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RESISTANCE TO CARBURIZATION OF VARIOUS HEAT-RESISTANT ALLOYS

by

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RESISTANCE TO CARBURIZATION OF

VARIOUS HEAT-RESISTANT ALLOYS

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ABSTRACT

Laboratory tests were conducted to determine the carburization resistance of various commercial iron-, nickel- and cobalt-base alloys. Test coupons were exposed isothermally at 871°, 927°, 982°C (1600°, 1700° and 1800°F) in a gas mixture containing H_2, CO and CH_4. Following exposure, the specimens were evaluated by determining the mass of carbon pickup per unit area of specimen. The microstructures of carburized samples were examined by optical metallography. Relative resistance to carburization for the alloys tested is presented. Possible correlation between alloying elements and the alloys' carburization resistance is discussed.

INTRODUCTION

Gaseous environments generated by many high-temperature industrial processes frequently contain carbonaeous gases. Selection of materials for elevated-temperature service in this type of environments require information and data pertaining to carburization of alloys. Carburization of metals and alloys has been the subject of numerous investigations (1-9). Most of this work has focused on cast alloys for ethylene cracking applications. For a number of investigations involving wrought alloys, the number of alloys studied in each case was relatively limited. Furthermore, most of the alloys investigated were 25 Cr- 20 Ni-type steels, such as HK-40 and its modified versions. Very few studies have examined superalloys which are characteristic of high elevated temperature strengths. Materials engineers or designers can only make an informed alloy selection only when they are provided with information and data of a sufficient number of alloys which exhibit various elevated temperature strength capabilities. In selecting materials for elevated temperature service, the materials' elevated temperature strength, in many cases, can be as important as the alloy's environmental resistance.

This paper presents the carburization data for a wide variety of alloys with elevated-temperature strengths ranging from low-strength stainless steels and Ni-Cr-Fe alloys to high-strength superalloys.

TEST PROCEDURES

The alloys investigated included a variety of commercial, wrought iron-, nickel- and cobalt-base alloys. The nominal chemical compositions of these alloys are tabulated in Table 1. Test coupons (approximately 0.10-0.15 cm x 2.2 cm x 2.2 cm) obtained from the annealed sheet stock were ground to a 120-grit surface finish. Exposure tests were performed in a carburizing environment with the inlet test gas composition being 5% H_2, 5% CO, 5% CH_4 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 coupns per test run) arranged in parallel with the gas flow direction were suspended by an alumina rod which was, in turn, supported by an alumina boat. Test coupons were isothermally exposed to the environment for 215 hours at 871° and 927°C (1600° and 1700°F) and for 55 hours at 982°C (1800°F).

Following the exposure, the test coupons were weighed and sectioned for carbon analysis and metallographic examination. The coupons exposed at 871° and 927°C (1600° and 1700°F) generally had small amounts of blackish carbon deposits. These deposits were removed from the samples with emery paper prior to carbon analysis of the samples. The coupons exposed at 982°C (1800°F) generally exhibited a surface scale (presumably carbide scale), which was not removed before carbon analysis.

The results are presented in terms of the mass of carbon pickup per unit area (mg/cm^2), which was obtained by the following equation:

$$\Delta M = \Delta C \, (W/A)$$

where, ΔM = Mass of carbon pickup per unit area (mg/cm^2),
ΔC = Difference in carbon (weight fraction) before and after exposure,
W = Weight of the unexposed specimen (mg), and
A = Surface area of the specimen exposed to the test environment(cm^2)

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© alloy No. 800H	.08	Bal	33	-	21	-	-	1.0+	1.5+	Al=.38, Ti=.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	Al=.2, Cb+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© 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 S	.02	3+	Bal	2.0+	15.5	14.5	1.0+	.4	.5	Al=.2, La=.02, B=.009
HASTELLOY alloy X	.10	18.5	Bal	1.5	22	9	.6	1.0+	1.0+	-
CABOT alloy No. 625	.10+	5+	Bal	-	21.5	9	-	.5+	.5+	Al=.4+, Ti=.4+, Cb+Ta=3.5
HAYNES alloy No. 230	.1	3+	Bal	3+	22	2	14	.4	.5	Al=.3, B=.005, La=.03
RA© alloy 333	.05	18	Bal	3	25	3	3	1.25	1.5	-
HASTELLOY alloy N	.06	5+	Bal	-	7	16.5	.5+	1.0+	.8+	Cu = .35+
HASTELLOY alloy G-30	.03+	15	Bal	-	29.5	5	2.5	.8+	-	Cu = 1.7, Cb = .7
CABOT alloy No. R-41	.08	5+	Bal	11	19	10	-	.5+	.1+	Al=1.5, Ti=3.0, B=.006
WASPALOY© 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 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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This method of presenting carburization data avoids ambiguities which could arise as a result of concurrent oxidation if the results were presented in terms of the specimen's weight changes (a commonly used method by many investigators for presenting carburization results).

