HIGH–TEMPERATURE CORROSION OF MATERIALS FOR HEAT RECOVERY SYSTEMS

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ABSTRACT

Metallic heat exchangers and recuperators used in industrial processes for extracting heat from flue gas streams can be subject to severely corrosive high-temperature environments. Principal modes of attack upon metals and alloys frequently encountered in various industrial processes are discussed. These corrosion modes include oxidation, sulfidation, carburization, and chlorination. The high-temperature alloys that are resistant to these types of environmental attack are discussed in terms of laboratory results. Suitable alloys for application in each principal environment are suggested.

INTRODUCTION

The waste heat recovery system is becoming an increasingly important design feature for modern high-temperature processing systems. Recovering heat from process or flue gas streams with a recuperator or heat exchanger and putting it back into the process can increase the system's thermal efficiency and significantly lower production costs. Flue gas streams generated by many high-temperature processing systems can be quite corrosive. The corrosive nature of the flue gas stream can vary from process to process. Understanding the corrosive nature of each specific flue gas environment and the resistance to corrosion attack of candidate alloys is of paramount importance in selecting the viable material for construction of the waste heat recovery system.

The corrosive species found in flue gas streams generally come from feedstock, fuels, fluxes, and/or chemical additives. The principal modes of high-temperature corrosion that have been frequently encountered in the industry include oxidation, sulfidation, carburization, and chlorination which can take place independently or jointly. The corrosion attack by any of these modes can be further accelerated by the presence of other contaminants such as vanadium, alkali metals, lead, ash, etc. In the present paper, such additional contaminant effects will not be addressed. Examples showing the corrosion of

alloys in flue gas environments generated by various industrial processes will be cited. Laboratory test results showing the relative performance of a wide variety of commercial alloys in environments typical of those responsible for these principal modes of corrosin are presented. The nominal compositions of the alloys investigated in this study are listed in Table 1.

OXIDATION

Excess air is often used to ensure a complete combustion of fuel in many industrial processes. When the combustion products thus generated contain little or no contaminants such as sulfur, carbon, chlorine, vanadium, alkali metals, and other impurities coming from the fuel, feedstocks, fluxes, or chemical additions, the dominant high-temperature corrosion is typically oxidation. Under these conditions, metals or alloys are oxidized mainly by oxygen.

Air oxidation data are readily available in the literature and alloy manufacturer data brochures for a variety of high-temperature alloys.[1-6] These data may be used as a qualitative guide to materials selection. Depending upon the operating temperature and other materials requirements, a materials engineer or designer has a wide selection of commercial wrought alloys from stainless steels to nickel- or cobalt-base superalloys (e.g., 304SS, 310SS, CABOT® alloys No. 800H and No. 600, INCONEL® alloy 601, HASTELLOY® alloy X, HAYNES® alloy No. 188, etc.). These alloys basically rely upon a Cr_2O_3 oxide scale for protection. However, these oxides tend to convert to volatile CrO_3 oxides at very high temperatures (i.e., above 1000°C).[7] At these temperatures, the alloys, such as CABOT alloy No. 214, that are capable of forming the more stable Al_2O_3 oxide scale are preferred.

Figure 1 illustrates the results of the air oxidation tests conducted at 1093°C (2000°F) for 1,008 hours. CABOT alloy No. 214 is compared with some high-temperature alloys that form chromia scales. CABOT alloys No. 800H and No. R-41 suffered severe oxidation attack; so did INCONEL alloy 601, which showed numerous internal voids. HASTELLOY alloy X, INCONEL alloy 617, and HAYNES Developmental alloy No. 230 (nickel-base superalloys) and HAYNES alloy No. 188 (cobalt-base superalloy) suffered much less attack. CABOT alloy No. 214, however, was essentially unaffected by the exposure. This alloy develops a tenaceous Al_2O_3 oxide film which remains intact, even after repeated thermal cycling from room-temperature to 1149°C (2100°F). Figure 2 shows the results of the oxidation tests conducted at 1149°C (2100°F). After exposure at 1149°C (2100°F) and thermal cycling once a day every day except during the weekends for 42 days (1,008 hours of accumulated exposure time), alloy 214 showed essentially no weight change. On the other hand, alloys 800H and 601 suffered significant weight loss.

SULFIDATION

Sulfur is the most common contaminant present in either process or flue gas streams. Accordingly, wide spread materials problems due to sulfidation

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attack have been encountered in various industrial processes. Waste incineration, glass manufacturing, petrochemical and refinery processing, fossil-fired power generation, and coal gasification are some of the industrial processes that have experienced sulfidation-related materials problems.

Figure 3 illustrates several examples of sulfidation problems encountered in several plants: (a) a waste incinerator burning waste oil (b), a refractory manufacturing plant (c), an oil-fired power plant, and (d) a petrochemical plant.

