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MATERIALS PERFORMANCE IN HIGH-TEMPERATURE, HALOGEN-BEARING ENVIRONMENTS

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ABSTRACT

Many industrial processes involve the exposure of materials to high-temperature environments which contain aggressive species such as chlorine. Little information concerning high-temperature corrosion resistance at temperatures greater than 760°C (1400°F) in these halogen-bearing environments has been available to guide materials selection. This study describes the behavior of various high-temperature materials subjected to both chlorine- and hydrogen chloride-bearing environments at 900°C (1650°F). Both weight-change data and metallographic evaluation of the modes of attack are presented, together with analysis of corrosion products by various analytical techniques. The possible relationships between alloy chemistry and performance are discussed.

INTRODUCTION

This paper presents preliminary results concerning the effect of halogen-bearing gases on the corrosion rate of commercial alloys at elevated temperatures. The data generated can serve as a guide for materials selection for such applications as waste incinerator and recuperator components when Cl₂ and/or HCl are known to be present.

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There have been several basic studies (involving halogen-O₂ environments) performed by previous investigators dealing with pure metals including nickel⁽¹⁾, cobalt⁽¹⁾, and chromium⁽²⁾, with binary systems Co-Cr⁽³⁾ and Co-Pt⁽⁴⁾, and with a ternary system, Ni-Cr-Al.⁽⁵⁾ In another work,⁽⁶⁾ commercial alloys INCOLOY[®] alloy 800 and INCONEL[®] alloys 600 and 601 were exposed to air at 800°C after being treated with the products of thermally decomposed PVC.

In the simplest terms, these investigators found that the halogen gas reacts with the basest elements present to form volatile chlorides, or in the presence of oxygen, to form both chlorides and oxychlorides such as CrO₂Cl₂. It appears that alloys having high aluminum contents are the best performers in these environments because of the high stability of Al₂O₃. But as indicated by the work of Viswanath, et al.⁽⁵⁾, if the O₂/Cl₂ ratio is too low, even Ni-Cr-Al alloys will undergo accelerated attack.

In this study, short-term tests of from 8 to 10 hours at 900°C (1650°F) were conducted with various commercially available alloys in environments of Ar-4%HCl-4%H₂ and Ar-20%O₂-2%Cl₂. Additional long-term tests were carried out at this temperature for times of from 250 to 400 hours in an Ar-20%O₂-1%Cl₂ atmosphere. The alloys investigated are listed in Table 1.

EXPERIMENTAL PROCEDURE

The short-term tests were performed with one specimen per run; they were nominally 1 cm x 1 cm with thicknesses ranging from about 0.10 cm to 0.15 cm. The test procedure and thermo-gravimetric apparatus utilized have been described elsewhere.⁽⁷⁾ The equipment consists of a Cahn RG-2 electrobalance, a Kanthal wound resistance furnace with associated temperature controller, and equipment for the purification, metering, and mixing of gases. Fixturing was via a quartz fiber from a specimen to the electrobalance. Most of the tests were run in duplicate. Specimens were descaled by a complex series of steps involving a hot alkaline bath followed by a series of acid rinses; washing in water, followed by a methanol rinse; and, finally, baking to dryness. The long-term tests were performed with four specimens per run. Figure 1 is a schematic of the apparatus used in the long-term tests.

The following experimental procedure was used for the long-term tests:

1. Specimens are prepared by polishing to 600-mesh emery paper and degreasing with acetone.
2. The initial mass and surface area of each specimen are recorded.
3. The specimens are placed in the furnace as shown in Figure 1, with at least 1 centimeter of separation between specimens.
4. The specimens are heated to 900°C in argon gas flowing at a linear velocity of 1.5 cm/sec.
5. When the furnace is at temperature, the argon is replaced by 79%Ar-20%O₂-1%Cl₂ at the same flow rate.

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6. The environment is maintained for 50 hours.
7. At the conclusion of each 50-hour exposure, the corrosive mixture is replaced by pure argon; the furnace is purged for one hour and is then cooled to room temperature.
8. The specimens are removed from the furnace, weighed, and photographed.
9. Deposits of corrosion products are collected from the top and bottom of the furnace.
10. The reaction tube is cleaned.
11. The specimens are then evaluated by optical and scanning electron microscopy.

TEST RESULTS

Ar-4%HCl-4%H₂ Environment

Figures 2 and 3 show the weight change data obtained for those alloys tested in this phase of the work. Reproducibility of results is good for HAYNES[®] alloy No. 188, HASTELLOY[®] alloys S and C-276, and CABOT[®] alloys No. 625 and No. 214. Differences in the results of duplicate test on HASTELLOY alloy X and CABOT alloy No. 600 may have resulted from slight differences in gas moisture content from run to run, a factor to which these alloys may be more susceptible than the others tested. Figure 4 shows photomicrographs of several of the alloys tested.