RESULTS AND DISCUSSION

The test gas mixture selected for this study was intended to produce a severe carburizing environment in which the chromium oxide scale protection would not be available for the alloys tested. The test environment was characterized by a low oxygen potential and unit carbon activity. The calculated equilibrium gas compositions at the test temperatures are given in Table 2. The 982°C (1800°F) equilibrium test environment plotted in a Cr-C-O stability diagram is shown in Figure 1. This figure implies that the formation of carbon soots and Cr_3C_2 carbides at the gas-metal interface is thermodynamically feasible at the temperature indicated.

Table 2

Inlet Test Gas Composition As Well As Calculated Equilibrium Gas Compositions at 871°, 927°, and 982°C (1600°, 1700°, and 1800°F)

	Inlet Gas Composition (Vol. %)	Calculated Equilibrium Composition (Vol. %) at 1 atm		
		871°C (1600°F)	927°C (1700°F)	982°C (982°C)
H_2	5.0	14.6	14.21	14.23
CO	5.0	4.69	4.74	4.75
CO_2	-	0.016	0.0046	0.0025
H_2O	-	0.044	0.018	0.011
CH_4	5.0	0.046	0.034	0.0264
Ar	Balance	Balance	Balance	Balance
a_c	-	1.0	1.0	1.0
P_{O_2}	-	1.5×10^{-22} atm	3×10^{-22} atm	9×10^{-22} atm

Carbon deposits were observed on the samples tested. In addition to carbon soots, a surface scale was observed to form on the metal surface for most alloys tested. Typical morphology of the scale is shown in Figure 2. This surface scale consists of mainly carbides with some oxides formed internally (within the scale) and/or at the scale-metal interface. X-ray diffraction analysis of selected samples indicated that the carbides in the scale were mainly Cr_3C_2. The above observations are in good agreement with the simple thermodynamic predictions.

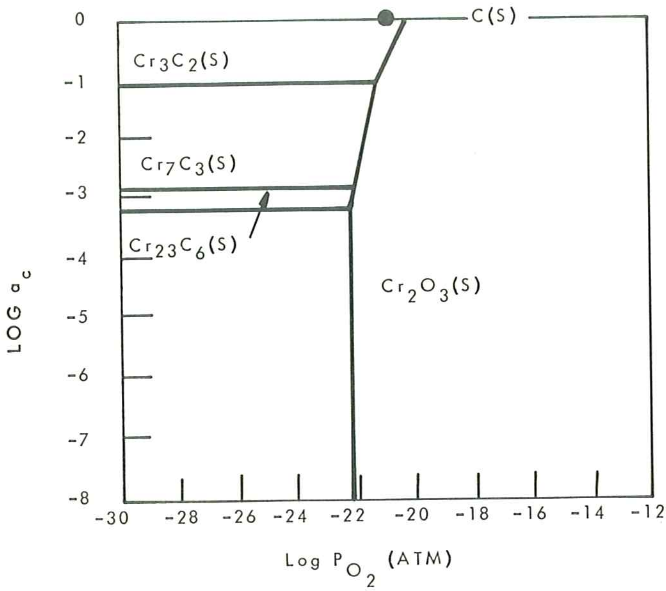


Figure 1: THE TEST ENVIRONMENT WITH RESPECT TO THE Cr-C-O SYSTEM AT 982°C (1800°F).

