HIGH-TEMPERATURE CORROSION AND EMBRITTLEMENT OF ALLOYS IN GASEOUS ENVIRONMENTS

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ABSTRACT - The structure and mechanical property response of a wide variety of alloy materials to laboratory exposure at temperatures up to 980°C (Ar + 5% H_2 + 5% CO + 5% CH_4) are described. The materials studied range from ordinary stainless steels to complex nickel- and iron-base, high-performance alloys. Data are presented which characterize the relative oxidation resistance of the materials, their resistance to carburization, and their susceptibility to property degradation as a function of thermal exposure. The influence of the various types of exposure, including air and severely carburizing environments, upon the residual tensile properties of a broad spectrum of alloys is fully described, as are the Charpy impact properties for both as-received and as-exposed specimens.

INTRODUCTION

Metallic components in industrial processes can undergo a significant degradation as a consequence of long-term exposure to aggressive high-temperature environments. The loss of component integrity experienced often can be related to the occurrence of one or more forms of high-temperature corrosion. Frequently, matters are further complicated by structural degradation of the alloy or metal due to thermal aging. In order to cope with such complex considerations, component designers need to have available detailed information on both high-temperature corrosion resistance and long-term thermal stability of candidate materials of construction.

In industrial processes such as heat treating, production of petrochemical feedstocks, and generation of synthesis gas, the forms of high-temperature corrosion usually encountered are carburization and oxidation. Carburization furnaces and facilities require carburization-resistant alloys for construction of furnace hardware, fixtures, brick anchors, heating elements, fans, and others. Pyrolysis furnaces for ethylene and olefins production require carburization-resistant alloys for cracker tubes, pigtail pipes, and fittings.

Carburization of metals and alloys has been the subject of many investigations.[1-12] Much of this work has focused upon cast materials, although several studies have invloved evaluation of selected wrought alloys.[4, 5, 7, 9-11] Little comprehensive data are available to guide the selection of wrought alloys for use in carburizing environments from among the numerous potential candidate materials. This is true for assessing relative resistance to carburization and, perhaps even more so, for evaluating mechanical property degradation experienced as a consequence of carburization.

In order to establish the relative performance capabilities of various candidate materials for long-term, elevated-temperature service, laboratory studies were conducted. These included evaluation of resistance to oxidation, carburization, and degradation of mechanical properties by exposure in air or carburizing environments. Environmental and mechanical property tests were performed upon annealed and annealed-plus-exposed sheet materials. Similarly, impact tests were performed upon standard Charpy V-notch specimens taken from hot-rolled plate products of the same alloys. The materials evaluated in these studies and their compositions are given in Table 1.

OXIDATION & THERMAL STABILITY TESTING

Oxidation resistance and thermal stability data for the various alloys of interest were developed in order to provide a basis for judging the further adverse effects of carburization. Oxidation tests were performed by exposing approximately 1- to 1.5-millimeter (40- to 60-mil) thick sheet samples of the various alloys for 1008 hours at 980°C (1800°F) in flowing air. Samples were cycled to room temperature once a week. Prior to exposure the 22 mm x 22 mm (0.88 in x 0.88 in) samples were ground to a uniform 120-grit surface finish to minimize the influence of variations in surface condition. Following exposure, the samples were cathodically descaled in a molten salt bath. The descaled samples were weighed and then metallographically examined to determine the extent of internal attack. Weight changes were converted to average sample thickness changes, or metal losses, from knowledge of the densities of the alloys and geometric considerations.