All of the alloys tested, with the exception of CABOT alloy No. 214, exhibited porosity with a concomitant depletion in chromium as found by semiquantitative SEM analyses. The alloy 214 specimens developed intergranular oxidation with precipitation of Al₂O₃. Figure 5 shows the average metal losses and continuous internal penetration experienced for selected alloys. The average metal losses were determined from weight-change measurements (original weight minus descaled weight) divided by the product of surface area and alloy density. It is apparent that the extent of internal attack overrides metal loss as a factor governing material performance. It is also clear that those aluminum-free alloys having chromium contents in excess of 20 percent are the worst performers in this respect. It is also interesting to note that the high molybdenum and lower chromium alloys HASTELLOY alloys C-276 and S, which are resistant to hydrochloric acid attack at low temperatures, performed very well in this high-temperature environment.

Ar-20%O₂-2% Cl₂ Environment

Figure 6 shows the weight change data obtained for those alloys tested in this oxidizing environment at 900°C (1650°F). Reproducibility of results was very good; the data represent the average of two tests. Figure 7 shows representative photomicrographs of selected alloys after testing. Again, CABOT alloy No. 214 exhibited the best corrosion resistance, but HASTELLOY alloys C-276 and S had very high metal losses. In addition, all of the high-

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chromium alloys exhibited a relatively high degree of intergranular attack. Results are summarized in Figure 8. It is interesting to note that with the exception of alloys C-276 and S the overall corrosion rates in the oxidizing environment were similar to those determined in the Ar-4%HCl-4%H₂ environment described above. The greater metal wastage encountered in the Ar-20%O₂-2%Cl₂ environment is offset by the reduced extent of observed continuous internal penetration.

Intergranular precipitates in those alloys which are aluminum free were shown by semiquantitative SEM analyses to be chiefly Cr₂O₃. Aluminum-bearing alloys such as INCONEL alloy 601 and CABOT alloys No. R-41 and No. 214 contained Al₂O₃ intergranular precipitates. This probably is a key reason for the lower metal losses encountered with the latter alloys since Cl₂ is capable of reacting with Cr₂O₃ to form the volatile CrO₂Cl₂.

Ar-20%O₂-1% Cl₂ Environment

The first group of alloys subjected to long-term tests consisted of HASTELLOY alloys C-276 and X, HAYNES alloy No. 188, and CABOT alloy No. 625. The HAYNES alloy No. 188 specimen disintegrated after 200 hours, and testing of the other three was terminated after 250 hours since it was obvious they would not survive the 400 hours.

The next group of alloys consisted of CABOT alloys No. 214, R-41, and 263 and INCONEL alloy 601. The CABOT alloy No. 263 specimen disintegrated after 350 hours of testing. Figure 9 shows photographs of the specimens after 250 hours and 400 hours. Figure 10 shows the weight-change data obtained for the eight specimens, and Figure 11 shows the metal loss and continuous internal penetration for those specimens which survived the tests. Figure 12 shows the through-thickness microstructures of the alloys subsequent to testing. (The data of Figure 11 were determined from a knowledge of initial sample thicknesses and direct measurements made of metal loss and continuous internal penetration from Figure 12.) As might have been expected, CABOT alloy No. 214 was the best performer; however, it is obvious that even that alloy cannot be utilized in this environment for any extended period of time.

SEM energy dispersive x-ray analyses of the surface oxides were performed. The results are shown in Table 2. As can be seen by comparison of Tables 1 and 2, each alloy scale shows an enrichment of its basest elements. Chlorine was not detected within the scale of any of the specimens. Figure 13 displays representative scanning electron micrographs for two of the coupon surfaces; the oxides are porous and fissured.

DISCUSSION AND CONCLUSION

Short-term tests (8-10 hours) on selected alloys at 900°C (1650°F) were conducted in environments of Ar-4%HCl-4%H₂ and Ar-20%O₂-2%Cl₂. Tests from 250 to 400 hours were similarly performed in an environment of Ar-20%O₂-1%Cl₂.

High molybdenum- and aluminum-bearing alloys were found to be the most resistant to the reducing (Ar-4%HCl-4%H₂) atmosphere. These include CABOT alloys No. 214 and No. R-41 and HASTELLOY alloys C-276 and S. Assuming linear kinetics, corrosion rates of from 40 to 55 mils per month were obtained;

however, long-term tests will be necessary to draw conclusions as to the usefulness of these alloys in commercial applications under these conditions. In general, continuous internal penetration was the major contributor to the corrosion rates obtained. With the exception of CABOT alloy No. 214, higher corrosion rates were encountered in the oxidizing (Ar-20%O₂-2%Cl₂) environment with metal wastage becoming more of a factor. Based on these results, long-term tests were carried out in the Ar-20%O₂-1%Cl₂ environment. Only CABOT alloys No. 214 and R-41 and INCONEL alloy 601 survived the 400 hours of testing. Alloy 214 exhibited the lowest observed corrosion rate of 27 mils per month.