Sulfur can be present in the process or flue gas stream as either SO_2 and SO_3 or H_2S depending upon the process or combustion conditions. In general, sulfur converts to SO_2 and SO_3 when the combustion takes place with excess air. The flue gas stream thus produced is generally highly oxidizing. However, oxygen-poor conditions can be established under certain conditions. When stoichiometric combustion conditions prevail, sulfur is generally present in the process gas stream as H_2S. Gas streams generated by many petrochemical processes and coal gasification are of this type. The atmosphere is generally reducing and is characterized by low oxygen potentials.

An investigation was undertaken at Cabot Corporation to generate sulfidation data for a wide variety of commercial alloys in both oxidizing and reducing environments covering both ends of the environmental spectrum encountered in industries. The results pertaining to the oxidizing atmosphere will be reported in the future. The following is a summary of the results generated in a reducing environment.

Figures 4 and 5 summarize the comparative performance ranking of various commercial iron-, nickel-, and cobalt-base alloys obtained from tests conducted at 760°C and 871°C (1400°F and 1600°F) in an environment with the inlet test gas mixture consisting of 5% H_2, 5% CO, 1% CO_2, 0.15% H_2S, 0.1% H_2O, and balance Ar (by volume percent). Cobalt-base alloys (e.g., HAYNES alloys No. 25, No. 150, and No. 188) were most resistant to sulfidation attack. Next to this group of alloys were the Fe-Ni-Cr-Co alloys (e.g., HAYNES alloy No. 556 and MULTIMET® alloy) and some nickel-base alloys with aluminum and titanium (e.g., CABOT alloy No. 263). High nickel alloys (e.g., HASTELLOY alloy X, CABOT alloy No. alloy 600, INCONEL alloy 601) and Fe-Ni-Cr alloys (e.g., 310SS and CABOT alloy No. 800H) suffered severe sulfidation attack.

CARBURIZATION

Flue gas streams containing carbonaceous gases can pose potential materials problems to metallic components as a result of carburization attack. As an example, Figure 6 shows the extensive carburization experienced by a Type 310SS part in a diesel engine preheater. In order to determine the carburization resistance of a wide variety of commercial wrought alloys, laboratory tests were performed in a highly carburizing environment. Figure 7 illustrates the relative alloy ranking for a wide variety of commercial alloys tested at 927°C (1700°F) for 215 hours in argon containing 5% H_2, 5% CO, and 5% CH_4

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(i.e., inlet gas composition by volume percent). The thermodynamic potentials for the test environment at 927°C (1700°F) were calculated to be

6.5×10^{-22} atm for the oxygen potential (P_{O_2}) and 1.0 for the carbon activity (a_c). The carbon deposits formed on the sample surface were removed by emery paper before the sample was cleaned and analyzed for carbon. The results were presented in terms of the mass of carbon pickup per unit area (mg/cm^2), which was obtained by the following equation:

$$M = C \left(\frac{W}{A}\right)$$

where,

M = mass of carbon pickup per unit area of specimen (mg/cm^2),
C = difference in carbon (weight fraction) before and after exposure,
W = weight of unexposed specimen (mg), and
A = surface area of the specimen exposed to the test environment (cm^2).

The present 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 method commonly used to present carburization results).

Several nickel- and iron-base alloys with excellent carburization resistance are available for materials selection. CABOT alloy No. 214 was found to be the best among the alloys tested.

CHLORINATION

Chlorine is another common contaminant in flue gases. In an aluminum-melting facility, for example, the flue gas may contain Cl_2 and/or HCl which come from either fluxes or chlorine gas used to purge molten aluminum. Incineration of wastes containing plastic materials (e.g., PVC) may also produce combustion products contaminated with chlorine and/or chlorides. Process gas streams generated by many chlorination processes contain Cl_2 and/or HCl.

The presence of Cl_2 or HCl in the flue gas stream can significantly accelerate the high-temperature corrosion of metals and alloys. The oxide scale may become less protective due to the concurrent formation of volatile metal chlorides and/or metal oxychlorides. As a result, oxidation of metals or alloys is greatly accelerated. An example showing extensive oxidation of an alloy 800 sample exposed to the chlorine-contaminated flue gas stream of an aluminum-melting furnace is illustrated in Figure 8.

Little high-temperature corrosion data with respect to the resistance to chlorination attack of engineering materials is available to guide materials selection. The most frequently referenced paper is the work by Brown et al.[8] which was published in 1947. Their tests were conducted in either 100% Cl_2 or 100% HCl environments which are really not pertinent to process or flue gas streams generated by many high-temperature process systems. Furthermore, many new high-temperature alloys have been developed and widely used in the industry since then. Therefore, chlorination tests were conducted for selected high-temperature alloys. The results are summarized in the following.