Results of the oxidation tests in terms of metal loss experienced and the amount of continuous internal penetration observed metallographically are presented in Figure 1. Some of the typical through-thickness microstructures of the test samples are shown in Figure 2. Although none of the alloys tested exhibited extensive oxidation attack, there were significant differences in the behaviors observed. CABOT alloy No. 214 was the best of the alloys, with a combined metal loss plus continuous internal penetration (CIP) of just 4.1 µm (0.18 mils) per

TABLE 1

Alloy	Chemical Composition (Weight Percent) C	Fe	Ni	Cr	Co	Mo	Si	Mn	Others
Type 310 Stainless Steel	0.05	Bal.	20	25			0.5	0.8	
CABOT® alloy No. 800H	0.08	Bal.	33	21			0.5	0.8	0.4 Al, 0.4 Ti
CABOT alloy No. 600	0.05	8	Bal.	15.5			0.2	0.5	
INCONEL® alloy 601	0.05	14	Bal.	23			0.2	0.5	1.4 Al
CABOT alloy No. 214	0.04	4	Bal.	16					4.2 Al, 0.02 Y
MULTIMET® alloy	0.10	Bal.	20	20	20	3	0.5	1.5	3W, 1Cb, 0.15N
INCONEL alloy 617	0.07	1.5	Bal.	22	12.5	9	0.5	0.5	1.2 Al, 0.3 Ti
HASTELLOY® alloy X	0.10	18.5	Bal.	22	1.5	9	0.4	0.7	
HAYNES® Developmental alloy No. 230	0.10		Bal.	22		2	0.5	0.65	14 W, 0.01 La
HASTELLOY alloy S	0.02		Bal.				0.5	0.65	0.01 La

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side. Assuming linear kinetics, this extrapolates to an oxidation rate of from 35 μm to 396 μm per year (1.4 to 15.6 mils per year) over the range of alloys tested.

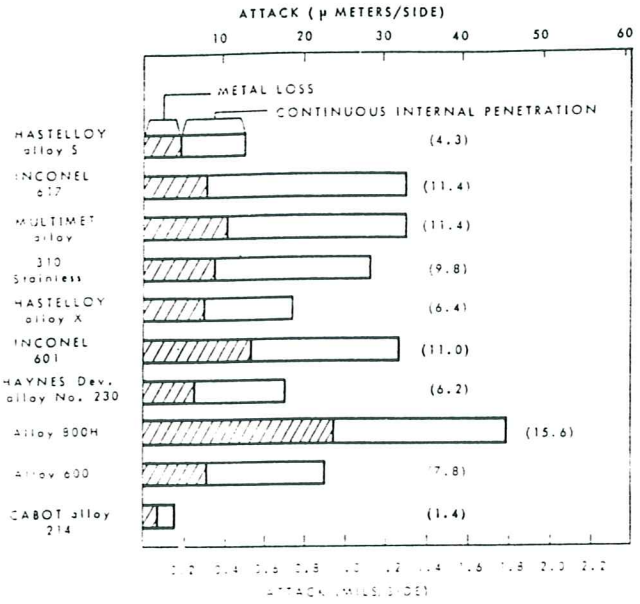

Fig. 1: Comparative oxidation resistance for a variety of alloys exposed to flowing air at 980°C (1800°F) for 1008 hours. The numbers in parentheses refer to linearly extrapolated rates of attack in mils/year.

The influence of long-term thermal exposure in an air environment upon alloy room-temperature tensile ductility was also determined for sheet product of the same materials. Tensile samples with a reduced section 1.27 cm (0.5 in) wide and 3.72 cm (2.25 in) long were exposed for 1000 hours in a large box furnace containing an air environment at 980°C (1800°F). Following exposure, these samples were tensile tested at room temperature (duplicate tests for each alloy), and the results were compared with those obtained from similar tests performed upon unexposed material. The comparison is shown in Figure 3.

Although all of the alloys, with the possible exception of INCONEL alloy 601, exhibited some apparent reduction in room-temperature tensile elongation, the only alloy to sustain major ductility loss was INCONEL alloy 617, which dropped from about 60 percent to about 30 percent. The smaller losses sustained by some of the other alloys, however, were sufficient to bring their ductilities down to a similar level. In any case, it is important to recognize that however small the reduction in ductility observed as a function of thermal aging/oxidation, the anticipated reduction in ductility as a consequence of carburization is likely to be additive.

