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MATERIALS BEHAVIOR IN HIGH-TEMPERATURE, SULFIDIZING ENVIRONMENTS

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ABSTRACT

The sulfidation behavior of a variety of commercial, wrought alloys ranging from stainless steels to nickel- and cobalt-base superalloys was investigated by performing laboratory tests in a reducing, sulfidizing environment at 760°C, 871°C, and 982°C (1400°F, 1600°F, and 1800°F). The relative performance ranking for these alloys is presented. The correlation between performance and alloy composition is discussed.

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. Process gas streams generated by many petrochemical and coal gasification processes 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 petrochemical processing, waste incineration, 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 comparative performance data for a wide variety of commercial alloys 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] More studies are needed to evaluate engineering materials that are resistant to sulfidation attack in other industrial processes. The intent of the present investigation was to generate such data in both oxidizing and reducing environments covering both ends of the environmental spectrum encountered in industries. The present paper reports the test results generated from a reducing, sulfidizing environment (i.e., sulfur is present as H_2S in the gas mixture). Data generated from an oxidizing, sulfidizing environment where sulfur is present as SO_2 and SO_3 will be reported in the future.

EXPERIMENTAL PROCEDURES

The alloys investigated included a variety of commercial, wrought, iron-, nickel-, and cobalt-base alloys. The nominal chemical compositions 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°C, 871°C, and 982°C (1400°F, 1600°F, 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.

RESULTS AND DISCUSSION

The test results generated at 760°C, 871°C, and 982°C (1400°F, 1600°F, and 1800°F) are summarized in Figures 2, 3, and 4, respectively. The results are presented in terms of weight gain per unit area of specimen. Representative test samples of iron-, nickel-, and cobalt-base alloys after testing at these three temperatures are shown in Figures 5, 6, and 7.

Sulfidation Behavior at 760°C and 871°C (1400°F and 1600°F)

Three high cobalt alloys (i.e., HAYNES STELLITE® alloy No. 6B and HAYNES® alloys No. 25 and No. 150) were found to be most resistant to sulfidation attack at 760°C (1400°F). Next to these alloys were HAYNES alloy No. 188, CABOT® alloy No. 263, HAYNES alloy No. 556, and MULTIMET® Alloy. CABOT alloy No. 600, HASTELLOY® alloy X, INCONEL® alloy 601, INCONEL alloy 617, Type 310 stainless steel, and CABOT alloy No. 800H suffered the worst attack.

At 871° (1600°F), all cobalt-base alloys performed best. These were followed by alloys 263 and 617 and then by MULTIMET alloy and alloy 556. Alloys 600, X, 601, 800H, and 310SS showed the worst performance.

It is known that high nickel alloys are prone to rapid sulfidation attack because of the formation of molten nickel sulfides. This was clearly indicated by the present results. The results also indicated that high iron alloys such as 310SS and alloy 800H suffered severe sulfidation attack as well. As shown in Figure 6, molten sulfides were found to occur on both high nickel and high iron alloys. An SEM/EDX analysis of the molten sulfides was performed on selected samples. In general, these molten sulfides were found to be highly enriched in nickel and iron. The results of an analysis performed on the alloy 800H sample tested at 871°C (1600°F) are illustrated in Figure 8. The iron-nickel rich sulfides were found to grow from the Fe-Cr-Ni rich sulfide scale (Figure 8). This is further illustrated in Figure 9, which shows the powdery sulfides enriched in mainly iron and nickel formed on the underlying sulfide scale enriched in iron and chromium. The cross section of this underlying (Fe, Cr) sulfide scale is shown in Figure 9b. A similar observation (i.e., Fe-Ni sulfides formed on an underlying Fe-Cr sulfide scale) was also made by Rao and Nelson in their investigation of 310SS in sulfidizing environments with low oxygen and high sulfur potentials.[5] For cobalt-base alloys (e.g., alloys 6B, 25, 150, and 188), small weight gains were observed after testing for 215 hours at 760°C and 871°C (1400°F and 1600°F). The corrosion products consisted mainly of sulfides. In some cases, small amounts of chromium oxides were also detected. It appears that slightly more oxides were detected at 871°C (1600°F) than at 760°C (1400°F). Sulfides were essentially chromium sulfides and/or (Cr, Co) sulfides. This is illustrated in Figure 10.

The overall behavior of the alloys tested in the present environment appears to follow a general trend when tested at both 760°C and 871°C (1400°F and 1600°F). Both high nickel and high iron alloys, in general, suffered the worst sulfidation attack. As the nickel and/or iron content in the alloy decreases, the alloy's sulfidation resistance tends to improve. The high cobalt alloys with low nickel and iron contents were found to be the best performers among the alloys tested. The results shown in Figures 2 and 3 were replotted as a function of (Fe + Ni) content in the alloy and are shown in Figure 11. The results suggest a qualitative correlation between the alloy's sulfidation resistance and the (Fe + Ni) content in the alloy. Apparently, it is related to the formation of (Fe, Ni) sulfides.

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Sulfidation Behavior at 982°C (1800°F)