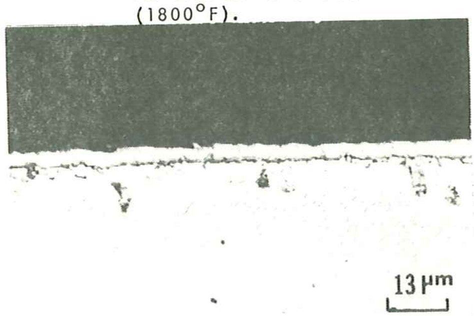


Figure 2: Optical photomicrograph showing a carbide scale formed on the alloy X sample tested at 982°C (1800°F) for 55 hours.

Alloy Ranking:

The test results in terms of the mass of carbon pickup per unit area of specimen generated at 871°, 927° and 982°C (1600°, 1700° and 1800°F) are presented in Figures 3, 4 and 5, respectively. For testing at 871°C (1600°F) for 215 hours, all the alloys except Type 310 stainless steel had relatively low levels of carbon ingress with the carbon pickup varying from 0.1 to 0.5 mg/cm^2 in each alloy base group. Type 310 stainless steel, which had a carbon pickup of about 2.4 mg/cm^2 after 215 hours at 871°C (1600°F), suffered severe carburization, as illustrated in Figure 6 (a). No carbide scale was observed on the metal surface. The alloy also suffered internal oxidation. All the other alloys tested showed a significantly lower carbon ingress than Type 310 stainless steel. MULTIMET® alloy, alloys 263, N, 214, 25 and 6B were among the alloys with very low carbon pickup (less than 0.2 mg/cm^2). The alloys with higher carbon ingress (more than 0.4 mg/cm^2) were alloys 800H, 333, X, R-41 and 188. Figure 6 (b) shows the carburized structure of alloy X with about 0.45 mg/cm^2 of carbon pickup. The alloy was only mildly carburized.