CARBURIZATION TESTING

Test coupons identical to those described for oxidation testing were exposed in a carburizing environment with an inlet gas composition of 5% H_2, 5% CO, 5% CH_4, and balance Ar (by volume percent). Tests were performed for both 215 hours at 925°C (1700°F) and 55 hours at 980°C (1800°F) in an alumina retort with a linear gas velocity of about 4 centimeters/minute. The test environment was characterized by a low oxygen potential and unit carbon activity.

Following exposure, test coupons were weighed and sectioned for both carbon analysis and metallographic examination. Surface scales, where encountered, were not removed prior to carbon analysis. Once carbon analyses were determined, a relative measure of the capability of each alloy to resist carburization was established by calculating the mass of carbon pickup per unit area of specimen (mg/cm^2) using the following equation:

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

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

A comparison of the extent to which the alloys were carburized is shown in Figure 4 for the 925°C (1700°F) exposures and in Figure 5 for

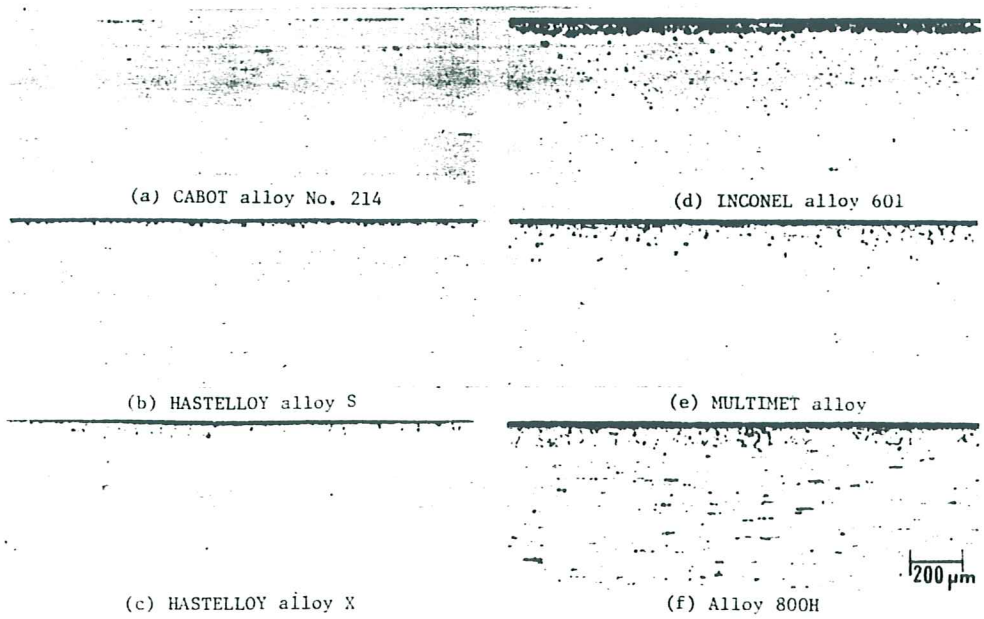

Fig. 2: Typical through-thickness microstructures for various alloys exposed to flowing air at 980°C (1800°F) for 1008 hours. The black area at the top of each photograph represents metal lost from the original thickness as a consequence of the exposure.

the exposures at 980°C (1800°F). The kinetics of carburization were observed to be much faster at 980°C (1800°F) than at 925°C (1700°F), as might be expected. As a whole, the group of alloys evaluated exhibited about twice as much carbon pickup at the higher temperature in just over a quarter of the exposure time. In both cases, CABOT alloy No. 214 was the least affected, while Type 310 stainless steel, which was only tested at 925°C (1700°F), showed severe carburization. For other alloys, the degree of carburization varied from slight for Alloy 800H and MULTIMET alloy to intermediate for HASTELLOY alloys S and X to more severe for INCONEL alloys 601 and 617.