The tests were conducted by exposing coupons in an oxidizing atmosphere of Ar + 20% O_2 + 2% Cl_2 (volume percent) and in a reducing atmosphere of Ar + 4% H_2 + 4% HCl (volume percent) at 900°C (1650°F) for eight hours. The ranking of the alloys tested in both atmospheres is shown in Figures 9 and 10. CABOT alloy No. 214 was found to be most resistant to the oxidizing environment. For the reducing environment, CABOT alloy No. 214 and HASTELLOY alloys C-276 and S were the most resistant among the alloys tested.

SUMMARY AND CONCLUSIONS

Principal modes of high-temperature corrosion frequently encountered in various industrial processes were discussed. These corrosion modes include oxidation, sulfidation, carburization, and chlorination. The relative performance ranking for a wide variety of commercial wrought alloys in resisting each type of corrosion attack was presented. General conclusions are briefly summarized as follows:

1. When the combustion process involves "clean" fuel and no major corrosive contaminants such as sulfur, chlorides, carbon, alkali metals, etc., in the flue gas, the dominant corrosion mode is typically oxidation. Under these conditions, a number of high-temperature alloys that rely on chromia scales for protection are available for application up to 1093°C (2000°F). These materials range from stainless steels to solid solution strengthened nickel- and cobalt-base superalloys (e.g., HASTELLOY alloy X, INCONEL alloy 617, HAYNES Developmental alloy No. 230, and HAYNES alloy No. 188). A new nickel-base alloy, CABOT alloy No. 214, which relies on an alumina scale for protection is significantly more resistant to oxidation than the chromia formers. CABOT alloy No. 214 retains its excellent oxidation resistance at extreme temperatures (i.e., above 1000°C) when the chromia formers begin to deteriorate because of the formation of volatile CrO_3 oxides.

2. For a reducing, sulfidizing flue gas stream, cobalt-base alloys such as HAYNES alloys No. 25, No. 150, and No. 188 are the best candidates. Fe-Cr-Co-Ni alloys with low nickel contents such as HAYNES alloy No. 556 and MULTIMET alloy are preferred to high-nickel alloys (e.g., alloy 600, INCONEL alloy 601, HASTELLOY alloy X) and Fe-Ni-Cr alloys (e.g., 310SS and alloy 800H). Nickel-base alloys with aluminum and titanium tend to suffer much less attack than those with little or no aluminum and titanium.

3. For carburizing environments, several nickel- and iron-base alloys exhibiting excellent carburization resistance are available for materials selection as illustrated in Figure 7. CABOT alloy No. 214 with significant amounts of aluminum was found to be the best among the alloys tested.

4. For the flue gas stream containing Cl_2 and/or HCl where oxidation/ chlorination or chlorination is the dominant mode of attack, CABOT alloy No. 214 is suitable in both oxidizing and reducing atmospheres. HASTELLOY alloys C-276 and S are suitable only in reducing atmospheres.

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7. Caplan, D., and Cohen, M. Journal of the Electrochemical Society, Vol. 108, No. 5, p. 438 (1961).

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Table 1

Nominal Chemical Composition of 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
CABOT alloy No. 600	.08+	8	Bal	–	16	–	–	.5+	1.0+	.35+	.3+	Cu=.5+
CABOT alloy No. 214	.04	4	Bal	–	16	–	–	–	–	4.5	–	Y=.01
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 S	.02	3+	Bal	2.0+	15.5	14.5	1.0+	.4	.5	.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+	.4+	.4+	Cb+Ta=3.5
CABOT alloy No. R-41	.08	5+	Bal	11	19	10	–	.5+	.1+	1.5	3.0	B=0.006
HASTELLOY alloy C-276	.01+	5.5	Bal	2.5+	15.5	16	–	.08+	1.0+	–	–	V=.35+
HAYNES Developmental alloy No. 230	.1	3+	Bal	3+	22	2	14	.4	.5	.3	–	B=0.005, La=0.03
RA*** alloy 333	.05	18	Bal	3	25	3	3	1.25	1.5	–	–	–
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	–	–	–