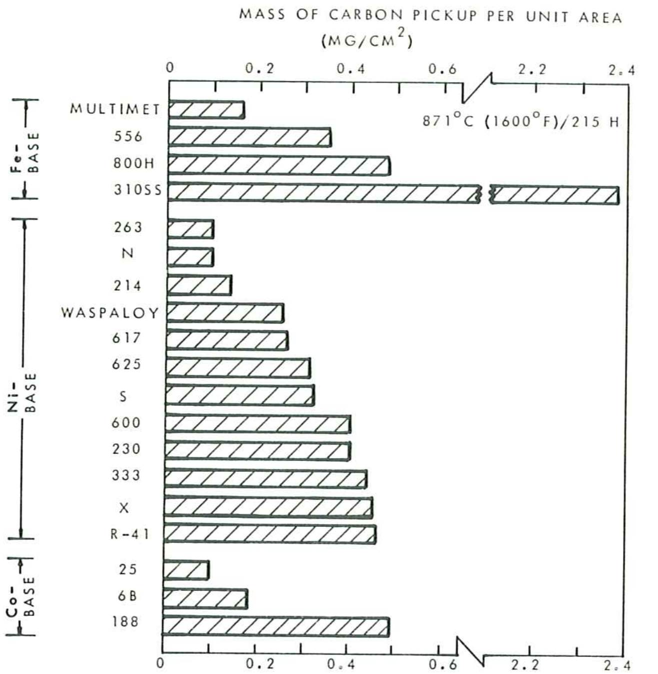


FIGURE 3: RESULTS OF CARBURIZATION TESTS CONDUCTED AT 871°C (1600°F) FOR 215 HOURS

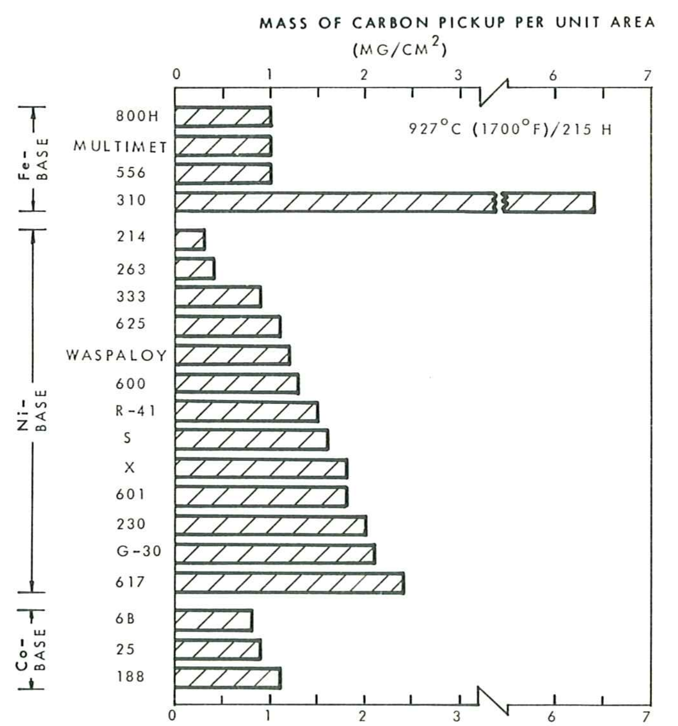


FIGURE 4: RESULTS OF CARBURIZATION TESTS CONDUCTED AT 927°C (1700°F) FOR 215 HOURS

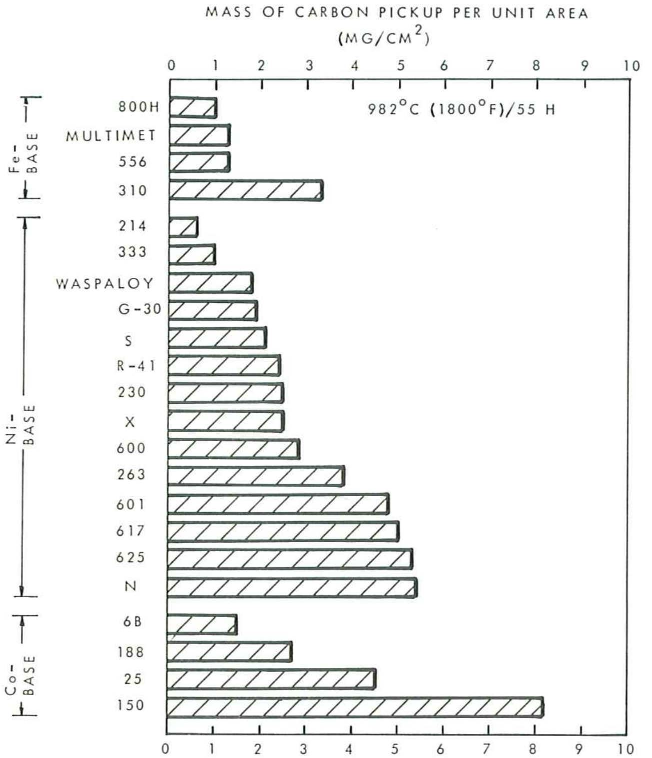
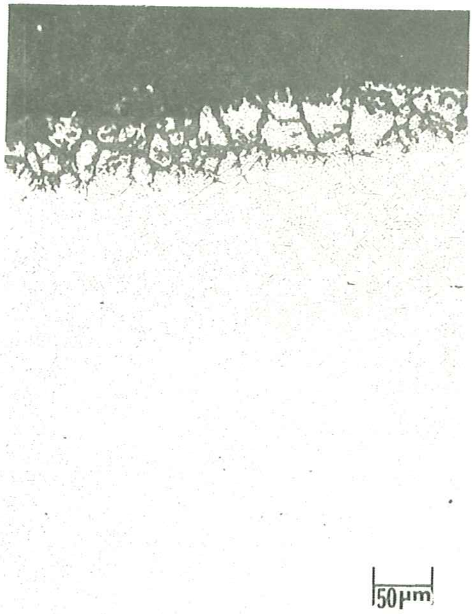


FIGURE 5: RESULTS OF CARBURIZATION TESTS CONDUCTED AT 982°C (1800°F) FOR 55 HOURS

The carburization kinetics were found to increase significantly when tested at higher temperatures (i.e., 927° and 982°C). The results generated at these two temperatures should be more discriminating than those generated at 871°C (1600°F) in terms of alloy ranking.