Alloys 600, 601, 617, X, and 800H showed the largest weight gains among the alloys tested. Samples of these alloys showed molten sulfides. Some of these samples are shown in Figure 7. On the other hand, alloys 6B, 25, 188, 556, and 310SS exhibited a negligible weight increase. The alloy with an intermediate weight gain was alloy 263. It was particularly interesting to note that 310SS, while showing significant weight increase due to the formation of sulfides at 760°C and 871°C (1400°F and 1600°F), showed little weight gain at 982°C (1800°F). The appearance of the 310SS sample tested at 982°C (1800°F) is shown in Figures 7d and 12a. The results of the SEM/EDX analysis of the surface scale indicated a mixture of oxides (marked as No. 3 in Figure 12b) and sulfides (marked as Nos. 1 and 2 in Figure 12b). Similarly, the scale formed on alloy 556, which showed little weight gain after testing, consisted of a mixture of oxides and sulfides. The cobalt-base alloys (e.g., 6B, and 188), however, exhibited only an oxide scale. Unlike the 760°C and 871°C (1400°F and 1600°F) tests, which involved mainly sulfidation, the 982°C (1800°F) tests involved oxidation for some of the alloys. Apparently under this test condition when oxidation is competing with sulfidation, the alloy composition appears to be important in determining the development of oxides, sulfides, or mixures 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 these alloys may favor the formation of oxides kinetically, as in the case of alloy 556. Increasing chromium content in these alloys may also accelerate the formation of oxides, as in the case of 310SS. Because of the competition between oxidation and sulfidation under the present test condition, there exists no apparent correlation between the alloy's sulfidation resistance and (Fe + Ni) content in the alloy, as was in the case of 760°C and 871°C (1400°F and 1600°F) testing. Figure 13 illustrates the 982°C (1800°F) test results plotted as a function of (Fe + Ni) content in the alloy.

SUMMARY AND CONCLUSIONS

A variety of commercial iron-, nickel-, and cobalt-base alloys was tested in a reducing, sulfidizing environment at 760°C, 871°C, and 982°C (1400°F, 1600°F, and 1800°F). The sulfidation data pertaining to the relative performance ranking for these alloys was presented. This information can be useful to guide materials selection for application in sulfur-contaminated environments.

In general, cobalt-base alloys (e.g., HAYNES STELLITE alloy No. 6B and HAYNES alloys No. 25, No. 150, and No. 188) were found to be most resistant to sulfidation attack among the three classes of alloys tested. Both high nickel and high iron alloys suffered severe sulfidation attack due to the formation of molten (Fe, Ni) sulfides. The present results appear to suggest that reducing nickel and/or iron content with a concurrent increase in cobalt in the alloy tends to improve the alloy's sulfidation resistance. Furthermore, under the conditions when oxidation is competing with sulfidation in the gas-metal reactions, either increasing chromium content or decreasing nickel content with a concurrent increase in cobalt would tend to improve the alloy's sulfidation resistance, presumably by accelerating the formation of oxides (or retarding the formation of Fe-Ni sulfides).

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Table 1

Nominal Chemical Composition of High-Temperature Alloys Under Investigation

Alloy	Nominal Chemical Composition (Wt. Pct.)											
	C	Fe	Ni	Co	Cr	Mo	W	Si	Mn	Al	Ti	Others
Type 310	.25+	Bal	20	-	25	-	-	1.5+	2.0+	-	-	-
CABOT* alloy No. 800H	.08	Bal	33	-	21	-	-	1.0+	1.5+	.38	.38	Cu=.75+
MULTIMET* alloy	.10	Bal	20	20	21	3	2.5	1.0+	1.5+	-	-	Cb+Ta=1,Cu=.5+,N=.15
HAYNES* alloy No. 556	.10	Bal	20	18	22	3	2.5	.4	1.0	.2	-	Cb+Ta=0.8,La=.02,N=.2,Zr=.02
CABOT alloy No. 600	.08+	8	Bal	-	16	-	-	.5+	1.0+	.35+	.3+	Cu=.5+
INCONEL** alloy 601	.10+	14.1	Bal	-	23	-	-	.5+	1.0+	1.35	-	Cu=1.0+
INCONEL alloy 617	.07	1.5	Bal	12.5	22	9	-	.5	.5	1.2	.3	Cu=.20
CABOT alloy No. 263	.06	.7+	Bal	20	20	6	-	.4+	.6+	.5	2	Cu=.20+
HASTELLOY* alloy X	.10	18.5	Bal	1.5	22	9	.6	1.0+	1.0+	-	-	-
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 alloy No. 150	.06	18	1.0	Bal	27	-	-	.3	.4	-	-	-
HAYNES STELLITE* alloy No. 6B	1.2	3+	3+	Bal	30	1.5+	4.5	2.0+	2.0+	-	-	-

+ Maximum

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** INCONEL is a registered trademark of the Inco family of companies.

Table 2

Inlet Test Gas Composition As Well As Calculated Equilibrium Gas Compositions At 760°C, 871°C, and 982°C (1400°F, 1600°F, and 1800°F)

	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	-	0.2×10^{-4}	0.1×10^{-5}	0.2×10^{-6}
Ar	Bal	Bal	Bal	Bal
P_{O_2}		5×10^{-22} atm	3×10^{-19} atm	3×10^{-17} atm
P_{S_2}		1×10^{-7} atm	0.9×10^{-6} atm	4×10^{-6} atm

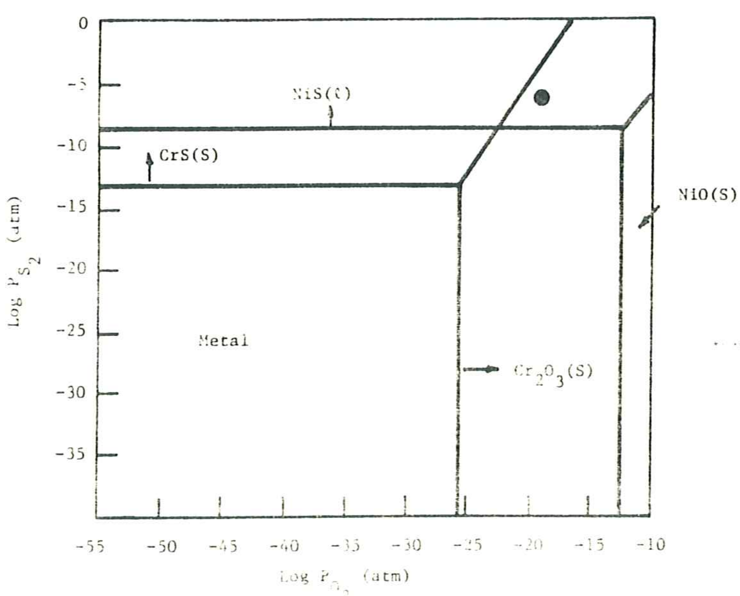


Figure 1: The test environment with respect to the M-S-O system at 871°C (1600°F).