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TABLE 1

Nominal Compositions of Alloys Investigated

<u>Alloy</u>	<u>Ni</u>	<u>Fe</u>	<u>Cr</u>	<u>Cb</u>	<u>Al</u>	<u>Ti</u>	<u>Mo</u>	<u>W</u>	<u>Y</u>	<u>Co</u>	<u>B</u>	<u>La</u>	<u>Si</u>	<u>Mn</u>
CABOT alloy No. 214	Bal.	4.0	16	-	4.2	-	-	-	.03	-	-	-	-	-
CABOT alloy No. R-41	Bal.	5.0*	19	-	1.5	3.0	10	-	-	11	.006	-	.5*	.1*
CABOT alloy No. 600	Bal.	8.0	16	-	-	-	-	-	-	-	-	-	.5*	1.0*
CABOT alloy No. 625	Bal.	5.0*	21	3.5	-	-	9.0	-	-	-	-	-	.5*	.5*
CABOT alloy No. 800H	33	Bal.	21	-	.38	.38	-	-	-	-	-	-	1.0*	1.5*
HASTELLOY alloy S	Bal.	3.0*	16	-	-	-	15	-	-	-	.009	.02	.5	.5
HASTELLOY alloy X	Bal.	19	22	-	-	-	9.0	0.6	-	1.5	-	-	1.0*	1.0*
HAYNES alloy No. 188	22	3.0*	22	-	-	-	-	14	-	Bal.	-	.04	.4	1.5*
HASTELLOY alloy C-276	Bal.	5.0	16	-	-	-	16	4.0	-	-	-	-	.08*	1.0*
INCONEL alloy 601	Bal.	14	23	-	1.4	-	-	-	-	-	-	-	-	-
Type 310SS	19	Bal.	25	-	-	-	-	-	-	-	-	-	.5	.8

* Maximum

TABLE 2

Semiquantitative Analyses of Surface Oxides
of Specimens Exposed to Ar-20% O₂-1%Cl₂
at 900°C (1650°F) for 250 to 400 Hours

Alloy	Ni	Cr	Fe	Co	Si	Al	Cb	Ti
HASTELLOY alloy C-276	25	40	34	-	0.6	0.3	-	-
CABOT alloy No. R-41	12	13	3.7	2.2	-	4.5	-	65
INCONEL alloy 601	18	52	18	-	1.0	3.4	-	4.1
CABOT alloy No. 214	5.1	26	1.7	-	-	67	-	-
HASTELLOY alloy X	22	29	42	-	4.4	0.8	-	1.2
CABOT alloy No. 625	14	38	16	-	3.7	0.8	25	3.1

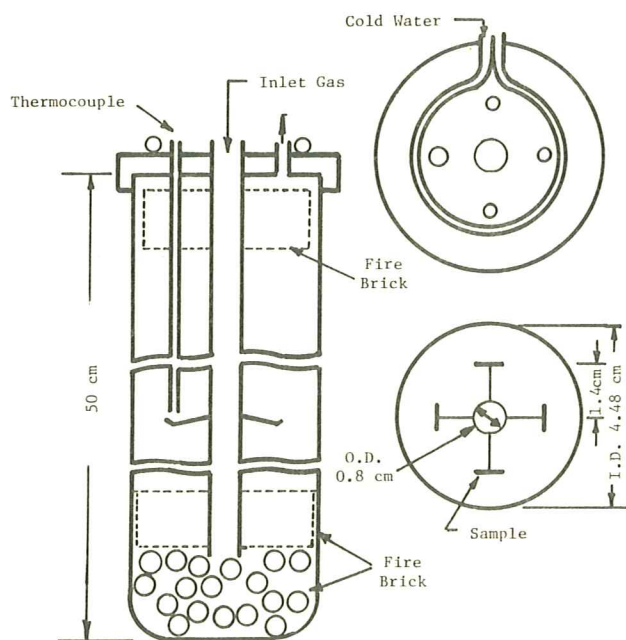


Figure 1: Schematic of apparatus utilized for long-term tests in halogen-oxygen environments.

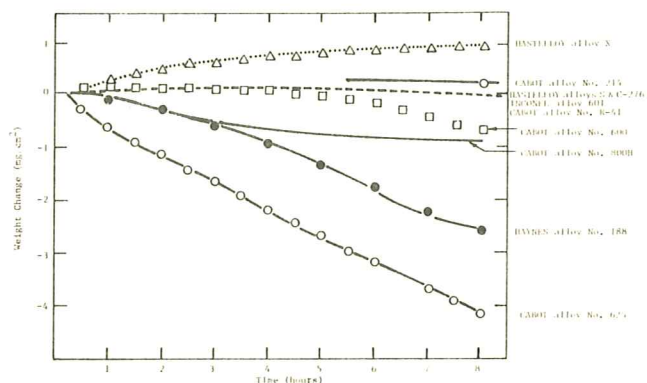


Figure 2: Weight change of selected alloys in an environment of Ar-4%Cl-4%H₂ at 900 C (1650 F).