At 927°C (1700°F), Type 310 stainless steel remained the worst performer among the alloys tested. The alloy was severely carburized after testing at 927°C (1700°F) for 215 hours. It also suffered internal oxidation. No carbide scale was observed on the metal surface. The morphology of attack was similar to that shown in Figure 6 (a). Other Fe-base alloys tested, such as alloys 800H, 556 and MULTIMET alloy, were found to be significantly better than Type 310 stainless steel. These three Fe-base alloys, although not as good as some of the Ni-base alloys (e.g., alloy 214), are much more resistant to carburization than many Ni-base alloys (e.g., alloys X, 601 and 617) and are about the same as the Co-base alloys tested (i.e., alloys 6B, 25 and 188). Ni-base alloys exhibited a wide range of resistance to carburization with the carbon pickup ranging from 0.6 mg/cm^2 for alloy 214 to about 2.5 mg/cm^2 for alloy 617.

For the test results generated at 982°C (1800°F) for 55 hours, it is interesting to note that Type 310 stainless steel was no longer the worst performer. Type 310 stainless steel, although still worse than other Fe-base alloys tested, was better than some of the Ni- and Co-base alloys (e.g., alloys 625, 601, 617, N, 25 and 150). X-ray diffraction analysis of the Type 310 stainless steel sample exposed at 982°C (1800°F) for 55 hours indicated that the surface scale was essentially Cr_3C_2 carbides. No



(a) Type 310 SS

(b) Alloy X

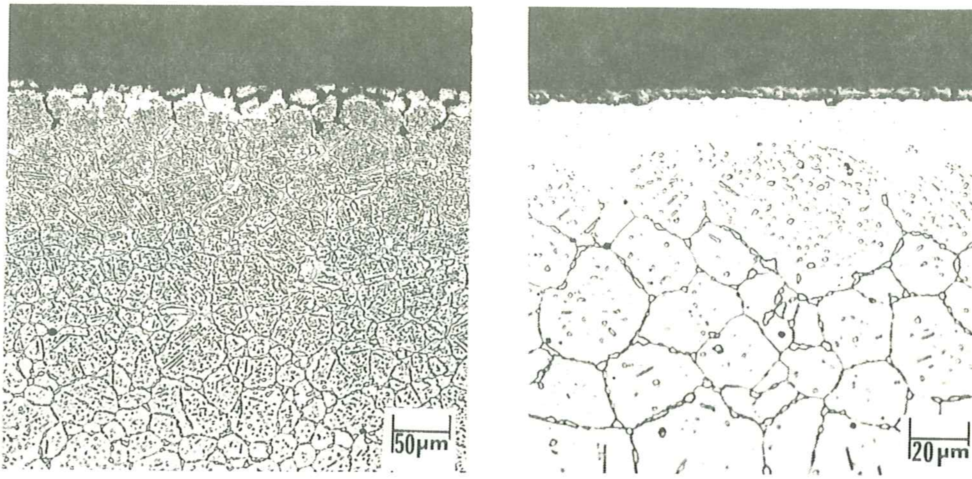
Figure 6: Optical photomicrographs showing typical carburized structure of Type 310 SS and Alloy X tested at 871°C (1600°F) for 215 hours. Unetched.

oxide scales were detected. Optical metallographic examination of the sample's cross-section revealed localized carburization attack. The area which suffered severe carburization attack showed internal oxidation with no carbide scales (Figure 7a). The area with a surface carbide scale, however, was only slightly carburized (Figure 7b). It appears that an exposure time of 55 hours is probably a threshold for rapid carburization of Type 310 stainless steel at 982°C (1800°F).

Again, Ni-base alloys exhibited a wide range of resistance to carburization with the carbon pickup varying from 0.6 mg/cm^2 for alloy 214 to slightly more than 5 mg/cm^2 for alloys 625 and N. For Co-base alloys, alloy 6B was the best performer (about 1.5 mg/cm^2 of carbon pickup), while alloy 150 was the worst (about 8 mg/cm^2 of carbon pickup). Typical carburized structures of selected alloys are illustrated in Figure 8.