+ Maximum

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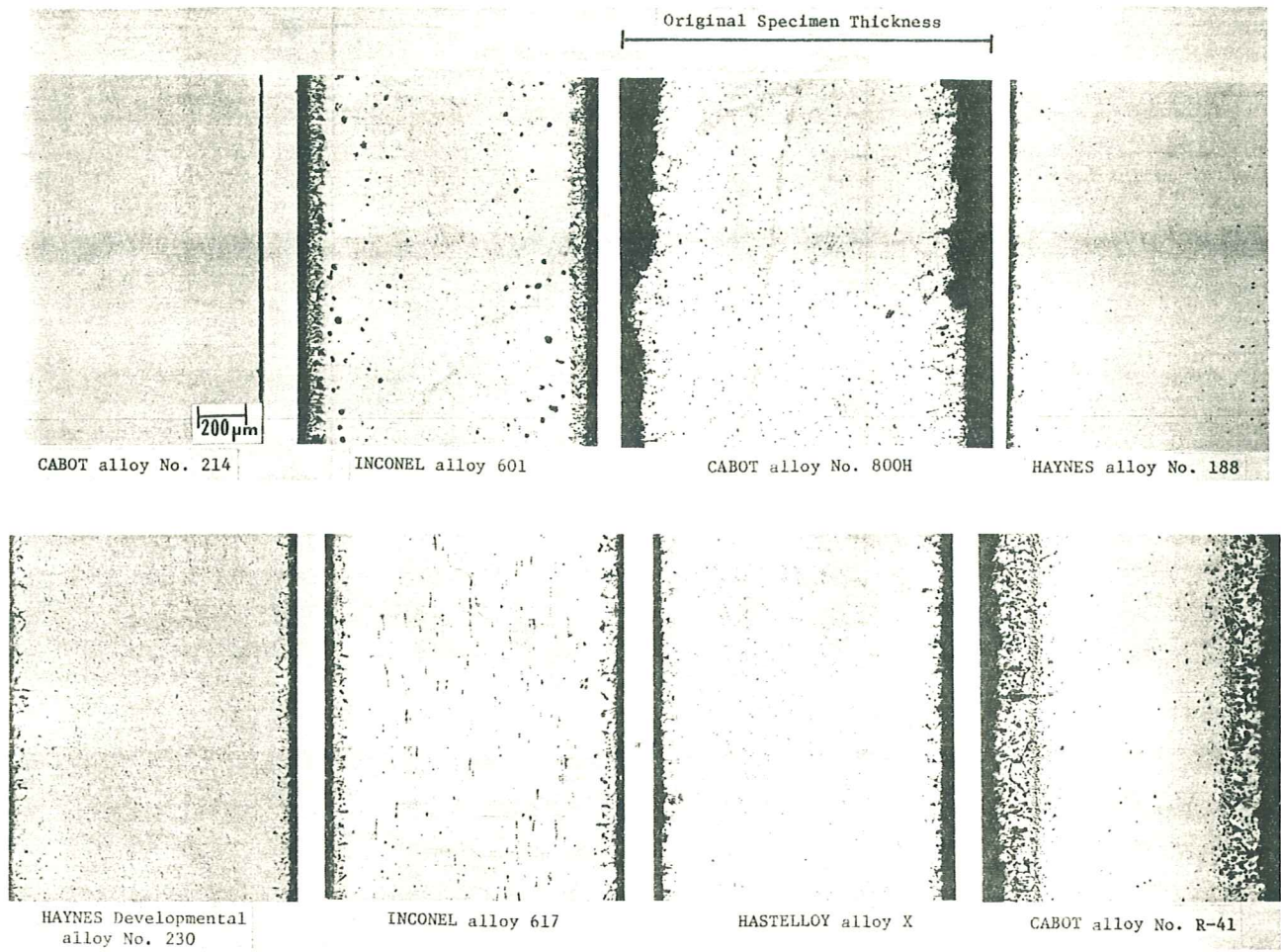*** RA is a registered trademark of Rolled Alloys.