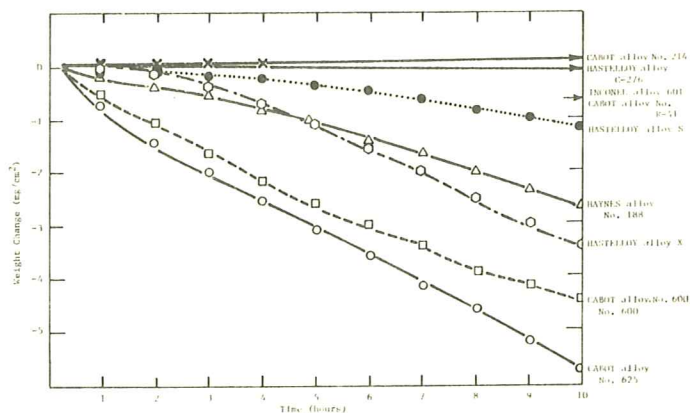


Figure 3: Weight change of selected alloys in an environment of Ar-4%Cl-4%H₂ at 900 C (1650 F) (second run).

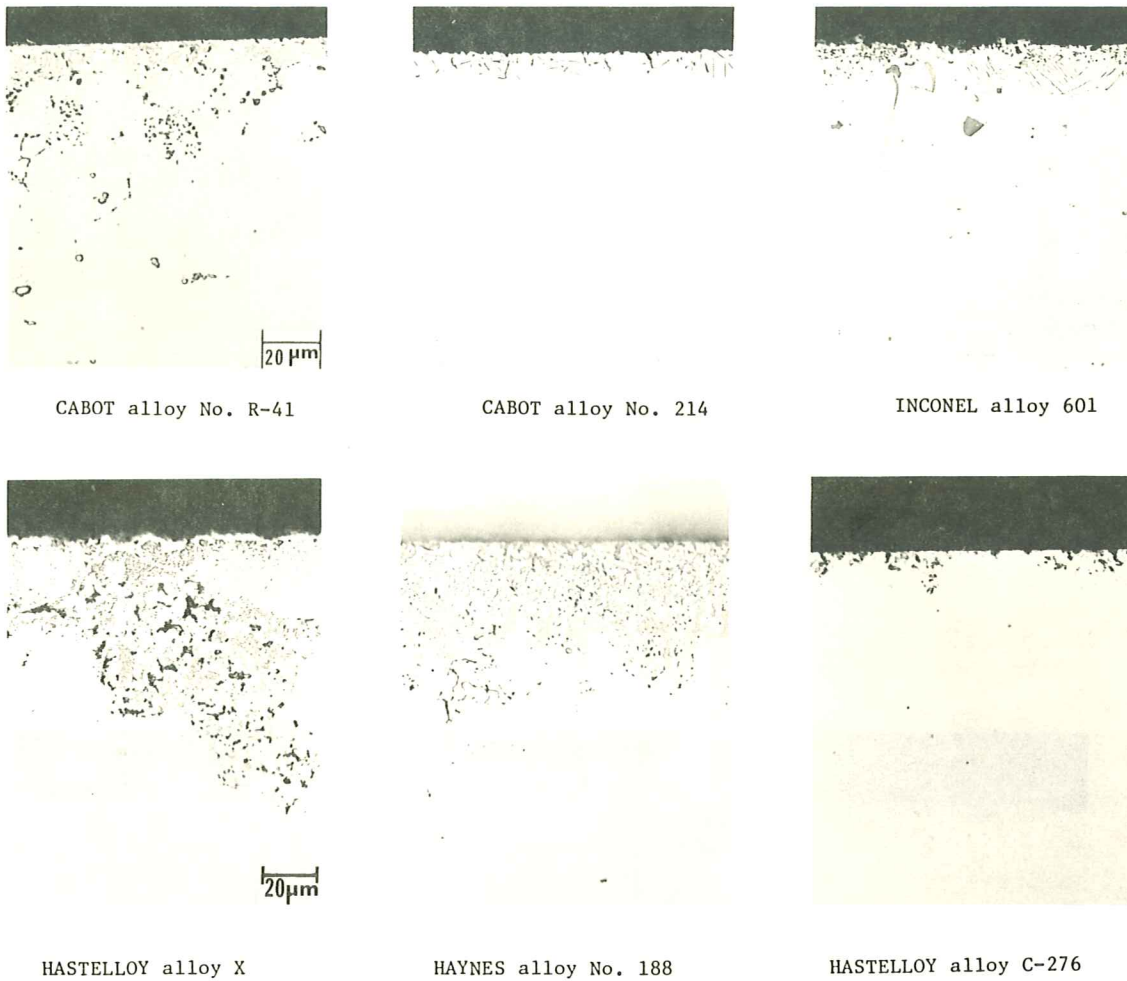


Figure 4: Optical photomicrographs showing corrosion attack upon various alloys in Ar-4%HCl-4%H₂ at 900°C (1650°F) for 8 hours.