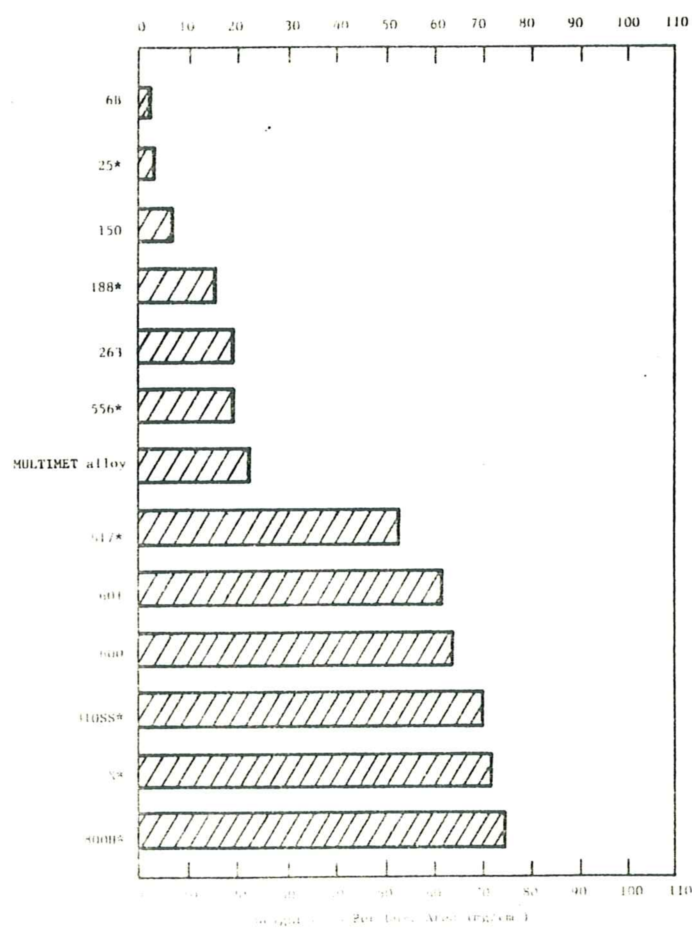


Figure 2: Results of sulfidation tests conducted at 760°C (1400°F) for 215 hours.

* Average of more than one test

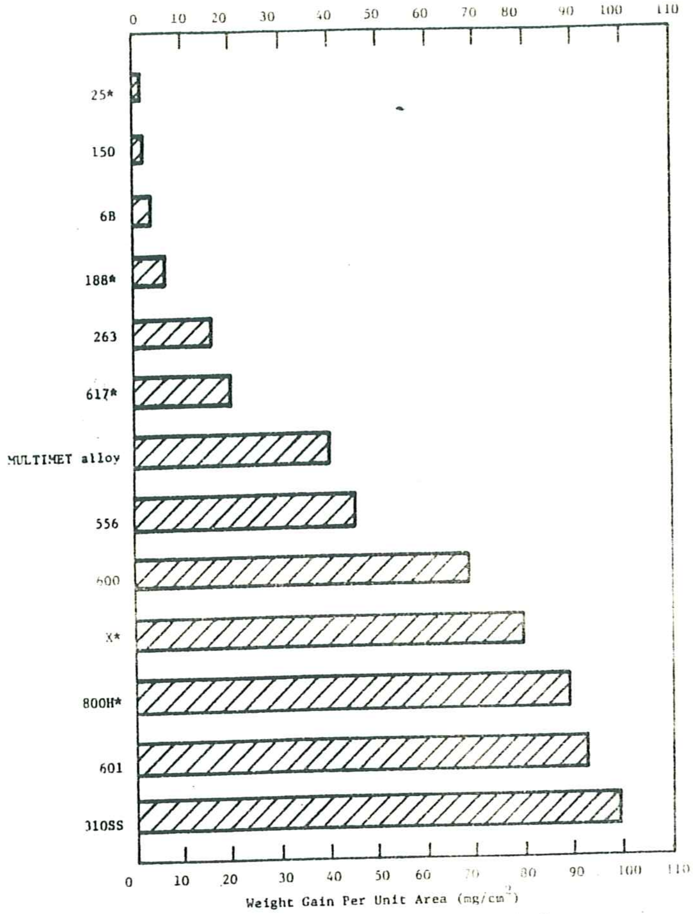


Figure 3: Results of sulfidation tests conducted at 871°C (1600°F) for 215 hours.

* Average of more than one test

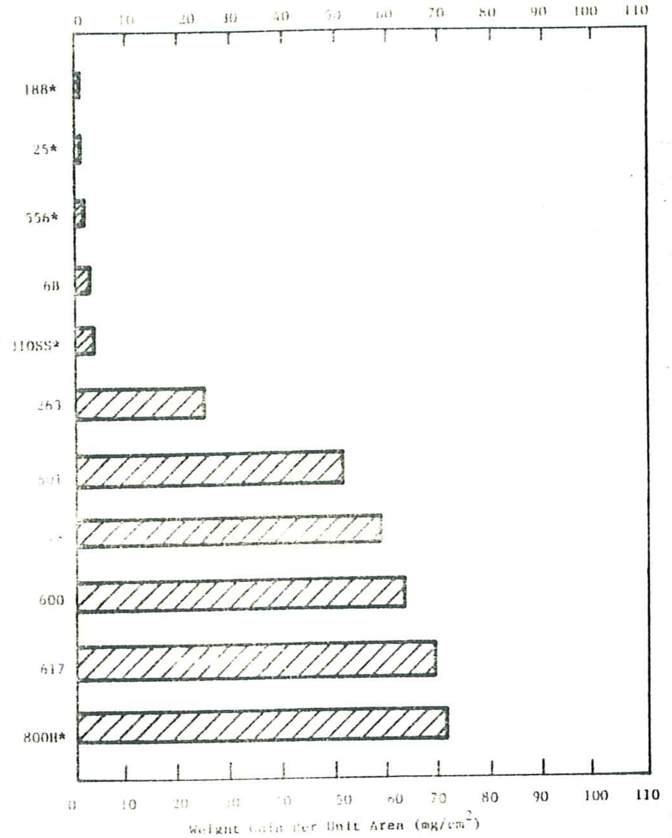


Figure 4: Results of sulfidation tests conducted at 982°C (1800°F) for 215 hours.

