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## HIGH TEMPERATURE CORROSION AND SELECTION OF MATERIALS FOR VARIOUS INDUSTRIAL PROCESSING EQUIPMENT

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### ABSTRACT

This paper discusses a wide variety of high-temperature corrosion problems frequently encountered in various industrial processes including metallurgical processing, chemical and petrochemical processing, glass manufacturing, heat treating and waste incineration. Examples of components' failures are given to illustrate the major modes of corrosion attack. Laboratory and field tests were performed in order to guide materials selection. Results of these tests are discussed.

### INTRODUCTION

Unscheduled plant shutdowns are frequently caused by the failure of the plant's equipment. A large number of these equipment failures are due to corrosion of alloys used

for construction of the equipment. Selection of viable alloys for application in corrosive environments requires a large body of materials information and data. The materials engineer has to understand the nature of the corrosive environment in question, particularly the principal corrosive contaminants that might be present in the environment. It is useful to have information with regard to the past materials experience in the same or similar environment (i.e., the alloys tried and failed in the same or similar environment, and the mode of corrosion attack). It is extremely desirable to have field test data (i.e., performance ranking of a group of candidate alloys) obtained from the corrosive environment prior to making the alloy selection. However, in many cases, it is not feasible to perform field tests due to a variety of rea-

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sons. Under these circumstances, the laboratory data coupling with the understanding of the corrosive environment can be extremely useful to the materials engineer for making an informed materials selection.

Cabot Corporation has been actively generating a corrosion data base in the area of aqueous corrosion for more than ten years. Significant amount of aqueous corrosion information regarding the nature of the corrosive environment in nearly every major industrial process, past materials experience, field and laboratory data has been disseminated to guide materials selection.

In the area of high-temperature alloys, Cabot has been meeting the demands of aerospace industry by providing high strength superalloys for gas turbine engines. HASTELLOY® alloy X, HAYNES® alloy No. 188 and HASTELLOY alloy S are few of those high-strength, superalloys widely used for hot-section components of gas turbine engines. The major characteristics of these alloys are high elevated-temperature strengths and excellent resistance to oxidation and hot corrosion. Due to increased operating temperatures for many industrial processes in the chemical processing and related industries, these high-strength, aerospace alloys are becoming attractive in these non-gas turbine industries. These include metallurgical processing, chemical and petrochemical processing, glass manufacturing, waste incineration, heat treating, waste heat recovery, and advanced energy conversion technologies.

Because of complex, corrosive environments frequently generated by these high-temperature processes, a large number of high-temperature corrosion problems have been encountered. In order to meet the

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demands of these industries for high-temperature corrosion-resistant alloys, Cabot Corporation started actively generating a high-temperature corrosion data base including both field and laboratory data several years ago. This paper describes various high-temperature corrosion problems encountered in these industries for past several years. The paper also present some of the laboratory and field data in order to guide materials selection for various industrial processing equipment. Alloys included in studies are shown in Table 1.

#### HIGH TEMPERATURE CORROSION PROBLEMS

The high-temperature corrosion problems encountered in various industries are summarized in this section. These materials problems are grouped into the following industrial sectors: metallurgical, chemical, petrochemical, waste incineration, glass manufacturing, heat treating, and pulp and paper industry. Highlights of some of these problems in each of the above industrial sectors are summarized in Tables 2 to 8.

In each problem area the information presented in the tables includes the type of process, the components that are suffering corrosion attack, the environment (e.g., the major corrosive contaminants), the flue gas temperature, and the major corrosion mode.

Oxidation can be considered to be the most important mode of high-temperature corrosion. It attacks metals or alloys either by itself or concurrently with other mode(s) of corrosion. Oxygen (or mostly air) is generally used for fuel combustion needed for most high-temperature processes. When little or no corrosive contaminants are present in the combustion products, metals or alloys degrade by oxidation. Burning natural gas, for example, produces combustion products relatively free of corrosive contaminants.



Sulfur is the most common contaminant present in the flue gas or process gas stream generated by high-temperature processes. Sulfur generally comes from fuels, feedstocks, fluxes or chemical additives used for a specific chemical reaction. Natural gas is a relatively clean fuel; its combustion yields little or no sulfur. No. 2 fuel oil contains up to 1% (by wt.) sulfur; while No. 6 fuel oil could contain up to 2 to 3% sulfur. The hydrocarbon feedstocks for chemical or petrochemical processing are also a source of sulfur. Some of the fluxes used for degassing in aluminum melting operation also contain sulfur. The typical chemical species of a flux used for aluminum melting operation are NaCl, NaF, CaF<sub>2</sub>, AlF<sub>3</sub> and Na<sub>2</sub>SO<sub>4</sub> (1). Sulfidation, therefore, is the most common mode of high-temperature corrosion responsible for many materials failures. An example is given to illustrate the severe sulfidation suffered by a stainless steel component in a waste pyrolysis furnace. The pyrolysis furnace was used to treat the wastes from pharmaceutical and chemical operations. The wastes (in a slurry form), which contained large amounts of sulfate salts (~ 4% by weight sulfur), were injected into the pyrolysis furnace which was heated to approximately 1500°F (816°C). The pyrolysis caused the liquid wastes to turn into ash which was then removed and discharged by a screw conveyor. The screw conveyor made of type 316SS failed in a week. The use of a STELLITE® alloy No. 6 weld overlay has been found to perform quite satisfactorily. Figure 1 (a) illustrates the severe sulfidation attack upon Type 316SS on the area where the 316SS substrate was not covered by an alloy 6 weld overlay. Figure 1 (b) shows the adjacent area with the alloy 6 weld overlay which was only slightly sulfidized.

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Chlorine (in form of Cl<sub>2</sub>, HCl, NaCl or KCl) is also a very important corrosive contaminant in high temperature corrosion for many industrial processes. Production of aluminum, silicon, chlorinated organic compounds, TiO<sub>2</sub>, titanium sponge and barium and strontium ferrite magnets all produces process gas streams containing chlorine. The flue gas stream generated by aluminum remelting operation also contains chlorine. The fluxes used for degassing in aluminum melting operations are a source for chlorine (1). Chlorine gas is generally used for degassing in aluminum scrap melting. The high temperature corrosion attack upon metals or alloys by a gas stream containing chlorine is extremely severe. Recuperators made of stainless steels (e.g., Type 316SS) have been found to fail after service for only several months in aluminum remelting furnaces. The high-temperature corrosion involving oxidation/chlorination, oxidation/chlorination/sulfidation or vapors and/or condensates of salts by aluminum melting furnace flue gas streams was discussed by Rothman et al. (2) and Russell et. al (3). Chlorine also plays a significant role in high temperature corrosion of metals or alloys involving incineration of municipal wastes (4).

Materials problems due to carburization in some of the petrochemical processes such as ethylene cracking are well known (5). Carburization problems are also common to heat treating components or equipment. Metal dusting, which is a form of carburization, has also been observed to take place on some of the furnace fixtures, such as brick anchors and fan housing assemblies, in carburizing furnaces. Metal dusting, which tends to occur in regions where carbonaceous gas atmosphere becomes stagnant normally results in rapid metal wastage. Figure 2 shows a sample of MULTIMET® alloy suffering severe metal dusting problem in a

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carburizing furnace environment. The sample was obtained from a furnace fan housing box. The metal dusting was initiated from the metal surface which was in contact with the furnace refractory lining. The metal temperature was believed to be between 1000°F and 1600°F (540°C and 871°C). Metal dusting problems in petrochemical processing were discussed elsewhere (5).

In some of the chemical processes involving regeneration of carbon materials, carburization is also the principal mode of corrosion attack for some metals.

The high temperature corrosion involving molten salts is responsible for many materials failures in high temperature industrial processes. A flue gas stream frequently contains Na and K (fuels and feedstocks are a source of these elements) which can react with sulfur and/or chlorine to form salts. The salts can then participate in the high-temperature corrosion by fluxing the protective oxide scale formed on the metal surface. This generally results in accelerated corrosion attack.