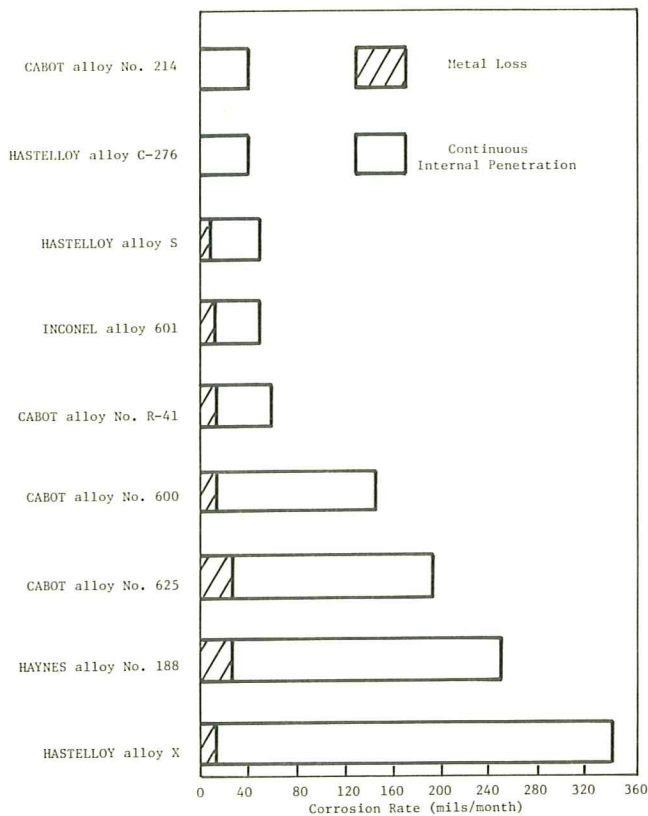


Figure 5: Corrosion rates of selected alloys in an Ar-4%HCl-4%H₂ environment at 900 C (1650 F). (Data based on 8-hour tests.)

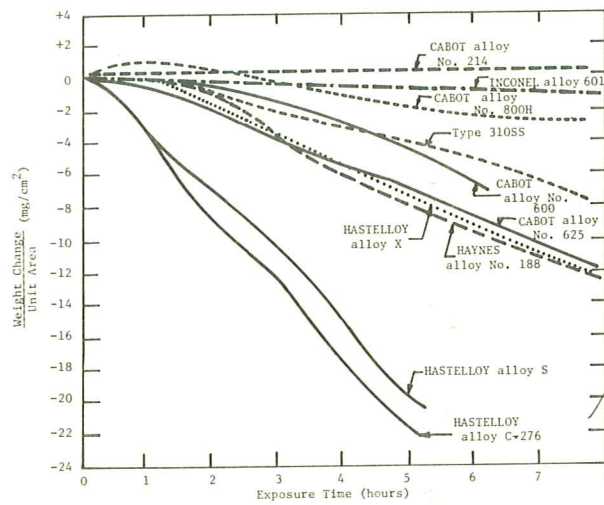


Figure 6: Weight change of selected alloys in an environment of Ar-20%O₂-2%Cl₂ at 900 C (1650 F).