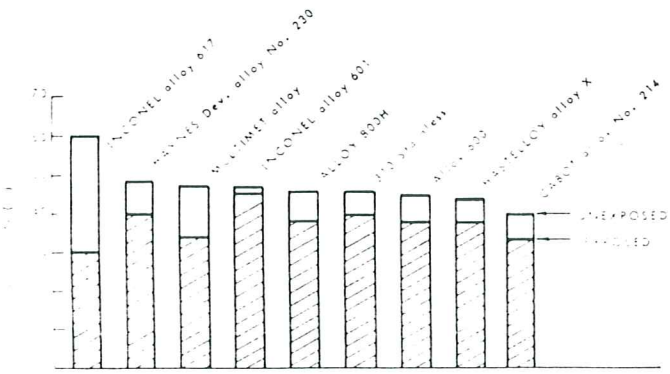

Fig. 3: Effect of 1000-hour exposure at 980°C (1800°F) in air upon the room temperature tensile elongation of sheet product of various alloys.

The excellent resistance of alloy No. 214 to carburization may well be related to the tightly adherent Al_2O_3 scale it forms even under very low oxygen potential conditions. The existence of this thin film has been confirmed by Auger analysis. The resistance of Alloy 800H to carburization is somewhat surprising, however, as its

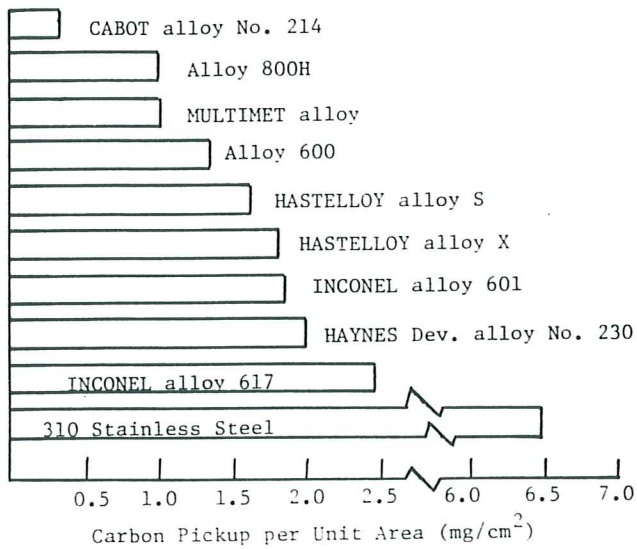

Fig. 4: Carburization of various alloys at 925°C (1700°F) after 215 hours in Ar-5%H_2-5%CO-5%CH_4.

poor oxidation resistance would indicate that an effective oxide scale barrier to carburization may not be a factor. Of course, it is possible that the formation of an adherent carbide layer on the surface might be involved. One possible clue to the behavior of Alloy 800H is illustrated in Figure 6, which shows the through-thickness microstructures of three of the alloys exposed to the 980°C (1800°F) carburizing environment for 55 hours. While alloy No. 214 (6c) shows virtually no subsurface carbide precipitation, and alloy X (6b) exhibits both grain boundary and matrix subsurface carbide precipitation, Alloy 800H (6a) exhibits carbide precipitation mainly along grain boundaries. This could be

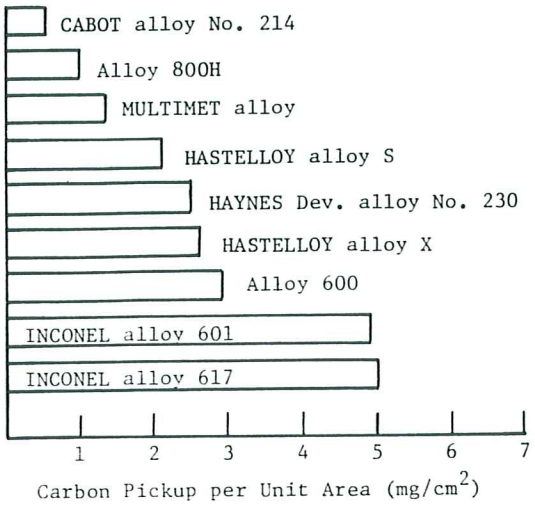

Fig. 5: Carburization of various alloys at 980°C (1800°F) after 55 hours in Ar-5%H_2-5%CO-5%CH_4.