The recovery boiler in pulp and paper industry is a good example. The recovery boiler is an ordinary steam boiler fired with the spent liquor from the digester. In the boiler, the organic residue is burned and the inorganic is reduced back to sodium sulfide and sodium carbonate. The corrosion of superheater tubes by the flue gas, and of waterwall tubes and smelt spout openings by the liquid (smelt) was discussed elsewhere (6,7). Major constituents of the smelt are  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_4$  with  $\text{NaOH}$  and  $\text{NaCl}$  as minor constituents. The molten smelt temperature is typically 1470°F (800°C).

Another example of high temperature corrosion involving molten salt attack is in heat treating industry where steel parts are annealed, normalized or hardened in molten salts. A typical heat treating salt for this application is a (Na,K,Ba) chloride salt. Type 309SS is widely used for the pots for holding this

molten salt at approximately 1550°F (840°C). Typical service life for the Type 309SS pot is several months.

A number of materials failures involving catastrophic oxidation have been observed. One involved a Type 316SS recuperator which was used to preheat the incoming combustion air to 1000°F (540°C) in a zinc-melting facility. The Type 316SS recuperator tubes with a tube wall thickness of .065-inch which were exposed to a 1800°F (982°C) flue gas on the OD of the tube, failed by perforation (or metal thinning) after two to three months of service. Zinc oxides were found to deposit on the tube surface. Evaluation of the failed sample showed no evidence of molten zinc attack.

The principal mode of attack was oxidation. However, the oxidation is believed to be accelerated by zinc vapor and/or zinc oxides. Detailed discussion of this corrosion problem was presented in a paper by Rothman et al. (2).

Another case of catastrophic oxidation involved alloy 601 (a nickel-base alloy). The strand annealing tubes made of alloy 601 were used for annealing cold drawn steel wires in air. The tube temperature was probably around 1900 - 2000°F (1040°-1090°C). The annealing was done following cold drawing of steel wires. A drawing compound was used during drawing. The tubes suffered severe high temperature corrosion attack in the front section of the tubes where steel wires entered into the annealing tubes following cold drawing. The general appearance of the failed tubes and the cross section of the tube illustrating the catastrophic oxidation are shown in Fig. 3. Examination of the corroded tube surface revealed molten phases which were enriched in Ca, as illustrated in Fig. 4. Apparently, oxidation was accelerated by the formation of molten phases which fluxed the protective oxide scale from the metal surface.

Formation of low-melting eutectic phases in the metal can also cause catastrophic oxidation. An example is



illustrated by the catastrophic oxidation of Type 304SS in the combustion environment generated by the manufacturing of phosphorus. An internal component made of Type 304SS failed catastrophically after service for two to three months in a combustion environment containing phosphorus (temperature was about 800°C), as illustrated in Fig. 5. The mode of attack is believed to be the formation of low-melting point eutectics of metal-phosphorus phases followed by rapid oxidation of these eutectic phases. Figure 6 illustrates oxidation of alloy 625 following the formation of Ni-P eutectics.

Figure 7 illustrates the accelerated oxidation attack upon alloy 253MA by a flue gas stream generated by calcining phosphate rocks. The part shown in the figure failed after service for approximately 150 days. The flue gas temperature could be 1800°F (982°C) or lower.

Some of the high-temperature processes can generate strong nitriding environments. Production of nitric acid and melamine, for example, involves processes that could produce nitriding environments. Heat treating fixtures and equipment of nitriding or carbonitriding furnaces are also exposed to strong nitriding environments. The materials resistance to nitriding is a prime consideration for alloys to be used in these environments.

#### SELECTION OF MATERIALS FOR APPLICATIONS IN CORROSIVE ENVIRONMENTS

The high temperature environments generated by industrial processes could vary from relatively simple environments where oxidation alone is the only mode of corrosion (e.g., environments generated by burning clean fuel such as natural gas) to environments contaminated with various corrosive species. The ideal approach to the selection of alloys for application in corrosive environments is to perform a field test in an operating plant in order to generate alloy performance ranking for a variety of

candidate alloys. This approach is being actively pursued at Cabot Corporation, and has been proven quite successful to guide materials selection. However, performing field tests, in many cases, is not feasible. The operator of the plant frequently needs a materials recommendation immediately after the equipment failure in order to minimize the financial loss due to unscheduled plant shutdowns. Under these conditions, the operator does not have time to perform a field test, which could take at least several months. In many other cases, field testing cannot be performed due to the lack of access to the operating system. Under these circumstances, an analysis of the failed component can generate valuable information with regard to the primary mode of corrosion attack. However, this information by itself is usually not adequate to guide materials selection. Additional information or data that are needed are laboratory data generated from the environment that is relevant to the environment in question. Therefore, laboratory testing is an integral part of the materials selection process.

From the discussion in the previous section it is clear that the major corrosion modes responsible for many materials failures include typically oxidation, oxidation/sulfidation, oxidation/chlorination, oxidation/chlorination/sulfidation, oxidation/carburization, nitriding, catastrophic oxidation due to metallic vapor species, molten salt attack and others. In order to generate the high temperature corrosion data base to guide materials selection for various industrial processing equipment, following evaluation and test programs have been underway at Cabot Corporation:

1. Field evaluation of alloy performance
  - Failure analysis of failed components
  - Field rack test and coupon exposure
  - Component trials



## 2. Laboratory tests

- Oxidation tests in air and combustion gas
- Hot corrosion tests
- Sulfidation tests
- Carburization tests
- Oxidation/chlorination
- Oxidation/chlorination/sulfidation
- Accelerated oxidation by vapors of salts, glass and metals
- Molten salts, molten glass and molten metals testing
- Nitriding tests

The above test programs are currently in progress. However, a significant amount of data have been generated so far. These test results are briefly described in this section in order to provide a general guidance to the selection of materials for application in various corrosive environments.

### Oxidation-Resistant Alloys:

Relative performance ranking for a wide variety of commercial alloys based on the laboratory tests performed in flowing air at 1800°F and 2000°F (982 and 1093°C) is presented in Figures 8 and 9. The tests were performed at the temperatures for 1008 hrs, cycled to room temperature once every 168 hours (a week). The results are presented in terms of linearly extrapolated depth of attack per year (mpy). The alloy with the best oxidation resistance was found to be alloy 214 followed by alloys S, 230, and 188.

Alloys containing titanium such as alloys R-41 and 263 exhibited the highest rate of oxidation among the alloys tested. Many alloys exhibited less than 30 mpy (0.75 mm/year) of oxidation rates at both temperatures.

These laboratory oxidation data are in good agreement with those obtained from the field tests. Figure 10 summarizes the results of a field test performed in a combustion atmosphere generated by burning natural gas. The samples were exposed for 4 months at approximately 1850°F

(1010°C). Alloy 214 exhibiting less than 5 mpy of oxidation attack was found to be the best performer, followed by alloy 601, alloy 230 and a number of other alloys with less than 20 mpy of oxidation rates.

### Sulfidation-Resistant Alloys:

Figures 11, 12 and 13 summarize the results of sulfidation tests performed at 1400, 1600 and 1800°F (760, 871 and 982°C) for 215 hours in a reducing, environment with the inlet test gas composition being 5% H<sub>2</sub>, 5% CO, 1% CO<sub>2</sub>, 0.15% H<sub>2</sub>S, 0.1% H<sub>2</sub>O and balance Ar (by volume percent). The detailed test procedures were described elsewhere (8). The calculated oxygen potentials P<sub>O<sub>2</sub></sub> in the test environment were 5x10<sup>-22</sup> atm at 1400°F (760°C), 3x10<sup>-19</sup> atm at 1600°F (871°C) and 3x10<sup>-17</sup> atm at 1800°F (982°C); the calculated sulfur potential P<sub>S<sub>2</sub></sub>

in the test environment were 1x10<sup>-7</sup> atm at 1400°F (760°C), 0.9x10<sup>-6</sup> atm at 1600°F (871°C) and 4x10<sup>-6</sup> atm at 1800°F (982°C). The environments were such that the formation of molten nickel sulfides was thermodynamically feasible.