Fig. 1 - Cross sections of descaled specimens of various alloys after testing at 1093 C (2000 F) for 1008 hours in flowing air. The specimens were thermally cycled to room temperature by air cool every 168 hours (a week). The original specimen thickness corresponds to the width of the individual photograph as indicated.
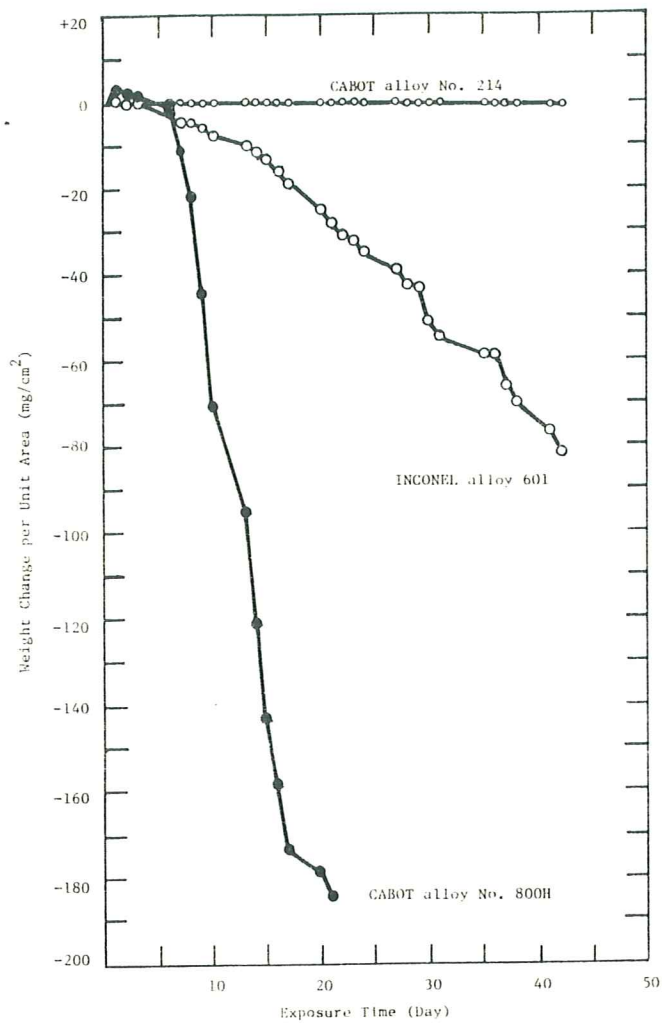
Fig. 2 - Results of oxidation tests at 1149 C (2100 F) in still air. The samples were thermally cycled to room temperature by air cool once a day every day except weekends.
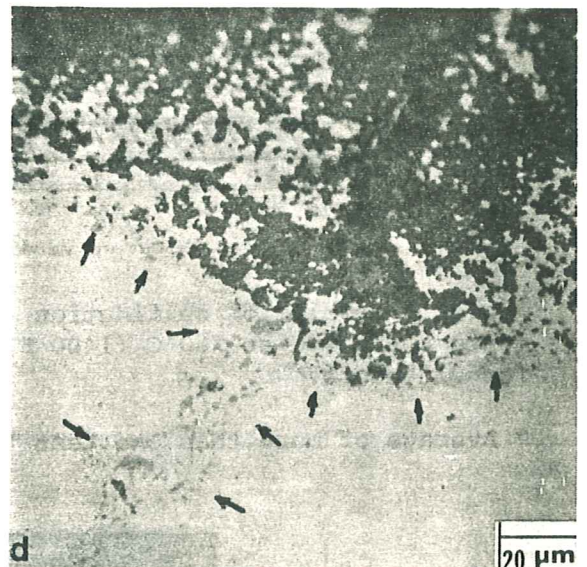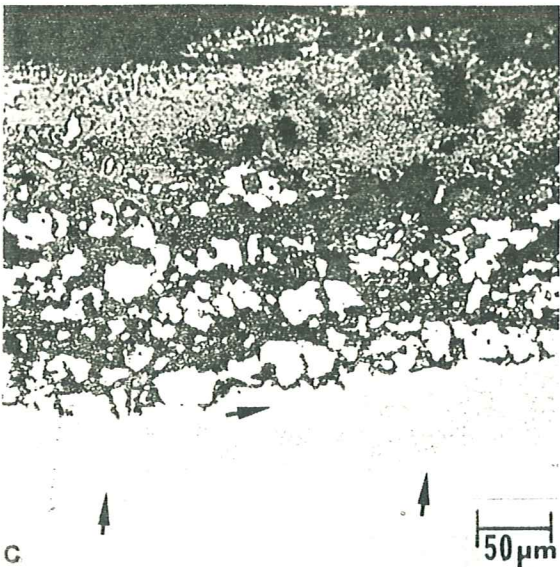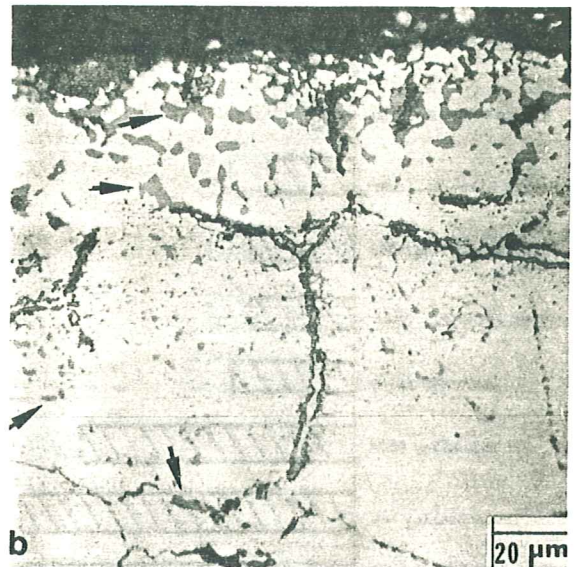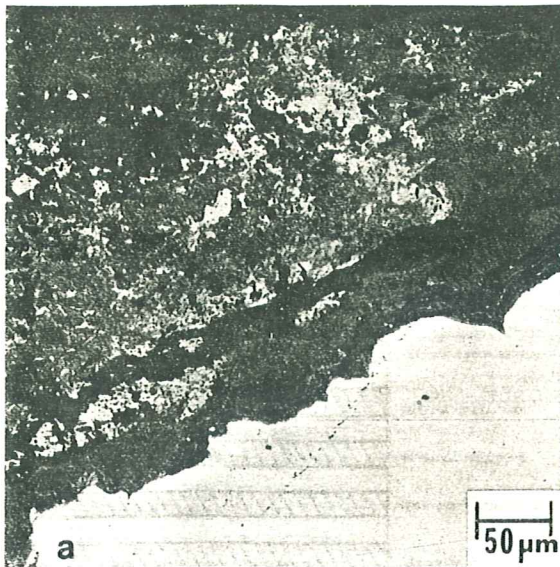
Fig. 3 - Examples of sulfidation-oxidation attack by
various flue gas streams. (a) Alloy X exposed to
combustion products of a waste incinerator incinerat-
ing waste oil (the corrosion scale consisted of a
mixture of nickel sulfides and chromium oxides),
(b) alloy 800H exposed to the flue gas of a refractory
manufacturing plant, (c) RA alloy 333 exposed to the
flue gas of an oil-fired facility, and (d) Type 316SS
exposed to the flue gas stream of a petrochemical
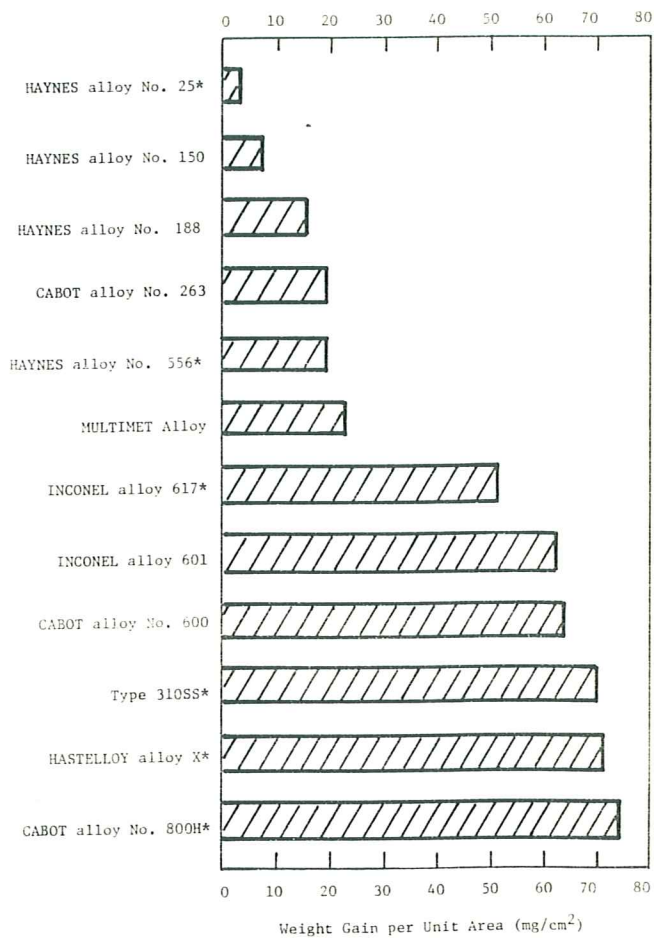plant. Arrows indicate sulfide phases in b, c, and d.