Alloying Elements and Carburization Resistance:

Chromium carbides are major carbides formed as a result of carburization. The type of chromium carbides formed would depend upon the carbon activities in the metal. Thermodynamically, Cr_3C_2 carbides should form on the metal surface because of the high carbon activities. This was confirmed by X-ray diffraction analysis of several exposed samples. As the carbon activity decreases with increasing distance away from the metal surface, carbides may change from Cr_3C_2 to Cr_7C_3 and to $Cr_{23}C_6$ as illustrated in Figure 1. Because chromium is the major element in the carbides resulting from carburization, it is generally



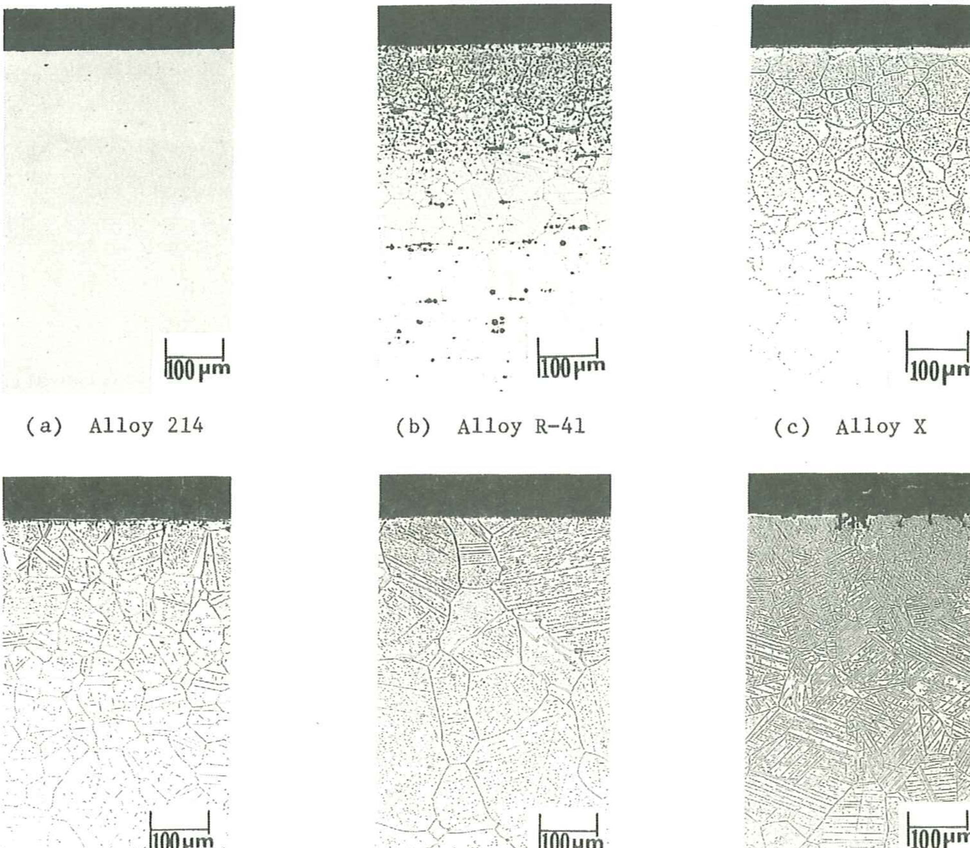
(a) (b)

Figure 7: Optical photomicrographs showing localized carburization attack upon Type 310 SS tested at 982°C (1800°F) for 55 hours: (a) severely carburized area, and (b) lightly carburized area.

believed that increases in Cr in the alloy can result in increased carburization rates. Chromium can also affect the alloy's carburization behavior in an opposite manner. The chromium oxide scale formed during exposure can be an effective barrier to carbon ingress, thus reducing carburization kinetics (10, 11). The present test environment, however, favors the formation of carbide scales instead of Cr_2O_3 oxide scales at the gas-metal interface (Figure 2). Oxides were observed to form beneath the carbide scale. These oxides are probably those of Cr, Mn, Si, Al and Ti.

The effect of Cr on the alloys' carburization resistance was examined for iron-, nickel- and Co-base alloys tested. In order to avoid complications introduced by the formation of oxides of Al, Ti and Si, alloys containing a significant amount of these elements were not included in the evaluation. Figure 9 illustrates the mass of carbon pickup as a function of Cr content in the alloys. The figure suggests no apparent correlation between chromium and the alloys' carburization resistance.

Increasing nickel in the alloy is generally believed to increase the alloy's carburization resistance. To avoid influences by other factors, only Ni-Cr alloys were examined for possible nickel effect. Also, Ni-Cr alloys with high Al, Ti or Si were not included in the analysis because of the possible influence by the oxides of these elements. As illustrated in Figure 10, increases in nickel content to not appear to incrase the alloy's carburization resistance. Although the data is somewhat scattering, the figure, however, suggests an optimum nickel content of approximately 30 to 40% wt. Similarly, an optimum iron content of approximately 30 to 45% wt. is also suggested for Ni-Cr alloys (Figure 11).