* Average of more than one test

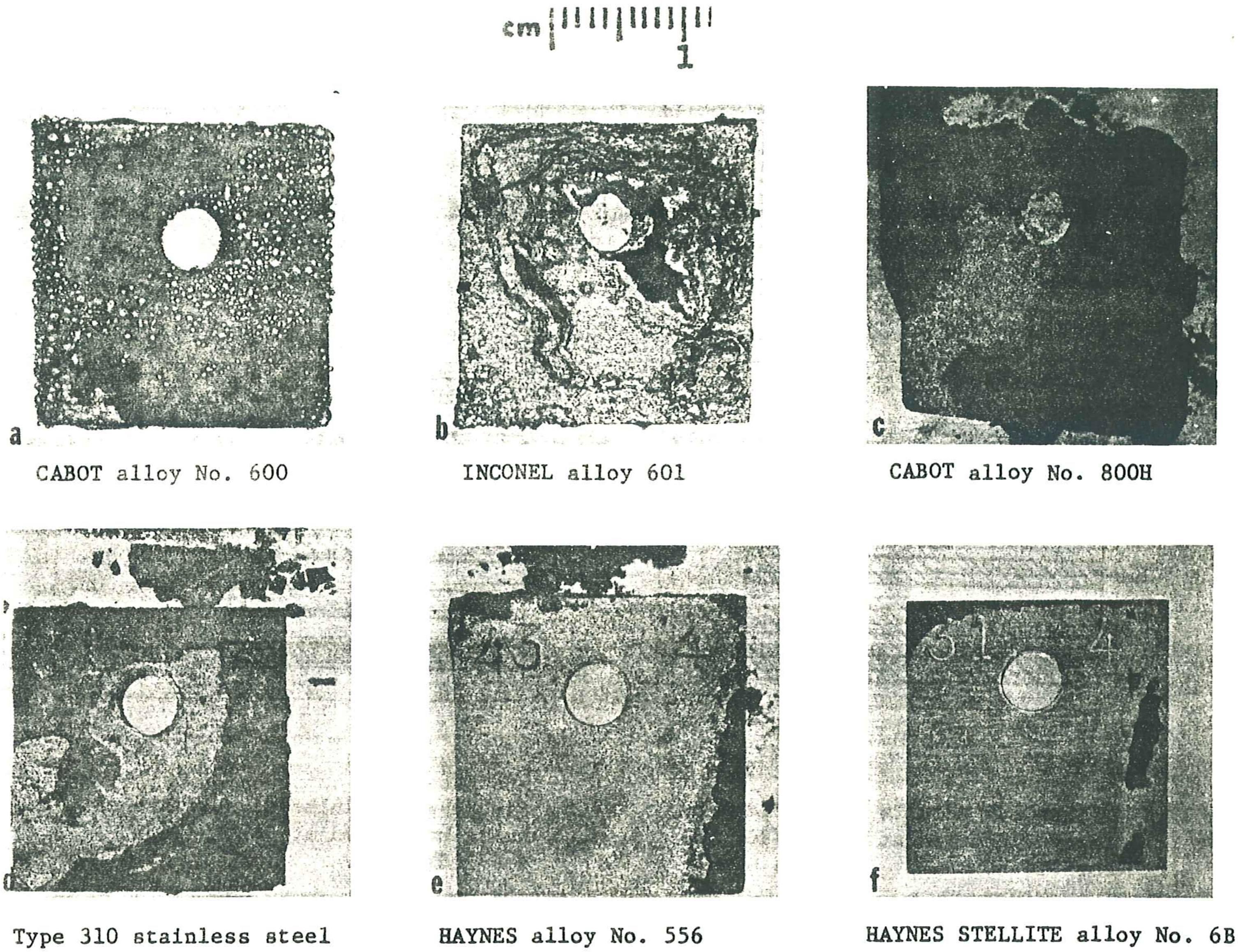
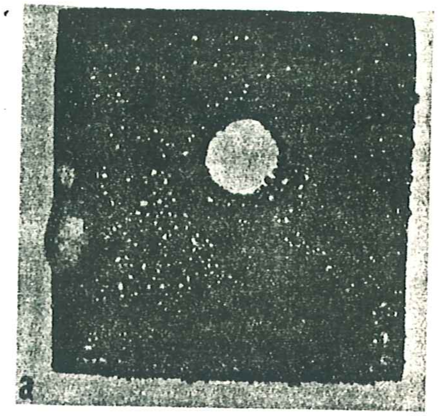
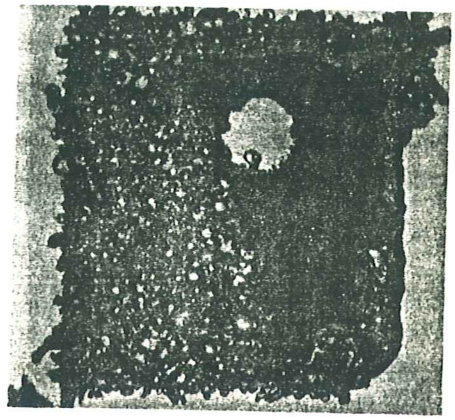


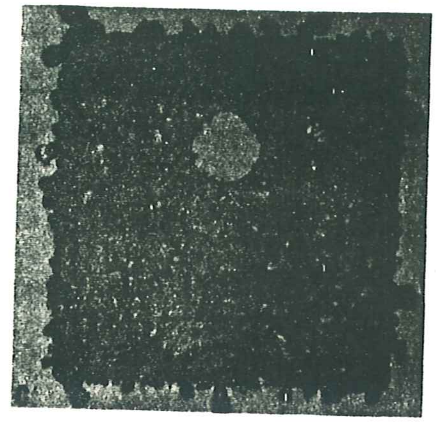
Figure 5: Representative test specimens of iron-, nickel-, and cobalt-base alloys tested at 760°C (1400°F) for 215 hours.