Cobalt-base alloys as a group were the best performers, followed by iron-base alloys with nickel-base alloys (as a group) being the worst. Although nickel-base alloys are most susceptible to sulfidation attack, several nickel-base alloys exhibited a sulfidation resistance approaching that of cobalt-base alloys in these short-term tests. They are alloy R-41 and WASPALOY alloy; both contain approximately 3% Ti. The excellent resistance displayed by these alloys is believed to be attributed to the formation of a protective (Cr,Ti) oxide scale. Not revealed by the bar-chart figures, these alloys have shown localized sulfidation attack after these short-term exposure tests. For applications in severe sulfidizing environments, it is prudent to avoid alloys containing high levels of nickel.

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These laboratory test results have been found to be in general agreement with the materials experience obtained from the field. Numerous cases of materials failures in operating plants have shown the following general trend: alloy 600 failed in a relatively short time; alloy 800/800H lasted slightly longer; 310SS, which showed better performance than 800/800H, was still not adequate in performance. Under these conditions, HAYNES alloy No. 556 (an Fe-Ni-Cr-Co alloy) will be a good alternate alloy. If the environment is much more severe, cobalt-base alloys such as alloys 188, 25 and 6B should then be considered.

The results of a field test performed in an incinerator burning municipal wastes are summarized in Fig 14. The principal mode of corrosion was found to be oxidation/sulfidation. The alloy ranking is similar to that obtained from laboratory tests (Fig. 11).

#### Carburization-Resistant Alloys:

Carburization resistance of various alloys was investigated by performing laboratory tests at 1700 and 1800°F (927 and 982°C) in a highly carburizing environment with the inlet test gas mixture being 5% H<sub>2</sub>, 5% CO, 5% CH<sub>4</sub> and balance Ar (by volume percent). This test gas mixture was selected in order 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 (calculated  $P_{O_2}$  were  $3 \times 10^{-22}$  atm at 927°C, and  $9 \times 10^{-22}$  atm at 982°C) and unit carbon activity. The detailed test procedures were described elsewhere (9).

The relative performance ranking for alloys tested is summarized in Figs. 15 and 16. Alloy 214 was found to be the most resistant to carburization among the alloys tested.

Figure 17 (a) shows severe oxidation/carburization of a Type

310SS sample obtained from an internal component of a carbon regeneration furnace. The part made of Type 310SS failed in 2 to 3 months of service (the temperature was approximate 1650°F). When the part was made of alloy 214, little environmental attack was observed after three months of similar service. The cross section of the alloy 214 sample is shown in Fig. 17 (b), illustrating slight oxidation with no evidence of carburization.

#### Chlorination-Resistant Alloys:

Materials resistance to chlorination attack was investigated by performing laboratory tests in an oxidizing environment with the inlet gas composition being 20% O<sub>2</sub>, 0.25% Cl<sub>2</sub> and balance Ar (by volume percent). The tests were performed at 1650°F (900°C) for 400 hours. The detailed test procedures were described elsewhere (10). The relative performance ranking for various alloys investigated is presented in Fig. 18.

The alloys containing highest levels of Mo or W (e.g., 15% Mo in alloy S and 14% W in alloy 188) suffered the worst attack, presumably due to the formation of highly volatile Mo or W oxy-chlorides. The best performer was alloy 214 followed by alloy 556 and Type 310SS. Type 310SS suffered significant amounts of metal wastage (more than three times that of alloy 214).

#### Materials Performance in other Aggressive Environments:

In a combustion environment containing phosphorus, such as the one generated by production of phosphorus, oxidation of metals or alloys was accelerated by the formation of low melting eutectics of metal-phosphorus phases. Table 9 illustrates the test results generated from a field test which involved the exposure of a test rack in a combustion atmosphere generated by the production of phosphorus. Alloy X appears to be the best performer among the alloys tested. The alloy performance ranking shown in the table failed to reveal



any compositional correlation. Better understanding on this type of corrosion may be achieved by future laboratory tests.

Materials resistance to nitriding environments was investigated by performing nitriding tests at 1200°F (649°C) for 168 hours (one week) in an environment with NH<sub>3</sub> as an inlet gas. The results in terms of both the depth of the nitrided layer and the mass of nitrogen pickup per unit area of specimen are presented in Table 10. Iron-base alloys performed poorly in this environment. Ni-base alloys are generally more resistant to nitriding. Alloy 188 (a Co-base alloy) was found to perform as well as alloy 600. Both alloys were among the best performers. More alloys as well as higher temperatures will be tested in the future.

Resistance to molten chloride salt attack was investigated by performing a field test in a heat treating salt (Na,K,Ba chloride salt) at 1550°F for one month. The results are summarized in Fig. 19. The environment was very corrosive. Alloy 600, for example, suffered a corrosion rate of approximately 100 mils per month. All simple alloys tested, such as 304SS, 310SS, 600 and 601, suffered high rates of attack. Aluminum or titanium (as an alloying element) appears to be ineffective in improving the alloy's resistance to molten chloride salt. It is illustrated by the performance of alloy 214 in comparison with that of alloy 600. Those complex solid-solution strengthened alloys (Fe,Ni or Co-base) containing W and/or Mo, such as alloys 188, X, S and 556, and MULTIMET alloy, were found to perform well. Alloy 188 was found to be the best performer among the alloys tested.

#### SUMMARY

A wide variety of high-temperature corrosion problems frequently encountered in various industrial processes were reviewed. These industrial processes included metallurgical, chemical, petrochemical, waste incineration, glass manufacturing, heat treating and pulp and paper industry. Highlights of some of these problems

in each of the above industrial sectors were summarized. The major corrosion modes responsible for many materials failures were found to include oxidation, oxidation/sulfidation, oxidation/chlorination, oxidation/chlorination/sulfidation, oxidation/carburization, nitriding, catastrophic oxidation due to metallic vapor species, and molten salt attack.

Laboratory data for a variety of commercial alloys to resist oxidation, sulfidation, carburization, chlorination and nitriding were presented. Field test data generated from various operating plants were also presented. The combustion environments in which field tests were performed were those associated with (1) burning of natural gas (oxidation), (2) incineration of municipal wastes (oxidation/sulfidation), (3) regeneration of carbon materials (oxidation/carburization), (4) manufacturing of phosphorus, and (5) a heat treating salt (molten Na,K, Ba chloride salt). Combination of both field and laboratory data provides a basis to guide materials selection for various industrial processing equipment. More laboratory and field tests are required in order to generate sufficient data base needed for making an informed materials selection.