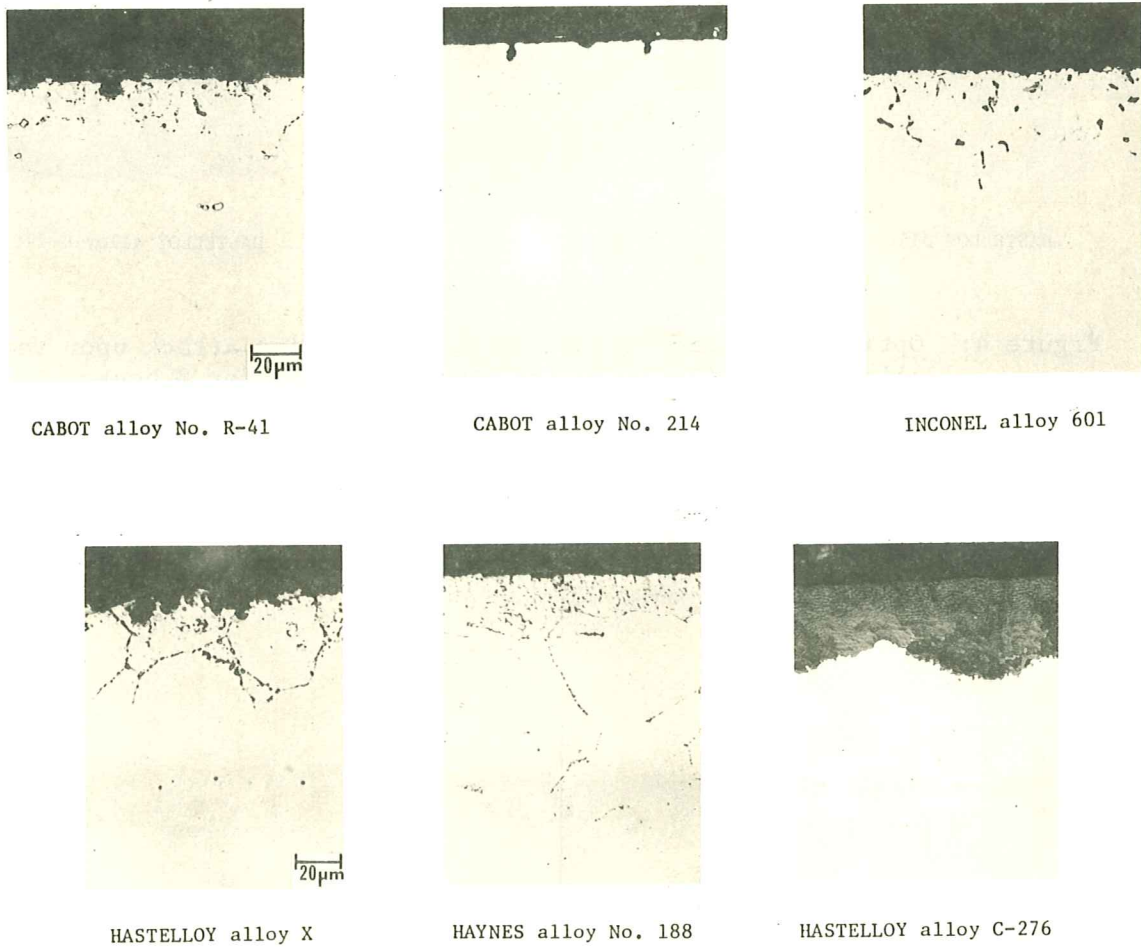


Figure 7: Optical photomicrographs showing corrosion attack upon various alloys in Ar-20%O₂-2%Cl₂ at 900°C (1650°F) for 8 hours.

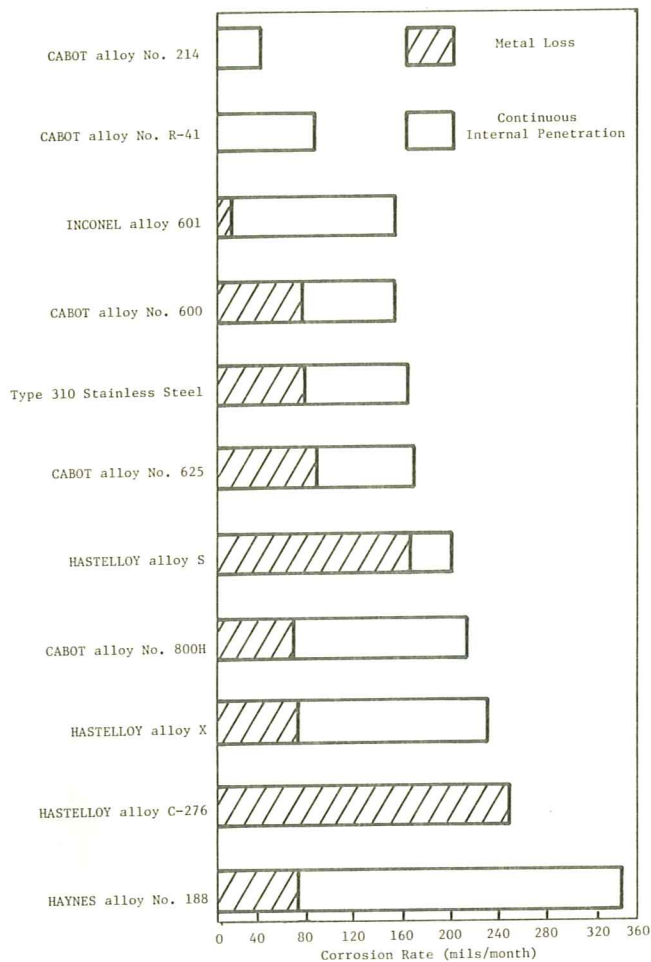


Figure 8: Corrosion rates of selected alloys in an Ar-20%O₂-2%Cl₂ environment at 900 C (1650 F). (Data based on 8-hour tests.)