(a) Alloy 214 (b) Alloy R-41 (c) Alloy X

(d) Alloy 601 (e) Alloy 617 (f) Alloy 150

Figure 8: Optical photomicrographs showing typical carburized structures of selected alloys tested at 982°C (1800°F) for 55 hours. Unetched.

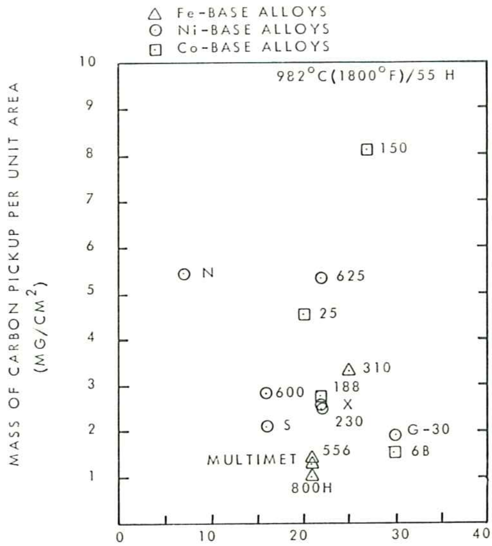


FIGURE 9: MASS OF CARBON PICKUP AS A FUNCTION OF Cr CONTENT IN THE ALLOY FOR Fe-, Ni- AND Co-BASE ALLOYS TESTED AT 982°C (1800°F) FOR 55 HOURS

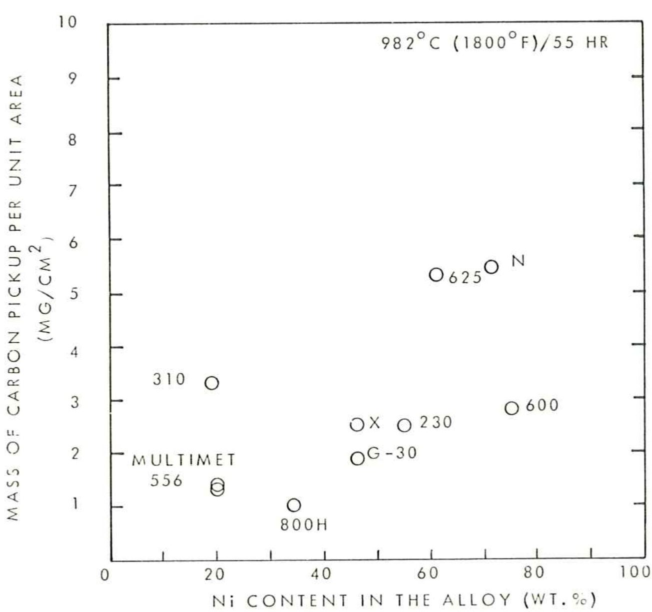


FIGURE 10: MASS OF CARBON PICKUP AS A FUNCTION OF Ni CONTENT IN THE ALLOY FOR Ni-Cr ALLOYS TESTED

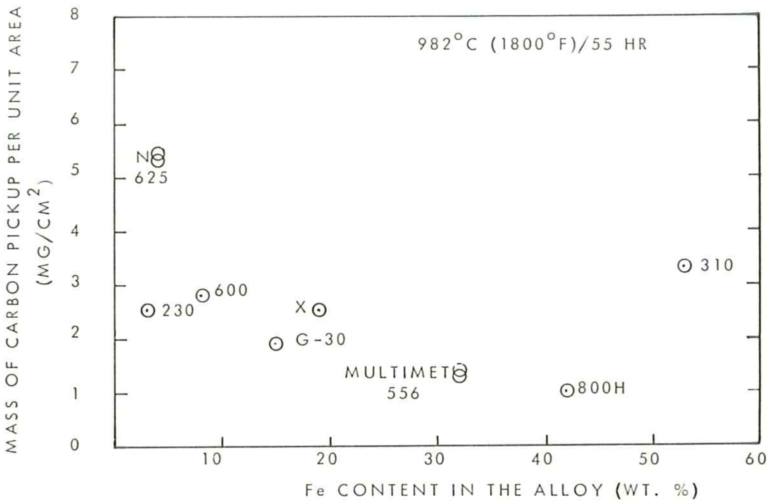


FIGURE 11: MASS OF CARBON PICKUP AS A FUNCTION OF Fe CONTENT IN THE ALLOY FOR Ni-Cr ALLOYS TESTED AT 982°C (1800 F) FOR 55 HOURS