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Table 1  
Nominal Chemical Compositions of Alloys Included in Studies

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+	-
Alloy 800H	.08	Bal	33	-	21	-	-	1.0+	1.5+	Al=.38, Ti=.38, Cu=75+
MULTIMET <sup>®</sup> alloy	.10	Bal	20	20	21	3	2.5	1.0+	1.5+	Cb+Ta=1, Cu=.5+, N=.15
HAYNES <sup>®</sup> alloy No. 556	.10	Bal	20	18	22	3	2.5	.4	1.0	Al=.2, Ta=0.8, La=.02, N=.2, Zr=.02
Alloy 600	.08+	8	Bal	-	16	-	-	.5+	1.0+	Al=.35+, Ti=.3+, Cu=.5+
CABOT <sup>®</sup> alloy No. 214	.04	4	Bal	-	16	-	-	-	-	Al=4.5, Y=.01
INCONEL <sup>®</sup> 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 <sup>®</sup> 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+	-
Alloy 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 <sup>®</sup> 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
WASPALLOY 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 <sup>®</sup> alloy No. 6B	1.2	3+	3+	Bal	30	1.5+	4.5	2.0+	2.0+	-

+ Maximum

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TABLE 2  
HIGH-TEMPERATURE CORROSION PROBLEMS IN METALLURGICAL PROCESSING

Process/Production	Components	Environment/Temperature	Corrosion Modes
Aluminum remelting	Recuperators	Flue gas contaminated with, Na, K, halogen (Cl <sub>2</sub> , F <sub>2</sub> ), sulfur up to 1800°F (980°C)	Oxidation/chlorination/sulfidation
Zinc melting	Recuperators	Flue gas contaminated with zinc vapor; up to 1800°F (980°C)	Oxidation accelerated by zinc vapor
Lead remelting	Recuperators	Flue gas contaminated with Cl <sub>2</sub> ; 1500°F (815°C)	Oxidation/chlorination
Copper (scrap) remelting	Recuperators	Flue gas contaminated with Cl <sub>2</sub> ; 1800°F (980°C)	Oxidation/chlorination
Refractory metals production	Reactor vessels	Molten Salts; up to 1800°F (980°C)	Molten salt attack
Aluminum production	Reactor vessels	HCl-bearing gas; up to 1300°F (700°C)	Oxidation/chlorination
Silicon production	Reactor vessels	Halogen-bearing gas; >1000°F (540°C)	Oxidation/chlorination
Steel reheating furnace	Recuperators	Flue gas contaminated with Na, V, S, Pb, etc., metal temps up to 1600°F (870°C)	Oxidation/fuel ash corrosion
Steel forging furnace	Recuperators	Combustion products; metal temps up to 1600°F (870°C)	Oxidation



TABLE 3

## HIGH-TEMPERATURE CORROSION PROBLEMS IN CHEMICAL PROCESSING

<u>PROCESS/PRODUCTION</u>	<u>COMPONENTS</u>	<u>ENVIRONMENT/TEMPERATURE</u>	<u>CORROSION MODES</u>
Chlorinated organic compounds	Pyrolysis furnace tubes	HCl-bearing gas; 1300-1500°F (700-815°C)	Oxidation/chlorination
Carbon regeneration in production of corn starch, herbicides, insecticides	Kiln internals, fluidized bed grid	Flue gas with carbonaceous gas; up to 1800°F (980°C)	Oxidation/carburization/sulfidation
Barium/Strontium ferrite magnets	Calciners	Flue gas with Cl <sub>2</sub> ; up to 2200°F (1200°C)	Oxidation/chlorination
Nitric acid	Catalyst grid support	Flue gas with carbonaceous gas; 1700°F (930°C)	Oxidation/carburization/nitriding
TiO <sub>2</sub> Production	Expansion joints	Cl <sub>2</sub> -bearing gas; up to 1900°F (1040°C)	Oxidation/chlorination
Ti production	Reactor vessels	Cl <sub>2</sub> -bearing gas; up to 1650°F (900°C)	Oxidation/chlorination
Mineral calcining processes	Calciners	Flue gas with possible sulfur contaminations; 1600°F-2200°F (870-1200°C)	Oxidation or oxidation/sulfidation
Nuclear fuel processing	Reactor vessels	HF-and F <sub>2</sub> -bearing gas; up to 1470°F (800°C)	Oxidation/fluorination
Phosphorus production	Reactor internals, air injection	Flue gas contaminated with P <sub>2</sub> O <sub>5</sub> ; up to 1500°F (816°C)	Oxidation, low melting metal-phosphorus eutectics

TABLE 4

## HIGH-TEMPERATURE CORROSION PROBLEMS IN PETROCHEMICAL PROCESSING

<u>PROCESS/PRODUCTION</u>	<u>COMPONENTS</u>	<u>ENVIRONMENT/TEMPERATURE</u>	<u>CORROSION MODE</u>
Ethylene cracking	Pyrolysis tubes, pigtails	H <sub>2</sub> , CO, CH <sub>4</sub> , H <sub>2</sub> O and other carbonaceous gases; up to 1800°F (980°C)	Oxidation/carburization
Steam reforming	Pyrolysis tubes, pigtails	H <sub>2</sub> , CO, CH <sub>4</sub> , H <sub>2</sub> O and others; up to 1800°F (980°C)	Oxidation/carburization
Refinery plant	Flare tips	Combustion products with SO <sub>2</sub> , SO <sub>3</sub> , or HCl, up to 2000°F (1090°C)	Oxidation/sulfidation, or chlorination/acid dew point corrosion
Petroleum coke calcining	Recuperators	Flue gas contaminated with S and V; 1500°F (816°C)	Oxidation/sulfidation

TABLE 5

## HIGH-TEMPERATURE CORROSION PROBLEMS IN WASTE INCINERATION

<u>WASTES INCINERATED</u>	<u>COMPONENTS</u>	<u>ENVIRONMENT/TEMPERATURE</u>	<u>CORROSION MODE</u>
Municipal Wastes	Superheaters	Flue gas with molten sulfate salts; Metal temp up to 900°F (480°C)	Oxidation/sulfidation/chlorination/molten salts
Municipal Wastes	Internal components	Flue gas with sulfur and others; up to 1700°F (930°C)	Oxidation/sulfidation
Pharmaceutical Wastes	Screw conveyors, plows, rakes	Flue gas with sulfur and salts; up to 1500°F (815°C)	Oxidation/sulfidation
Packaging materials	Bypass damper	Flue gas with S, Zn, Ca, etc., up to 2000°F (1090°C)	Oxidation/sulfidation
Paint sludges	Air injection pipe, internal components	Flue gas with Ti, Zn, Ca, etc., up to 2000°F (1090°C)	Oxidation
Chemical wastes from Si production	Recuperator	Cl <sub>2</sub> -bearing gas stream; up to 1800°F	Oxidation/chlorination

TABLE 6

## HIGH-TEMPERATURE CORROSION PROBLEMS IN GLASS MANUFACTURING

<u>PROCESS/PRODUCTION</u>	<u>COMPONENTS</u>	<u>ENVIRONMENT/TEMPERATURE</u>	<u>CORROSION MODE</u>
Fiberglass	Recuperators	Flue gas contaminated with S, Na, chlorides, sulfates, etc.; up to 2000°F (1090°C)	Oxidation/sulfidation/molten salts
Fiberglass	Spinners	Molten glass; up to 1800°F (980°C)	Molten glass attack/erosion
Fiberglass	Melting pots	Molten glass; up to 1700°F (930°C)	Molten glass attack



TABLE 7

## HIGH-TEMPERATURE CORROSION PROBLEMS IN HEAT TREATING

PROCESS/PRODUCTION	COMPONENTS	ENVIRONMENT/TEMPERATURE	CORROSION MODE
Gas carburizing	Furnace components	Carburizing atmospheres; 1600°-2000°F (870°-1090°C)	Carburization
Gas carburizing	Furnace brick anchors, fan housing assemblies	Carburizing atmospheres; metal temp 1000-1500°F (540°-820°C)	Metal dusting
Heat treating carbon steel parts	Hangers	Oxidizing atmospheres at 1600°F (870°C) and molten nitrate salts at 500°F (260°C); thermal cycling	Oxidation/thermal fatigue
Heat treating	Radiant tubes	Oxidizing atmospheres (O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub> , etc.); 1500-2000°F (820-1090°C)	Oxidation
Pottery kilns	Kiln components	Oxidizing atmosphere (O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub> , etc.); up to 2100°F (1150°C)	Oxidation
Strand annealing	Annealing furnace tubes	Oxidizing atmospheres contaminated with Ca and others from drawing compounds; 1800-2000°F (980-1090°C)	Oxidation accelerated by Ca and others
Heat treating	Molten Salt pots	Molten (Na, K, Ba) chloride salts; 1550°F (840°C)	Molten salt attack