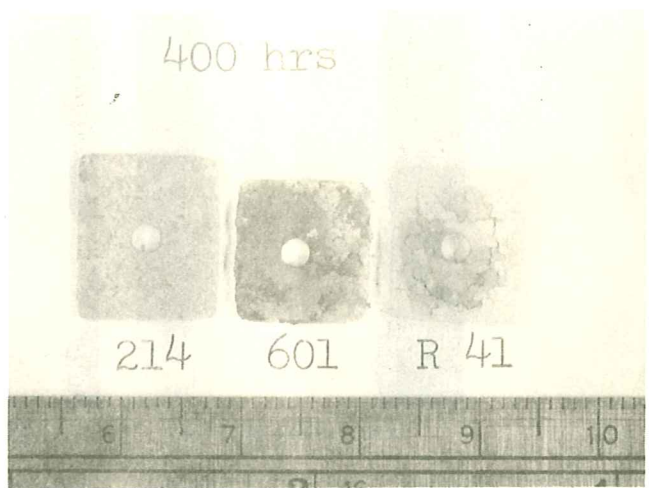
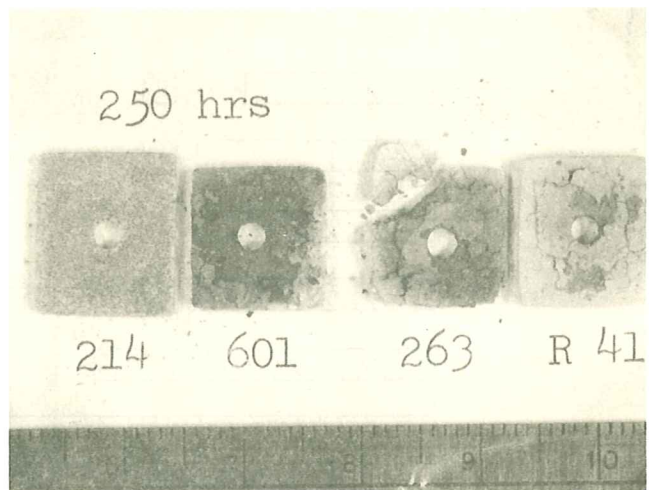


Figure 9: Photographs of selected alloys after times indicated in an environment of Ar-20%O₂-1%Cl₂ at 900 C (1650 F).

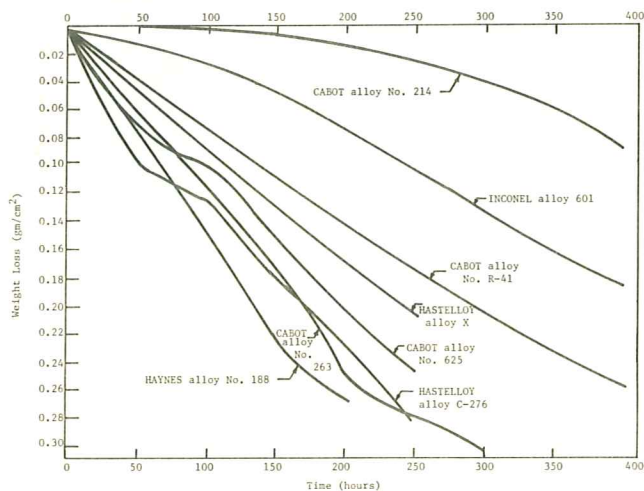


Figure 10: Weight change of selected alloys in an einvironment of Ar-20%O₂-1%Cl₂ at 900 C (1650 F).

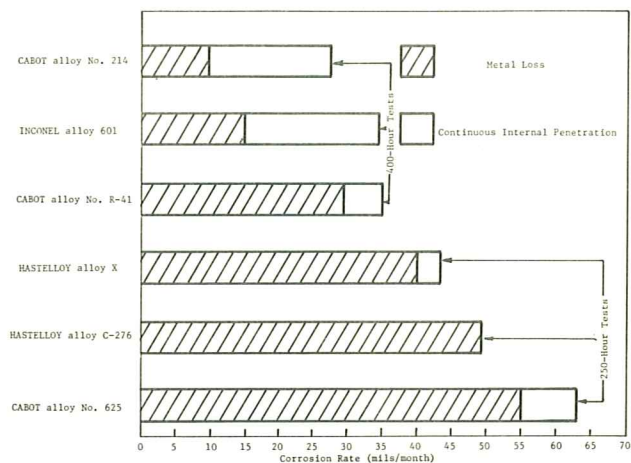


Figure 11: Corrosion rates of selected alloys in an Ar-20%O₂-1%Cl₂ environment at 900 C (1650 F).