Fig. 4 chart

Weight Gain per Unit Area (mg/cm²) — scale 0 to 80

- HAYNES alloy No. 25*
- HAYNES alloy No. 150
- HAYNES alloy No. 188
- CABOT alloy No. 263
- HAYNES alloy No. 556*
- MULTIMET Alloy
- INCONEL alloy 617*
- INCONEL alloy 601
- CABOT alloy No. 600
- Type 310SS*
- HASTELLOY alloy X*
- CABOT alloy No. 800H*

Fig. 4 - Results of sulfidation tests conducted at 760 C (1400 F) for 215 hours.
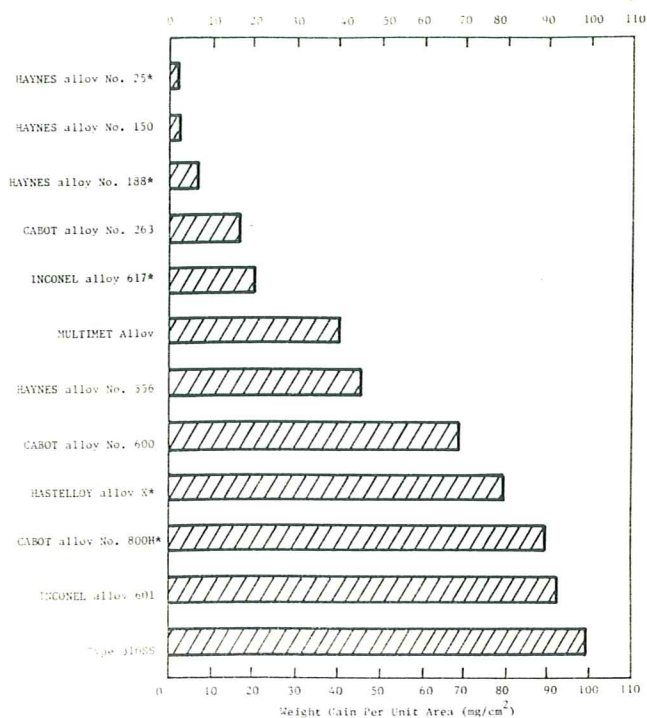
* Average of more than one test