TABLE 8

## HIGH-TEMPERATURE CORROSION PROBLEMS IN PULP AND PAPER INDUSTRY

PROCESS/PRODUCTION	COMPONENTS	ENVIRONMENT/TEMPERATURE	CORROSION MODE
Recovery boilers	Smelt spouts; "six packs"	Molten smelts (Na <sub>2</sub> S, Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> CO <sub>3</sub> and NaCl); 1500-1700°F (820-927°C)	Molten salt attack
Recovery boilers	Superheaters, internal components	Flue gas contaminated with salts; up to 1500°F (820°C)	Oxidation/molten salts

TABLE 9

Metal loss and Maximum Depth of Pitting Attack Values For Samples Exposed in a Combustion Environment\* Containing Phosphorus, at about 800°C for 30 Days

ALLOY	Metal Loss, mil (μm)	Max Depth of Pitting Attack,	
		mil (μm)	(μm)
	-1.90** (-48)	3.0	(76)
556	2.18 (55)	6.0	(152)
263	2.26 (57)	6.0	(152)
214	-0.54** (-14)	8.0	(203)
R-41	2.19 (56)	8.0	(203)
S	1.4	9.0	(229)
188	2.20 (56)	9.0	(229)
68	0.67 (17)	10.0	(254)
800H	2.21 (56)	11.0	(279)
230	1.35 (34)	15.0	(381)
304	3.00 (76)	15.0	(381)

\*The environment was generated during calcining sodium triphosphate in phosphorus production.

\*\*The negative metal loss numbers are believed to be caused by the incomplete removal of the tenacious chemical deposits on the samples.

TABLE 10

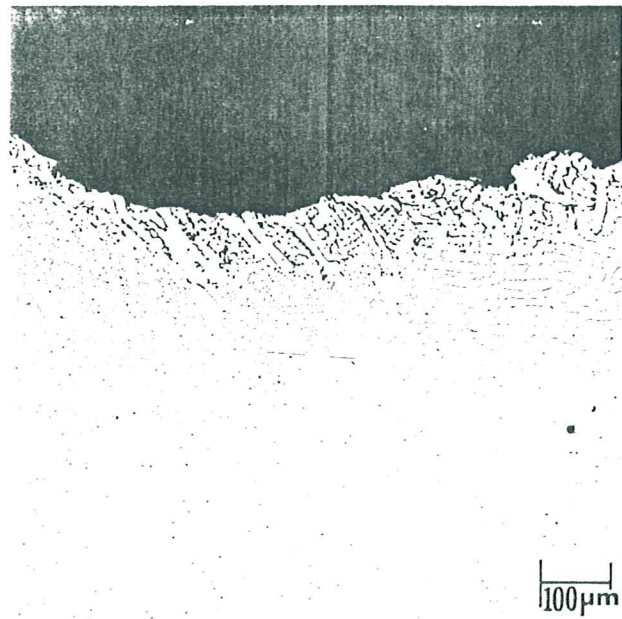
Nitriding Resistance\* of Various Alloys

Alloy	Depth of Nitrided Layer, Mile (μm)	Mass of Nitrogen Pickup per Unit Area, mg/cm <sup>2</sup>
600	1.3 (33)	0.8
188	0.6 (15)	1.2
S	1.1 (30)	1.3
617	1.0 (25)	1.3
214	1.5 (38)	1.5
X	1.5 (38)	1.7
800H	4.1 (102)	4.3
556	3.5 (89)	4.9
310	6.0 (152)	7.4
304	8.4 (213)	9.8

\*Tested in NH<sub>3</sub> at 1200°F (649°C) for 168 hours (one week).

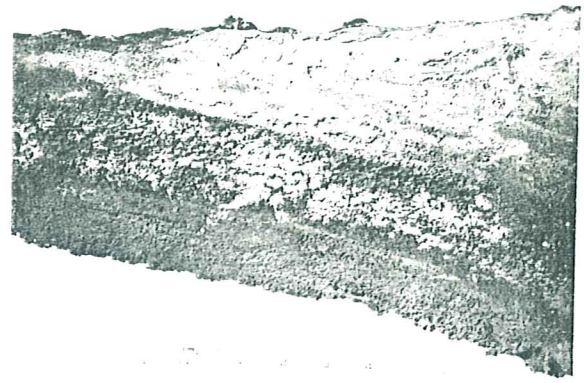


(a)

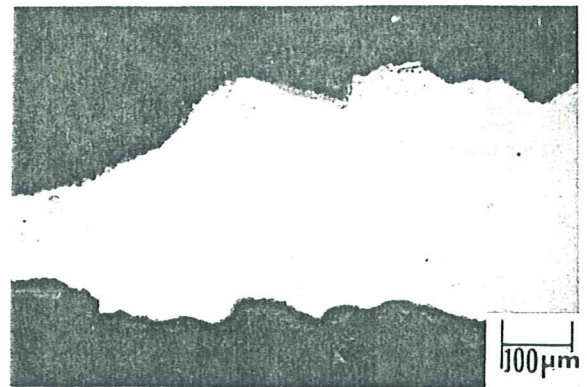


(b)

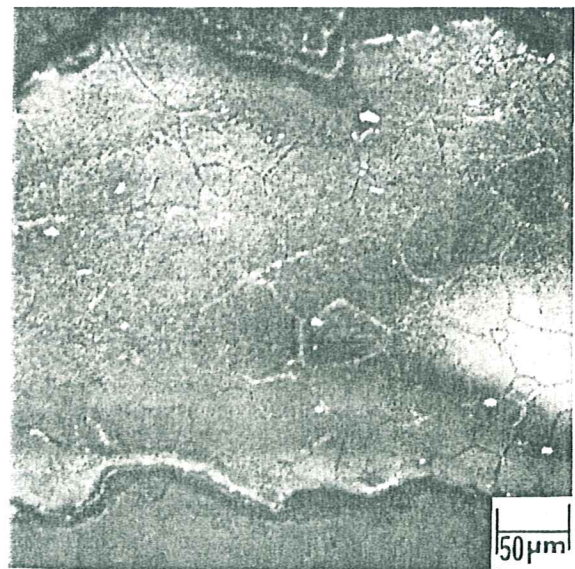
Fig. 1 - Optical photomicrographs showing sulfidation attack upon (a) type 316SS (the area which was not covered by the alloy 6 weld overlay) and (b) the alloy 6 weld overlay, in an environment generated by pyrolysis of pharmaceutical and chemical wastes.



(a)



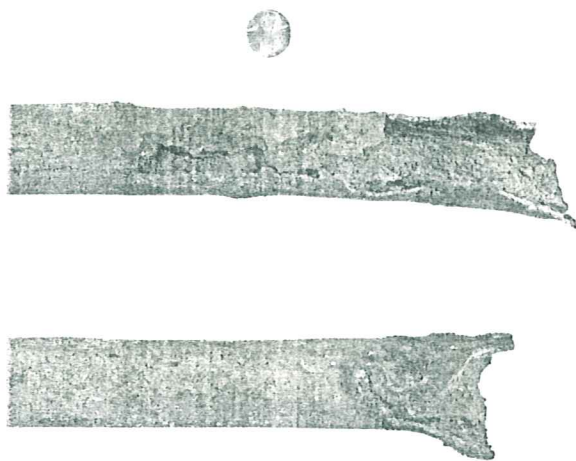
(b)



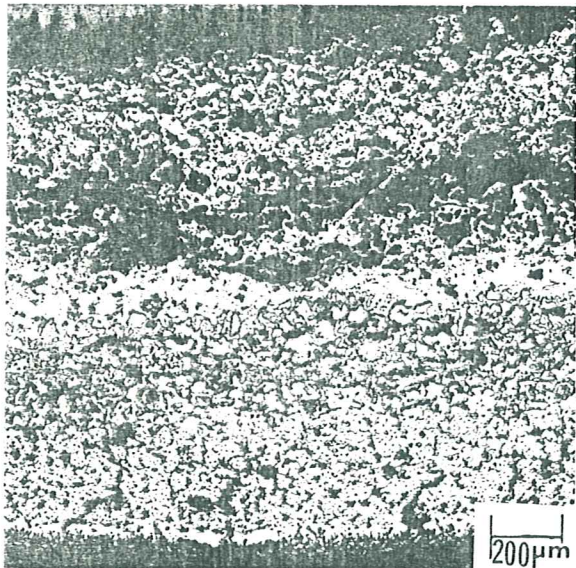
(c)

Fig. 2 - Optical photomicrographs showing metal dusting attack upon MULTIMET ALLOY (a carburization furnace fan box): (a) overall view of the sample, (b) cross-section of the sample showing pitting attack, and (c) severe carburization underneath the pitted area.