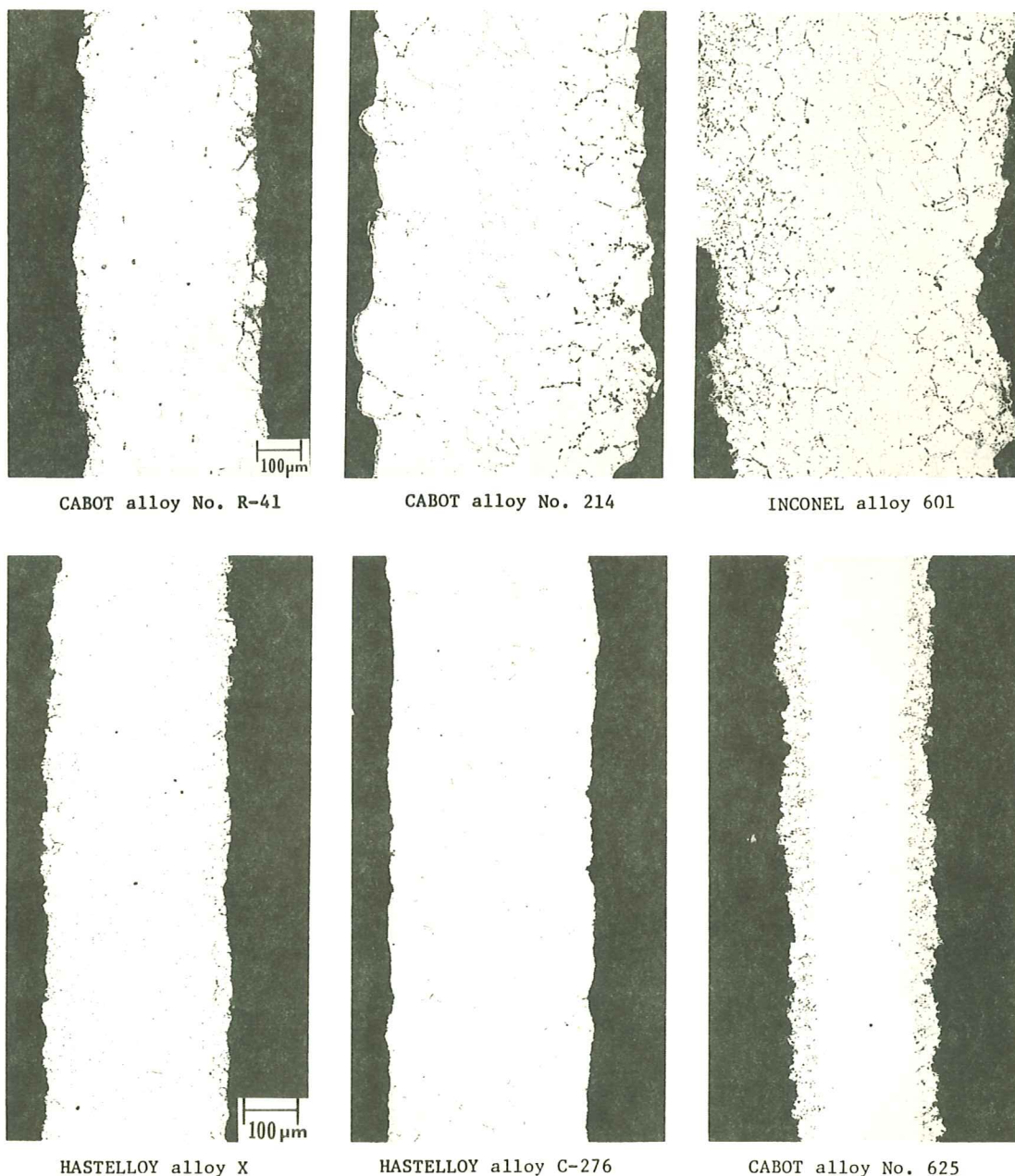
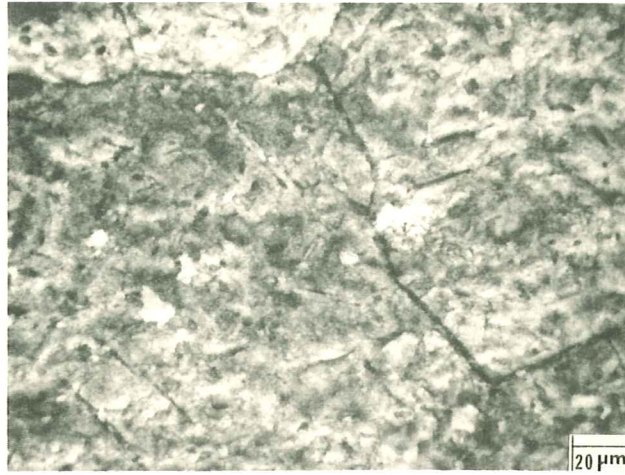


Figure 12: Photomicrographs of alloys tested in Ar-20%O₂-1%Cl₂ at 900°C (1650°F) run for 400 hours; 100X.
NOTE: Original specimen thicknesses were not the same.



(a) HASTELLOY alloy C-276 (250 hours)



(b) CABOT alloy No. 214 (400 hours)

Figure 13: Scanning Electron Micrographs (BSE) of specimens after testing in Ar-20%O₂-1%Cl₂ at 900°C (1650°F); 500X.