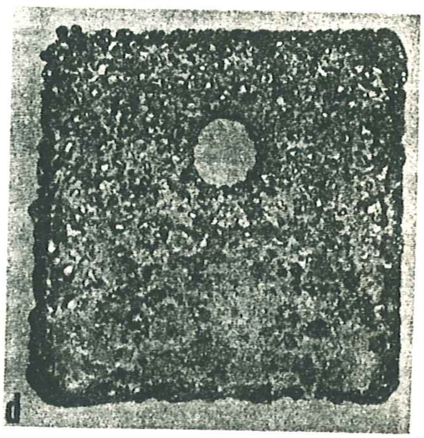
CABOT alloy No. 600



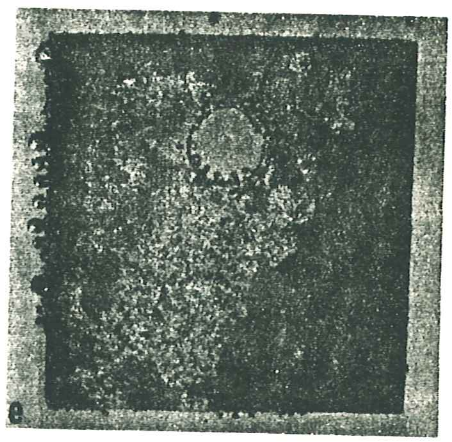
INCONEL alloy 601



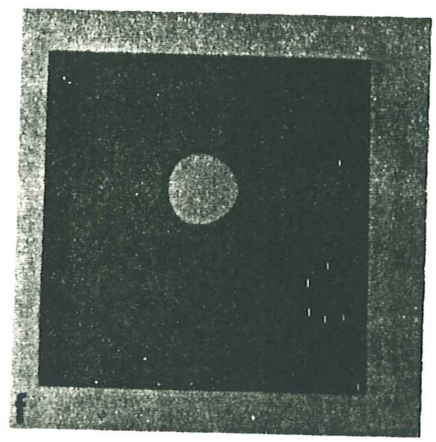
CABOT alloy No. 800H



Type 310 stainless steel

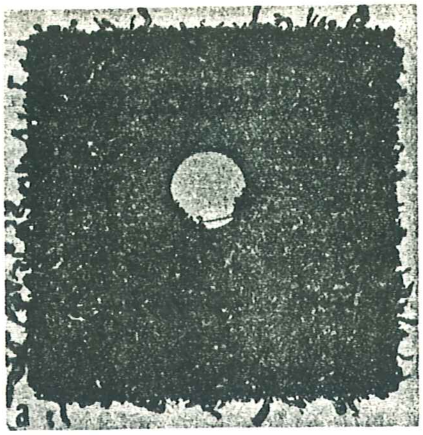


HAYNES alloy No. 556

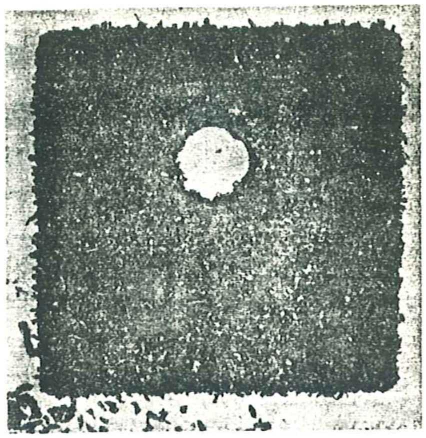


HAYNES STELLITE alloy No. 6B

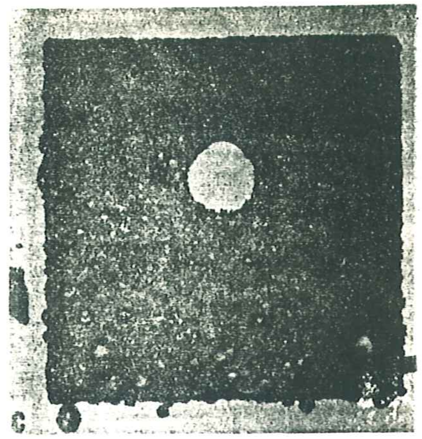
Figure 6: Representative test specimens of iron-, nickel-, and cobalt-base alloys tested at 871°C (1600°F) for 215 hours.