Fig. 5 chart

Weight Gain Per Unit Area (mg/cm²) — scale 0 to 110

- HAYNES alloy No. 25*
- HAYNES alloy No. 150
- HAYNES alloy No. 188*
- CABOT alloy No. 263
- INCONEL alloy 617*
- MULTIMET Alloy
- HAYNES alloy No. 556
- CABOT alloy No. 600
- HASTELLOY alloy X*
- CABOT alloy No. 800H*
- INCONEL alloy 601
- Type 310SS

Fig. 5 - Results of sulfidation tests conducted at 871 C (1600 F) for 215 hours.
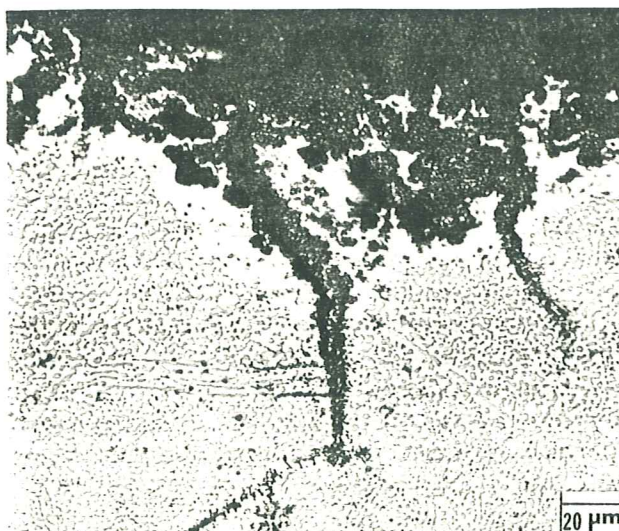
* Average of more than one test

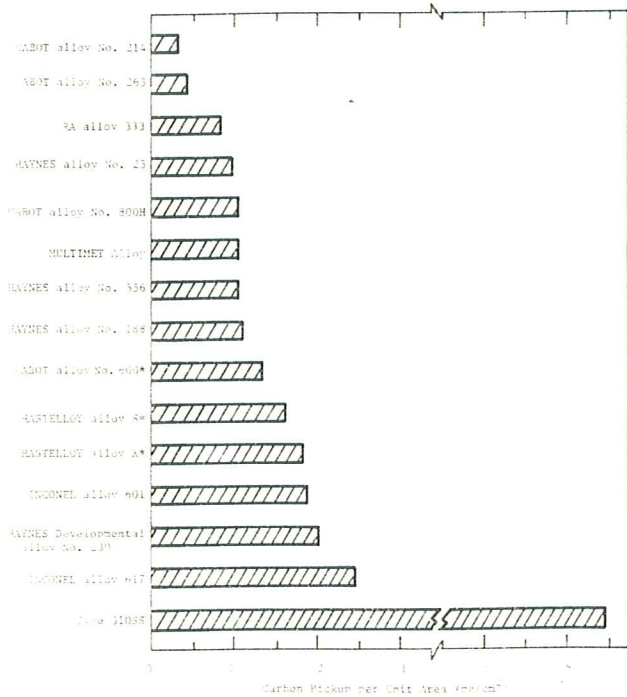Fig. 6 - Extensive carburization of the Type 310SS sample obtained from a diesel engine preheater

Fig. 7 - Results of carburization tests conducted at 927 C (1700 F) for 215 hours.
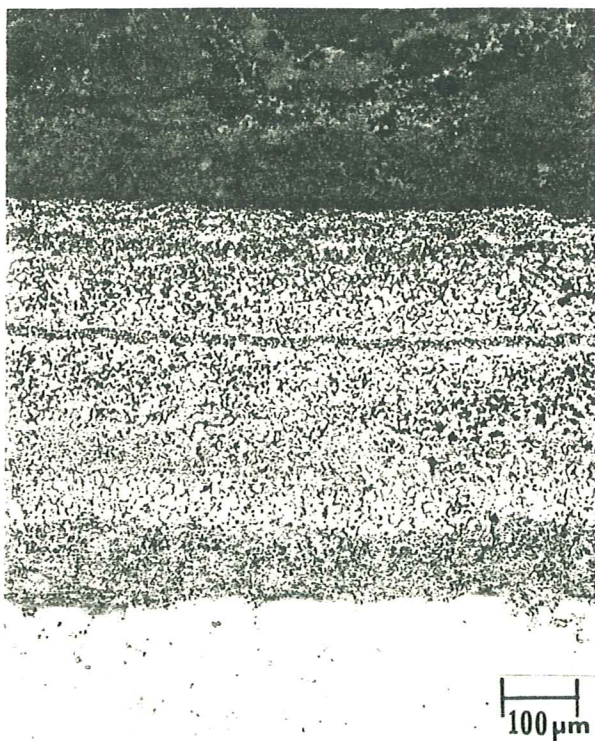
* Average of more than one test