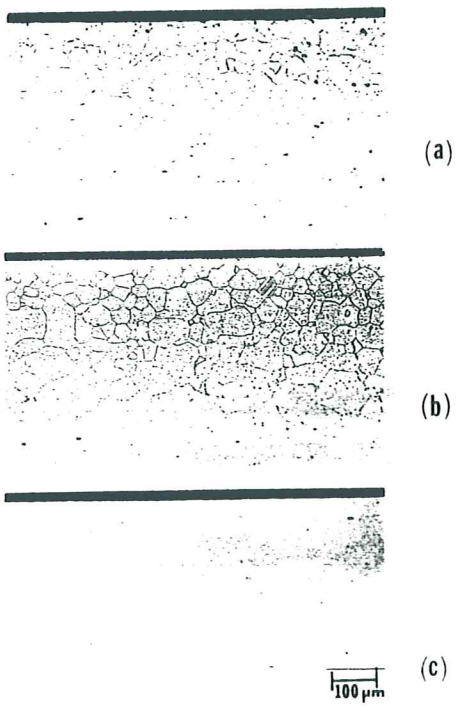

Fig. 6: Morphology of carburization observed for three alloys exposed for 55 hours at 980°C (1800°F) in Ar-5%H_2-5%CO-5%CH_4. (a) Alloy 800H, (b) HASTELLOY alloy X, (c) CABOT alloy No. 214.

indicative that matrix carbon diffusion is somehow inhibited in this alloy, although matrix versus grain boundary carbon solubility considerations could also certainly be involved.

CARBURIZATION EFFECT UPON TENSILE & IMPACT PROPERTIES

Tensile test specimens with reduced sections 0.64-cm (0.25 in) wide and 2.86-cm (1.125 in) long were exposed to both air and carburizing environments in manners similar to those described previously. Exposures were performed at both 925°C (1700°F) and 980°C (1800°F) for 24 hours. Tensile tests were conducted in duplicate at room temperature for samples as-received, exposed in air, and exposed in carburizing environments. Results of these tests are given in Table 2.

These tests indicate that all of the materials tested undergo drastic loss of room temperature tensile ductility as a consequence of the 980°C (1800°F)/24 hour carburization exposure, as opposed to the air exposure at the same temperature. Only Alloy 600 exhibits a reasonable residual tensile elongation at 11.9 percent. Alloy 800H and CABOT alloy No. 214 are better than the rest, but still quite low at 5.5 and 6.5 percent, respectively. The most unexpected result is that obtained for MULTIMET alloy. Where the majority of the poor tensile ductility results exhibited by the various alloys are in keeping with the carbon pickup per unit area rankings developed from the 980°C (1800°F) carburization tests, the poor ductility behavior of MULTIMET alloy is inconsistent with its good resistance to carbon pickup.

One factor which may be contributing to the tensile test behavior of both Alloy 600 and MULTIMET alloy following the 980°C (1800°F) carburization exposure is examined in Figure 7. This figure illustrates the observed hardness levels as a function of distance below the sample