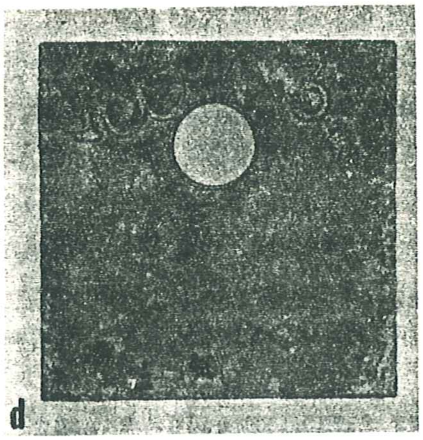
INCONEL alloy 601



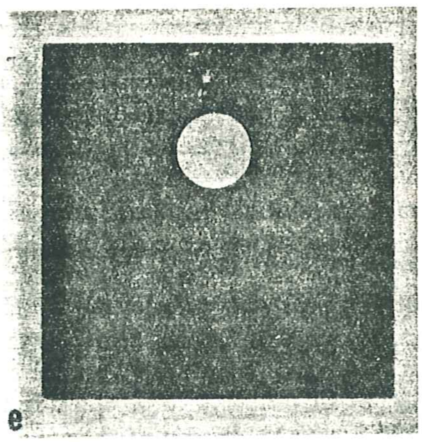
HASTELLOY alloy X



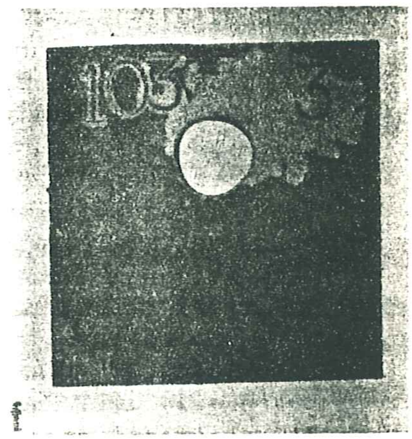
CABOT alloy No. 800H



Type 310 stainless steel



HAYNES alloy No. 556



HAYNES STELLITE alloy No. 6B

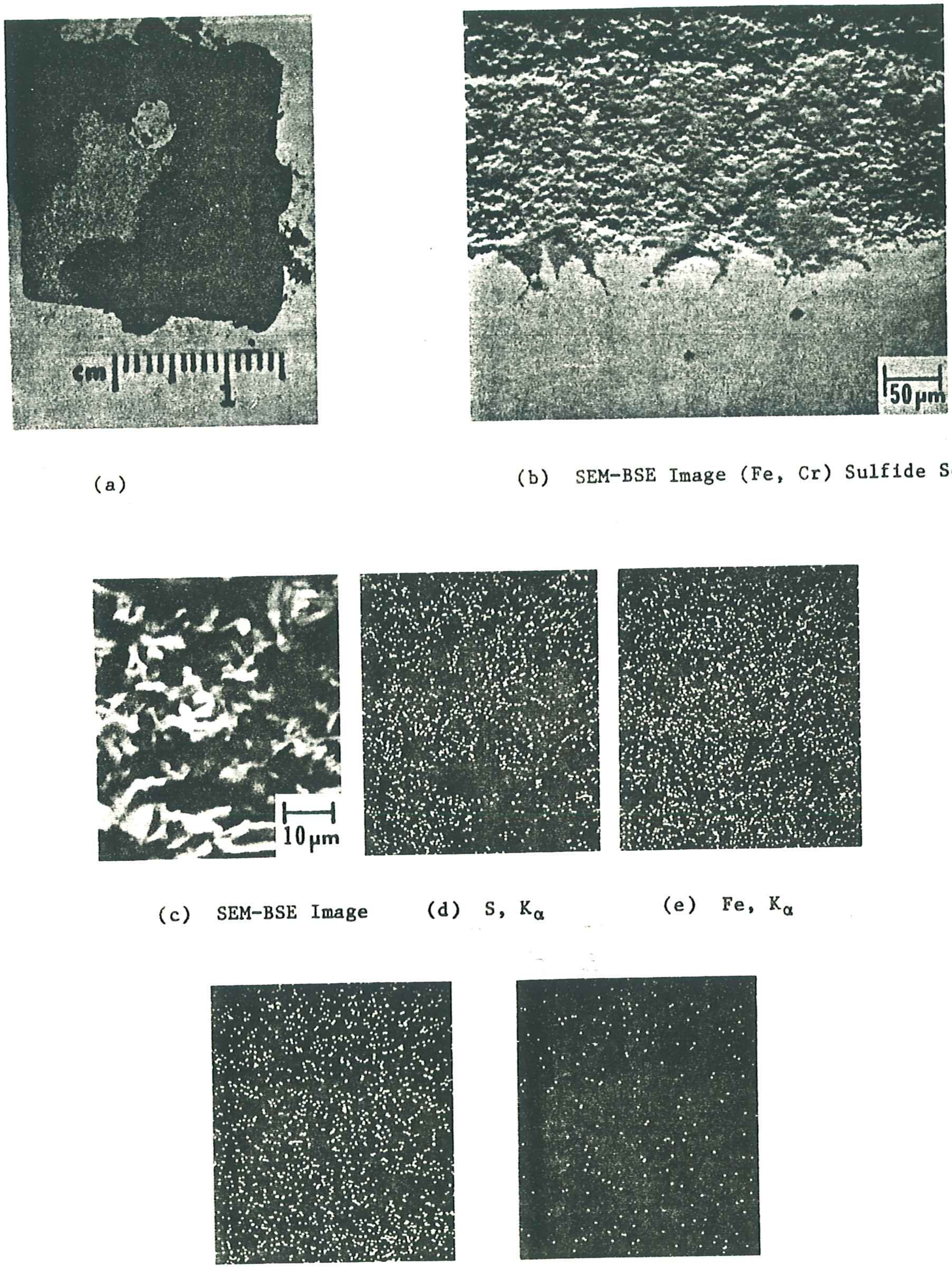
Figure 7: Representative test specimens of iron-, nickel-, and cobalt-base alloys tested at 982°C (1800°F) for 215 hours.

SEM/EDX Semi-Quantitative Analysis (Percent)

Phase:	S	Cr	Fe	Ni
1	26.7	33.7	27.2	12.5
2	37.2	4.6	36.8	21.3
3	45.3	2.6	35.3	16.9

SEM-BSE Image

Figure 8: Results of an SEM/EDX semiquantitative analysis of the surface scale formed on the CABOT alloy No. 800H sample tested at 871°C (1600°F) for 215 hours. Note the Fe-Ni rich sulfide nodules (marked as Nos. 2 and 3).