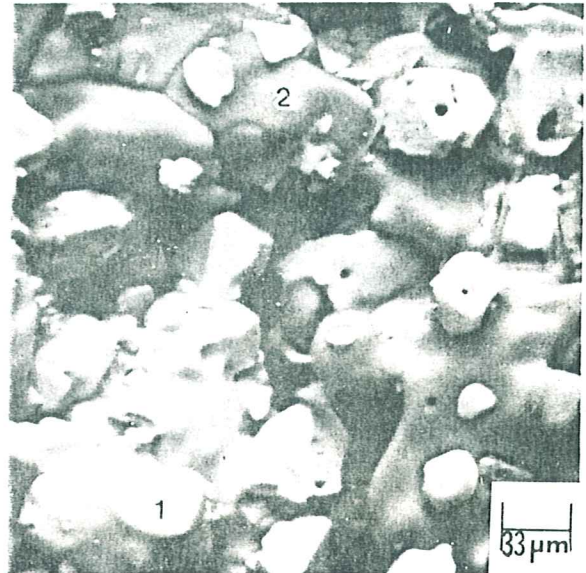


(a)



(b)

Fig. 3 - Optical photomicrographs showing the failure of INCONEL alloy 601 strand annealing tubes presumably due to accelerated oxidation attack by impurities of drawing compounds remained on the steel wires being annealed: (a) overall view of the failed tube samples, and (b) cross-section of the tube sample.



Area	Semi-Quantitative Analysis*				
	Ca	Ni	Fe	Cr	Si
1	1.55	91.85	5.13	0.60	0.87
2	97.43	1.77	0.24	0.14	0.09

\*Relative intensity

Fig. 4 - SEM photomicrograph showing the corrosion products formed on the ID of the alloy 601 tube (Fig. 3a) as well as the results of a SEM/EDX analysis of these corrosion products.

304 SS burner mixing plate

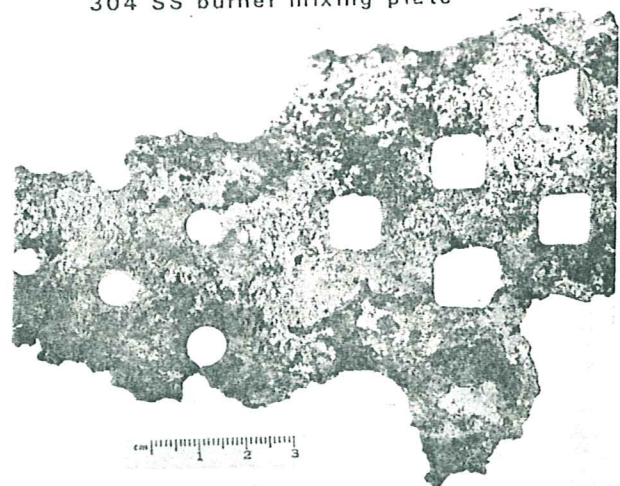


Fig. 5 - Optical photomicrograph showing severe high temperature corrosion attack upon a type 304SS component in an environment generated by calcining sodium triphosphate in phosphorus production.

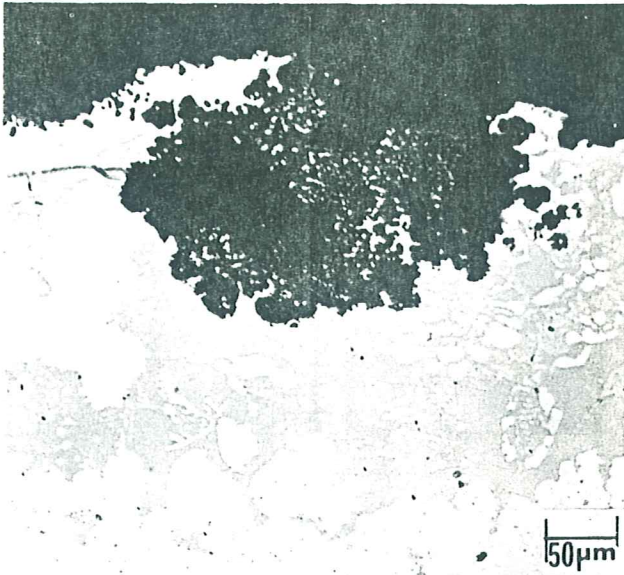


Fig. 6 - Optical photomicrograph showing oxidation of alloy 625 following the formation of low melting Ni-P eutectic phases in an environment generated by calcining sodium triphosphate in phosphorus production.

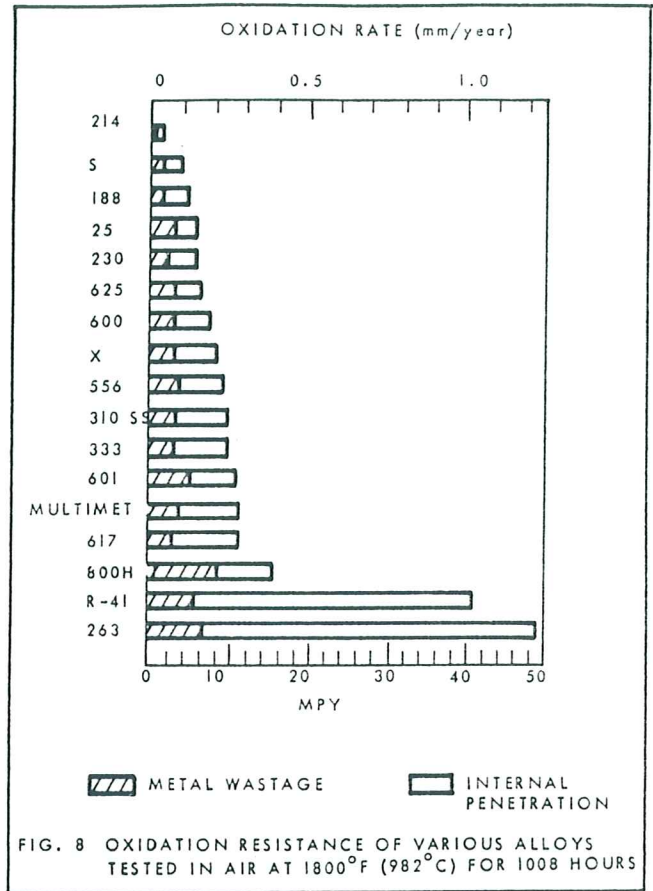


FIG. 8 OXIDATION RESISTANCE OF VARIOUS ALLOYS TESTED IN AIR AT 1800°F (982°C) FOR 1008 HOURS

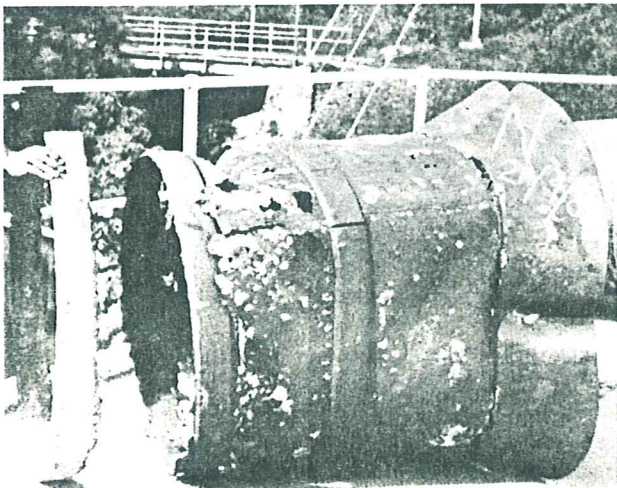


Fig. 7 - Failure of a component made of alloy 253MA in an environment generated by calcining phosphate rocks.