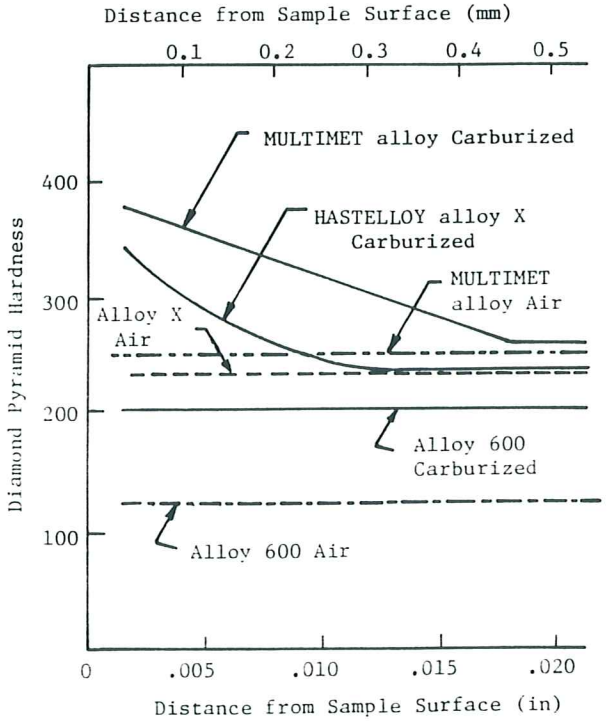

Fig. 7: Hardness as a function of distance from the sheet sample surface for MULTIMET alloy, Alloy 600, and HASTELLOY alloy X exposed 24 hours at 980°C (1800°F) in air and in Ar-5%H_2-5%CO-5%CH_4.

TABLE 2

Room Temperature Tensile Ductility of

Air- and Carburizing Atmosphere-Exposed Samples of Various Alloys

Alloy	Elongation				
	As-Received (%)	Exposed 980°C (1800°F)/24 Hours		Exposed 925°C (1700°F)/24 Hours	
		Air (%)	Carburizing (%)	Air (%)	Carburizing (%)
Alloy 600	45.2	44.9	11.9	44.5	36.0
CABOT alloy No. 214	39.8	29.9	6.5	27.5	14.0
Alloy 800H	46.3	42.5	5.5	41.5	36.4
HASTELLOY alloy S	56.8	54.2	4.6	52.3	11.8
HASTELLOY alloy X	47.6	37.7	2.9	31.5	10.6
HAYNES Dev. alloy No. 230	47.2	36.8	2.8	37.1	11.4
INCONEL alloy 601	47.4	43.5	2.7	48.6	16.4
Type 310 Stainless Steel	47.7	43.9	1.9	40.7	8.3
INCONEL alloy 617	59.5	25.1	1.5	35.8	15.9
MULTIMET alloy	47.8	30.7	1.1	36.0	37.5

surface for the 980°C (1800°F) carburized specimens of MULTIMET alloy, Alloy 600, and HASTELLOY alloy X in comparison to the results observed for simple air exposures. Although both MULTIMET alloy and Alloy 600 exhibit case depths greater than 0.5 to 0.6 millimeters (20 to 25 mils), Alloy 600 shows a uniform increase in hardness as a consequence of carburization, while MULTIMET alloy exhibits a pronounced gradient in hardness from the surface to almost the limits of the case depth. HASTELLOY alloy X, which exhibits a case depth of about 0.25 millimeters (10 mils), displays behavior similar to MULTIMET alloy.

These hardness profiles are consistent with the microstructural observations made concerning carbide volume fraction and morphology in the samples. HASTELLOY alloy X and MULTIMET alloy both exhibited high volume fractions of carbides near the surface, decreasing gradually over the depth of the carburization case. Alloy 600, on the other hand, exhibited uniform low volume fraction carbide precipitation throughout the extent of the case zone, with the carbides exhibiting a relatively discontinuous morphology.

Examination of the fracture surfaces of broken room temperature tensile samples, photographs of which are shown in Figures 8 to 10, reveals that MULTIMET alloy exhibits a complete intergranular failure with no sign of any plastic deformation, even in the material below the case zone. Conversely, Alloy 600 exhibits complete ductile failure behavior, with no sign of intergranular crack propogation. HASTELLOY alloy X fails in a mixed mode, showing a few signs of plastic deformation in the case zone itself and a readily apparent transition to combined intergranular and transgranular failure in the material below the carburized case.