(a)

(b) SEM-BSE Image (Fe, Cr) Sulfide Scale

(c) SEM-BSE Image

(d) S, K_α

(e) Fe, K_α

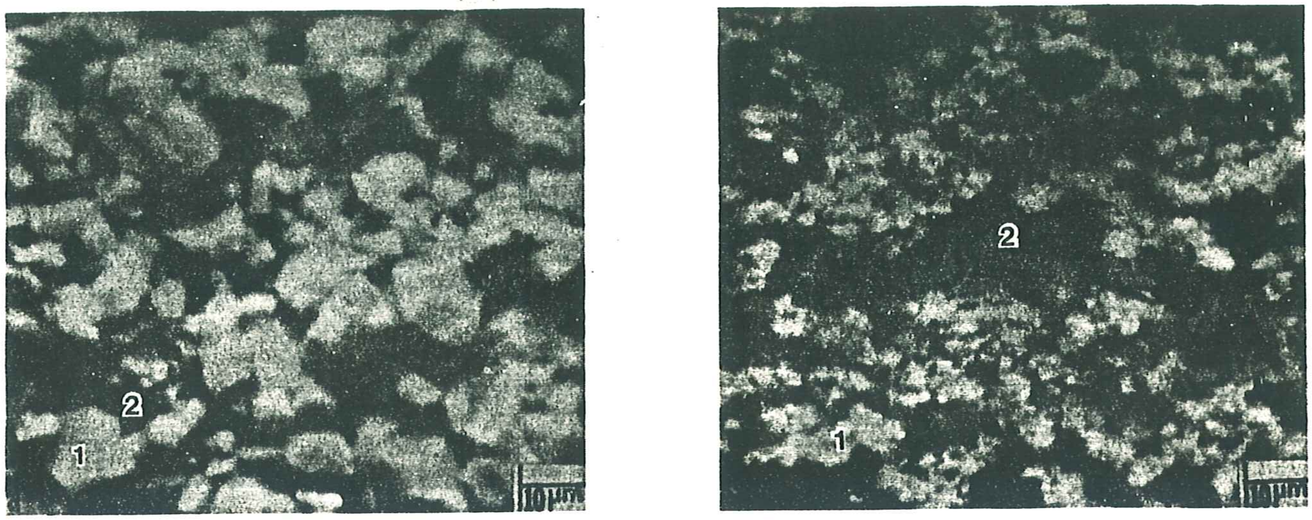
(f) Ni, K_α

(g) Cr, K_α

Figure 9: Photomicrographs showing the formation of (Fe, Ni) sulfides on an underlying (Fe, Cr) sulfide scale for the CABOT alloy No. 800H specimen tested at 760°C (1400°F) for 215 hours. (a) Specimen after testing; (b) SEM photomicrographs showing the cross section of the (Fe, Cr) sulfide scale; (c) SEM photomicrograph showing the powdery sulfides; (d), (e), (f), and (g) SEM photomicrographs showing the corresponding x-ray mappings of sulfur, iron, nickel, and chromium.

760°C (1400°F)/215 Hours

871°C (1600°F)/215 Hours



1. (Cr, Co) Sulfides
2. Cr Oxides

1. Cr Sulfides
2. Cr Oxides

Figure 10: SEM photomicrographs showing the phases formed on the HAYNES STELLITE alloy No. 6B samples tested for 215 hours at (a) 760°C (1400°F) and (b) 871°C (1600°F). Note that small amounts of oxides were detected.

