack.

## References

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