The key influence of carburization case depth upon the residual ductility in the alloys is apparent from the comparison of the room temperature tensile elongation of 925°C (1700°F) carburization exposed samples to that of 980°C (1800°F) exposed samples in Table 2. While MULTIMET alloy was the most embrittled at 980°C (1800°F), it is the least embrittled following the 925°C (1700°F) exposure. All of the materials displayed ductile failure characteristics with the less severe carburization exposure, which would suggest that the failure mode is very dependent upon the case depth. Following MULTIMET alloy, Alloys 600 and 800H were once again among the best performers. CABOT alloy No. 214 displayed somewhat lower ductility after the 925°C (1700°F) carburizing exposure than might have been expected, although still a quite reasonable 14.0 percent. INCONEL alloys 601 and 617 were noticeably improved in their response to the less severe exposure, having tensile elongations of 16.4 and 15.9 percent, respectively.

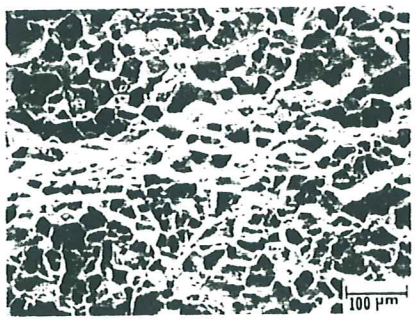

Fig. 8: Scanning electron micrograph of the fracture surface of a MULTIMET alloy sheet sample exposed to carburizing environment at 980°C (1800°F) for 24 hours and tensile tested at room temperature.

Studies were also performed to determine the effect of carburization exposure upon room temperature impact properties. Standard size Charpy V-notch samples were tested both in the as-received condition and following exposure for 200 hours at 980°C (1800°F) in the Ar-5%H_2-5%CO-5%CH_4 carburizing environment already described (samples

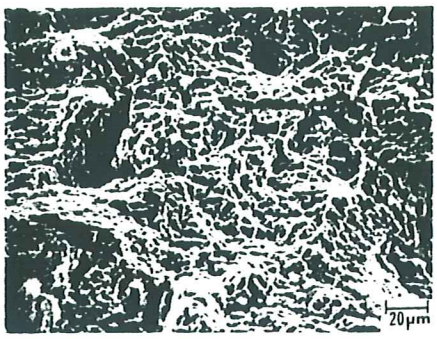

Fig. 9: Scanning electron micrograph of the fracture surface of an Alloy 600 sheet sample exposed to carburizing environment at 980°C (1800°F) for 24 hours and tensile tested at room temperature.

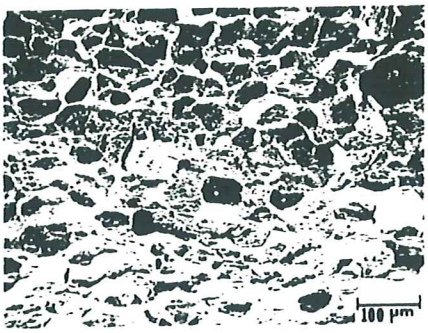

Fig. 10: Scanning electron micrograph of the fracture surface of a HASTELLOY alloy X sheet sample exposed to carburizing environment at 980°C (1800°F) for 24 hours and tensile tested at room temperature.

were machined prior to exposure). Results are presented in Table 3.