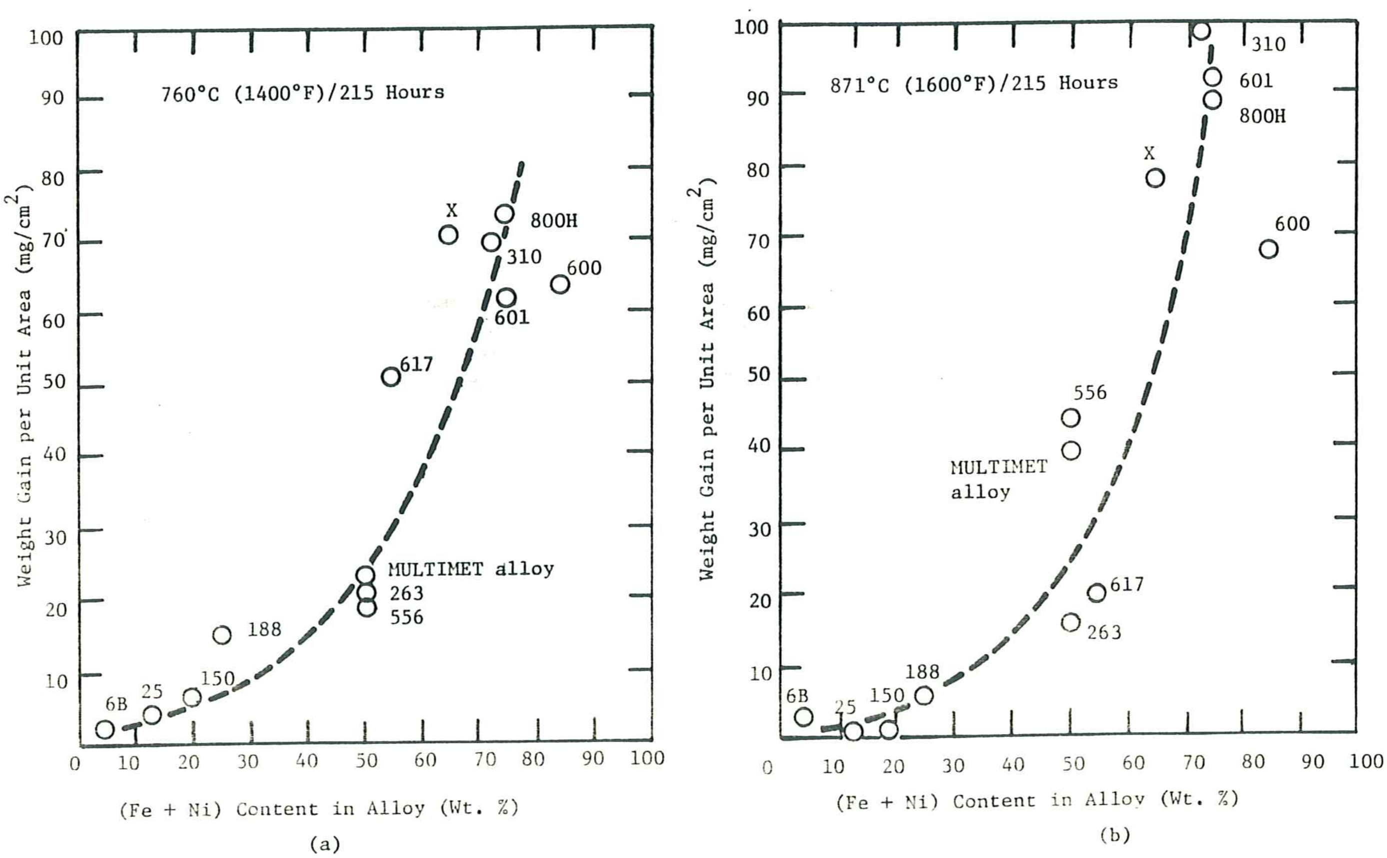
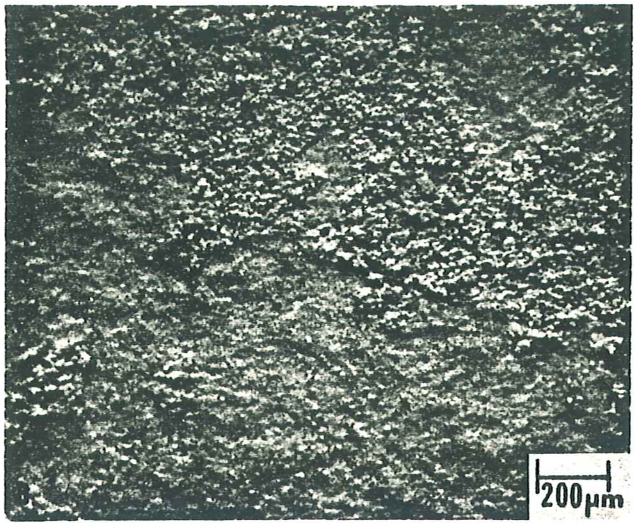
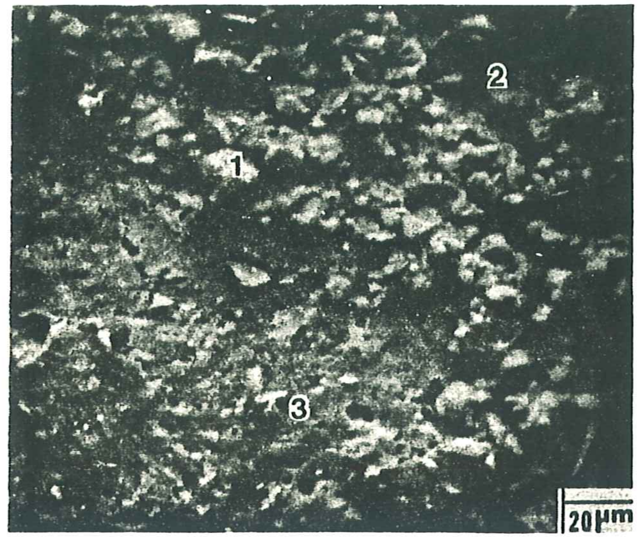


Figure 11: Test results plotted as weight gain per unit area as a function of (Fe + Ni) content in the alloys tested at 760°C (a) and 871°C (b).



SEM-BSE Image



SEM-BSE Image

SEM/EDX Semi-Quantitative Analysis (Percent)

Phase:	Cr	Fe	Ni	S	Al
1	71.5	13.7	0.5	12.7	1.6
2	79.9	13.2	0.3	6.5	0.1
3	95.9	1.2	0.3	2.5	0.1

Figure 12: SEM photomicrographs showing the scale formed on the 310SS sample tested at 982°C (1800°F) for 215 hours. (a) General scale morphology and (b) the analysis of phases in the scale.

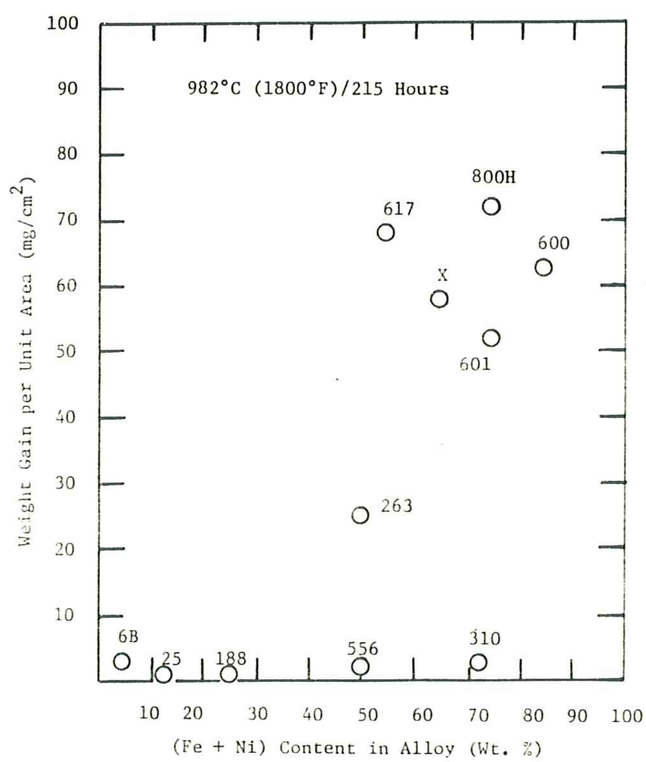


Figure 13: Test results plotted as weight gain per unit area as a function of (Fe + Ni) content in the alloys tested at 982°C (1800°F) for 215 hours.