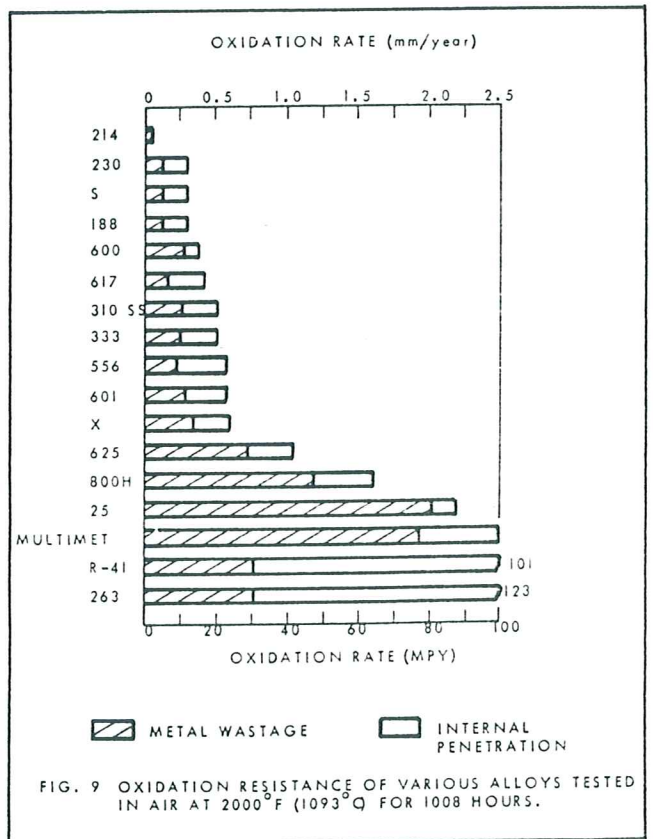
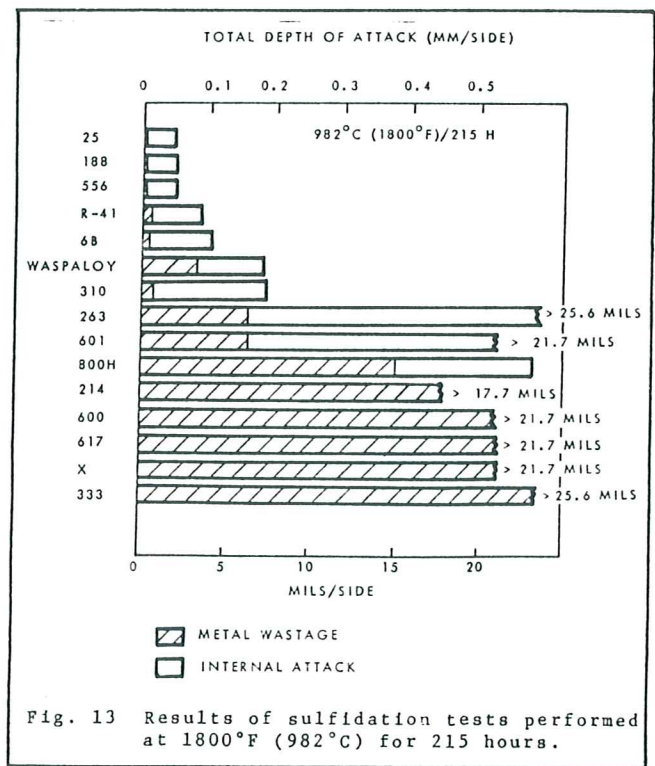
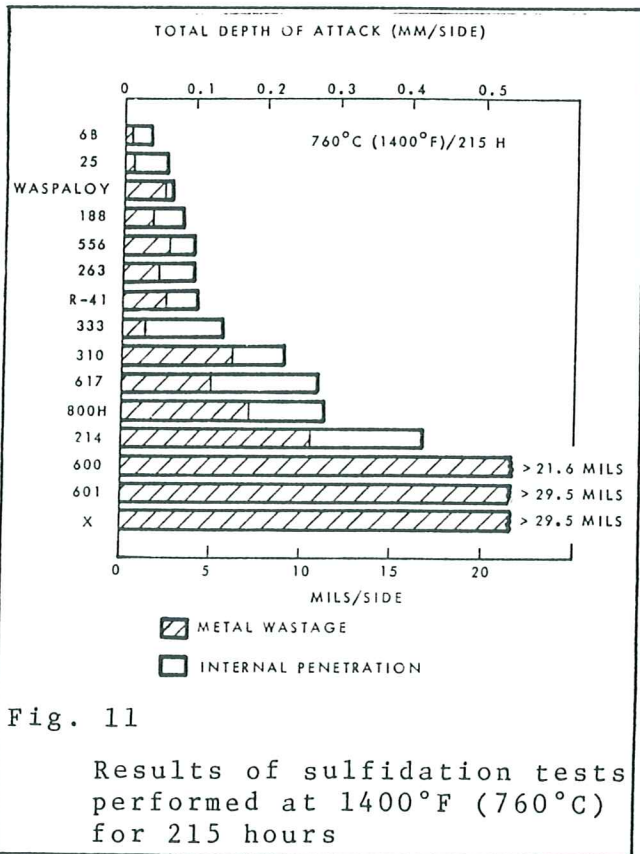
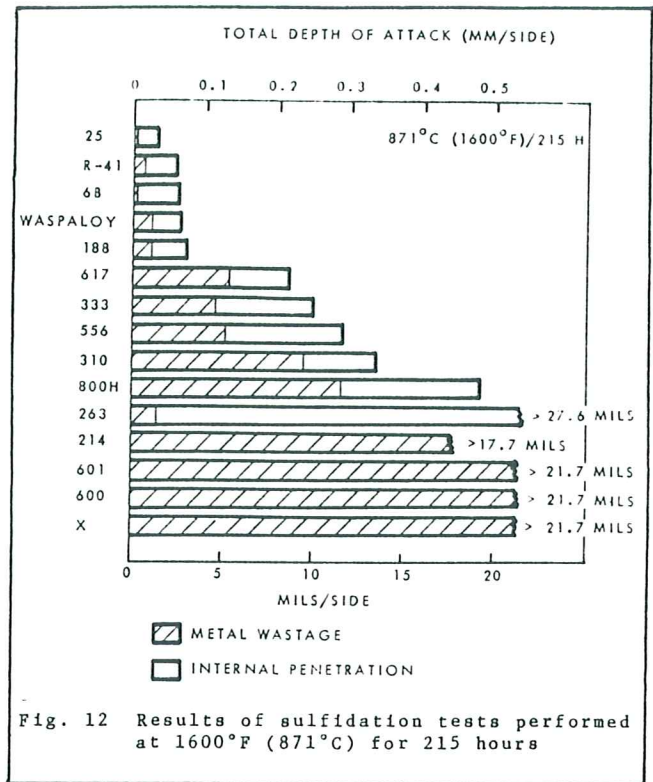
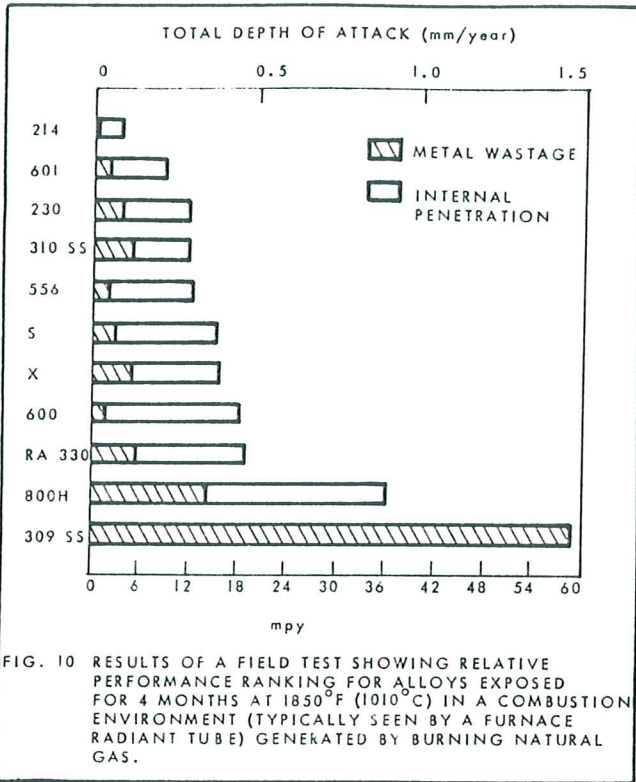