TABLE 3

Charpy V-Notch Impact Properties for Various Alloys Before and After Carburization Exposure for 200 Hours at 980°C (1800°F) in Ar-5%H_2-5%CO-5%CH_4

Alloy	Impact Strength - Joules (ft-lb) Unexposed		Exposed	
310 Stainless Steel	> 348	(257)*	122	(90)
INCONEL alloy 601	> 329	(243)*	47	(35)
Alloy 800H	> 293	(216)*	92	(68)
CABOT alloy No. 214	> 193	(142)*	45	(33)
MULTIMET alloy	167	(123)	9	(7)
INCONEL alloy 617	132	97)	26	(19)
HASTELLOY alloy S	113	83)	49	(36)
HASTELLOY alloy X	100	74)	14	(10)
HAYNES Dev. alloy No. 230	77	57)	26	(19)

* Specimens Did Not Break

Unfortunately, results have not yet been generated for Alloy 600; however, it is apparent from the results obtained for the other alloys that the influence of carburization at 980°C (1800°F) upon impact properties is not necessarily the same as that exerted upon tensile ductility. This is clear from the post-carburization impact strength of Type 310 stainless steel and the relatively good strengths exhibited by HASTELLOY alloy S, INCONEL alloy 601, and CABOT alloy No. 214. Some results are consistent with those of the tensile tests, such as for MULTIMET alloy, but the significant differences in the behavior of the other alloys suggest that it is prudent to evaluate both tensile and impact properties in an attempt to rank alloy capabilities.

SUMMARY AND CONCLUSIONS

The oxidation resistance, thermal stability, and resistance to carburization of a variety of commercially available wrought materials have been characterized. It has been shown that an order of magnitude variation in resistance to oxidation at 980°C (1800°F) is manifested by the alloys studied, CABOT alloy No. 214 being the most resistant and Alloy 800H the least resistant. However, even Alloy 800H did not exhibit extensive oxidation after 1008 hours of exposure in flowing air at 980°C (1800°F).

Studies were performed to describe the relative thermal stability of these alloys in terms of residual room-temperature tensile ductility following 1000-hour exposure in air at 980°C (1800°F). It has been shown that most of the alloys exhibited some apparent reduction in room-temperature ductility as a consequence of this exposure, but only INCONEL alloy 617 sustained a major loss of tensile elongation (from about 60% to about 30%). All of the alloys tested still exhibited 30 percent more tensile elongation subsequent to exposure.

Data have been presented which demonstrate that, as in the case of oxidation resistance, a wide range in observed resistance to carburization is exhibited by the alloys studied. In terms of the mass of carbon pickup per unit area following exposure in a low oxygen potential, highly carburizing environment, CABOT alloy No. 214, Alloy 800H, and MULTIMET alloy were found to be the most resistant materials tested at both 980°C (1800°F) and 925°C (1700°F). Type 310 stainless steel was found to be the least resistant.

In terms of the embrittling effects observed as a consequence of carburization exposure, it was determined that both the residual room temperature tensile properties and room temperature impact properties of carburized samples are not necessarily consistent with behavior which would be expected from mass of carbon pickup measurements. Although Alloy 800H and CABOT alloy No. 214 exhibited reasonable resistance to embrittlement, the most resistant material in terms of tensile test results was Alloy 600, which was found to be considerably more susceptible to carbon pickup than either of these two alloys. MULTIMET alloy, one of three alloys most resistant to carbon pickup at both 980°C (1800°F) and 925°C (1700°F) exhibited the worst post-exposure

tensile ductility and impact strength following sample exposure at 980°C (1800°F). On the other hand, it was the least embrittled alloy evaluated in the post-925°C (1700°F) exposure tensile tests.

Perhaps the most notable inconsistency in behavior was the post-980°C (1800°F) exposure impact strength of Type 310 stainless steel, which was the highest for the alloys tested. This material exhibited the worst resistance to carbon pickup at 925°C (1700°F) and was among the lowest in post-exposure tensile ductility for both exposure temperatures. Its excellent impact properties and the relatively better performance of INCONEL alloy 601 and HASTELLOY alloy S in impact tests rather than tensile tests all point to the importance of viewing the embrittling influence of carburization from several vantage points. It is evident from this work that the effect of carburization upon mechanical properties is complex and requires further study before full understanding can be achieved.

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