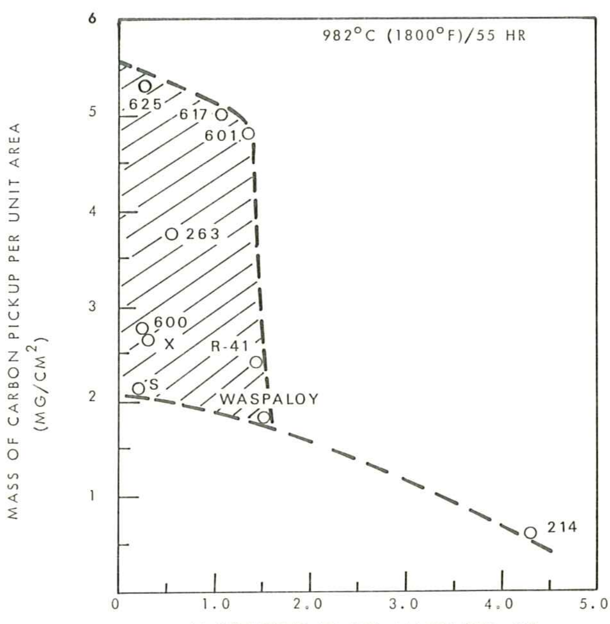


FIGURE 12: MASS OF CARBON PICKUP AS A FUNCTION OF Al CONTENT IN THE ALLOY FOR Ni-BASE ALLOYS.

Norton et al. (8) found that the Ni/(Cr + Fe) ratio was an important factor in influencing the carburization resistance in Fe-Ni-Cr alloys and Schnaas and Grabkes (5) suggested the ratio Ni/Fe = 4/1 for a Ni-Cr-Fe alloy with the optimum carburization resistance. No such dependence is apparent for either case in the present study. It may very well be because some of the Ni-Cr alloys investigated in the present study contained significant amounts of Mo, W or Co.

Aluminum with its oxide scale being extremely protective against oxidation attack should be an important alloying element in resisting carburization attack. The excellent resistance to carburization displayed by alloy 214 is believed to be attributed to the Al_2O_3 film formed on the metal surface during exposure. The existance of this film has been confirmed by Auger analysis. Apparently, alloy 214 contains a sufficient amount of aluminum (nominally 4.5% wt.) to form a continuous Al_2O_3 film. Other nickel-base alloys, such as alloys 601 (nominally 1.35% wt.) and 617 (nominally 1.2% wt.) were significantly less resistant to carburization. The levels of aluminum in these two alloys were not high enough to form a continuous Al_2O_3 film. Figure 12 illustrates the mass of carbon pickup as a function of aluminum content for Ni-base alloys containing various amounts of aluminum. Significant data scattering exists for alloys with aluminum contents less than 1.5% wt. It appears to imply that aluminum may not be an important alloying element when it is less than 1.5% wt. More data points are needed for alloys containing more than 1.5% aluminum in order to characterize the possible dependence of aluminum at high levels of concentrations.

Silicon is also known to improve the alloy's carburization resistance (4). However, the alloys investigated contained relatively low levels of silicon. Therefore, the analysis of a possible silicon effect could not be performed in this study.

SUMMARY

A wide variety of commerical, wrought alloys were tested in a highly carburizing environment at 871°, 927° and 982°C (1600°, 1700° and 1800°F). The relative performance ranking for these alloys in resisting carburization was presented. CABOT® alloy No. 214 was found to be the most resistant to carburization among the alloys tested. This appears to be attributable to the formation of a tenaceous Al_2O_3 scale arising from the significant amount of aluminum (nominally 4.5% by weight) present in the alloy. Possible correlation between other alloying elements and the alloys' carburization resistance was also discussed.

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