Fig. 8 - Extensive oxidation of the alloy 800 sample exposed to the chlorine-contaiminated flue gas of an aluminum-melting furnace. The deposit was highly enriched in Cl and K.
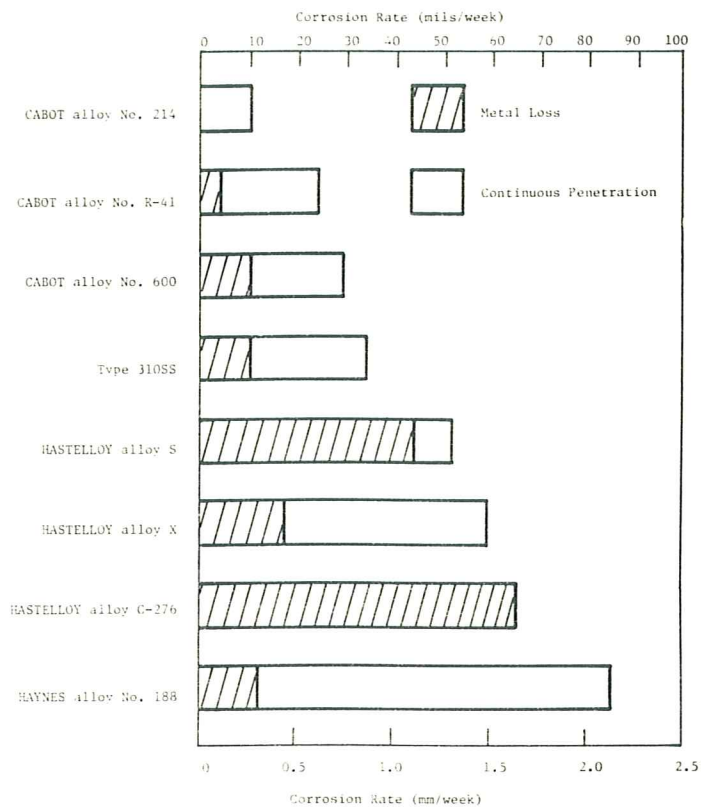

Fig. 9 - Corrosion rates of various alloys obtained from tests conducted at 900 C (1650 F) for 8 hours in argon containing 20% O_2 and 2% Cl_2 (volume percent).
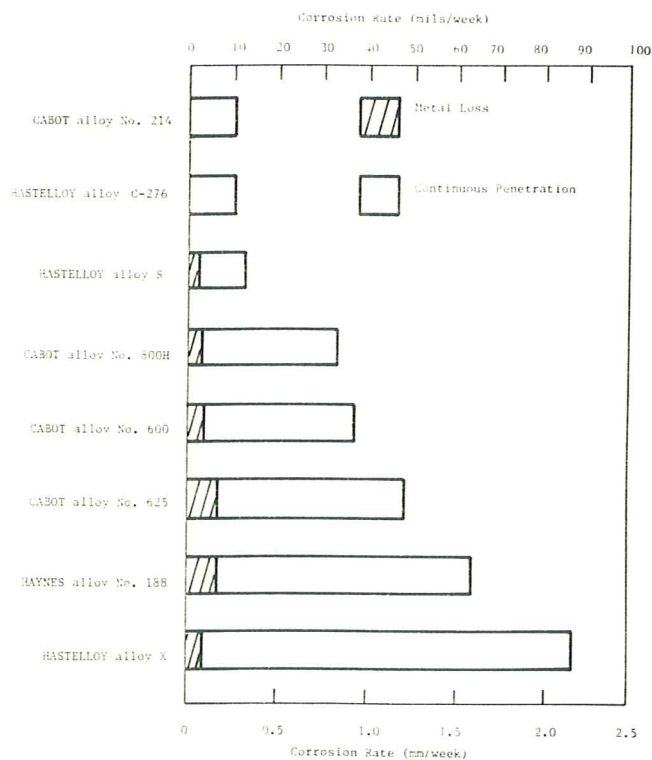

Fig. 10 - Corrosion rates of various alloys obtained from tests conducted at 900 C (1650 F) in argon containing 4% H_2 and 4% HCl (volume percent).