FIG. 9 OXIDATION RESISTANCE OF VARIOUS ALLOYS TESTED IN AIR AT 2000°F (1093°C) FOR 1008 HOURS.





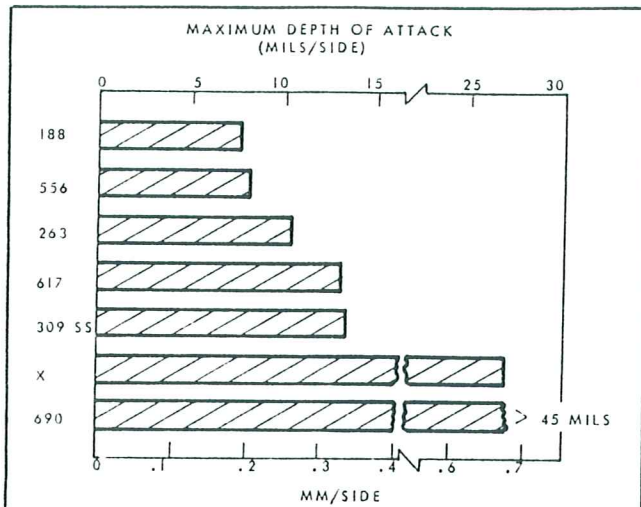


FIG. 14 RESULTS OF A FIELD TEST SHOWING RELATIVE PERFORMANCE RANKING FOR ALLOYS EXPOSED FOR 950 HOURS AT 1475°F (800°C-AVERAGE TEMPERATURE) WITH A MAXIMUM TEMPERATURE OF 1750°F (950°C) IN A COMBUSTION ENVIRONMENT GENERATED BY INCINERATION OF MUNICIPAL WASTES. THE PRINCIPAL MODE OF CORROSION WAS OXIDATION/SULFIDATION

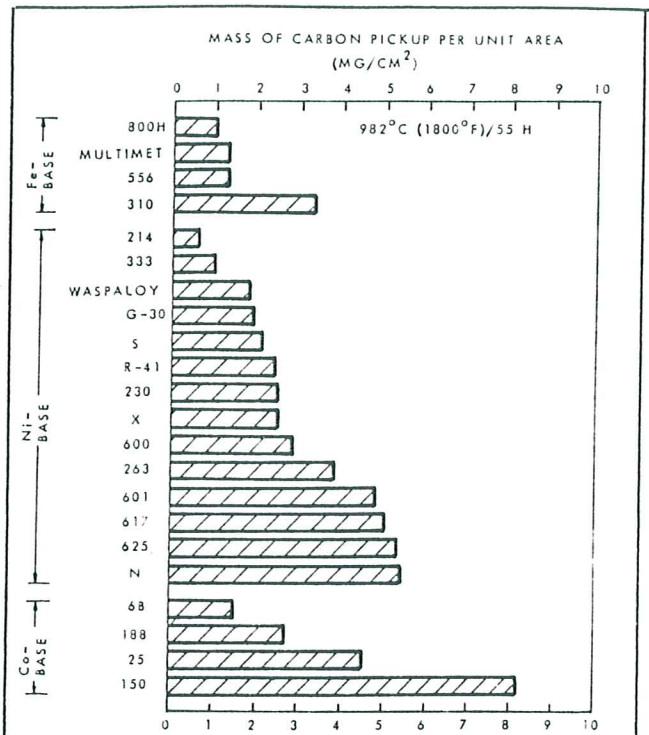


Fig. 16 Results of carburization tests conducted at 1800°F (982°C) for 55 hours.

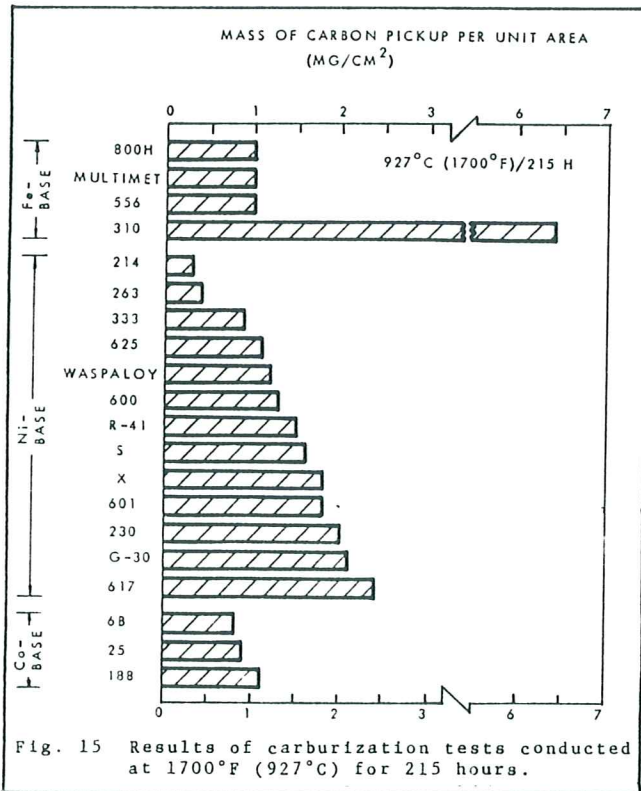
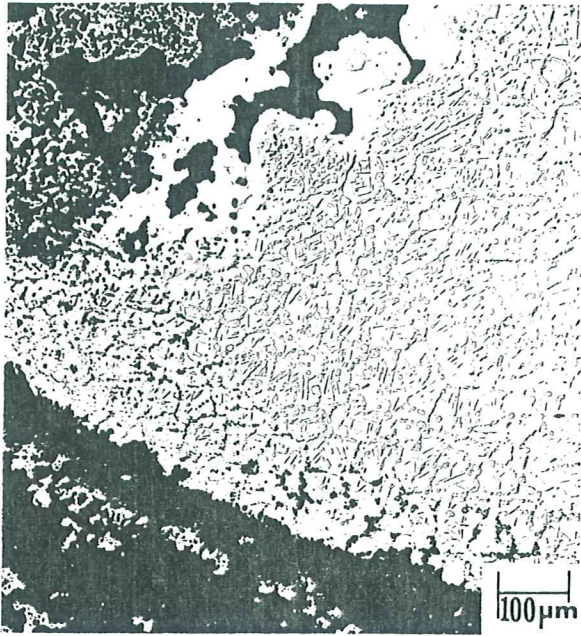
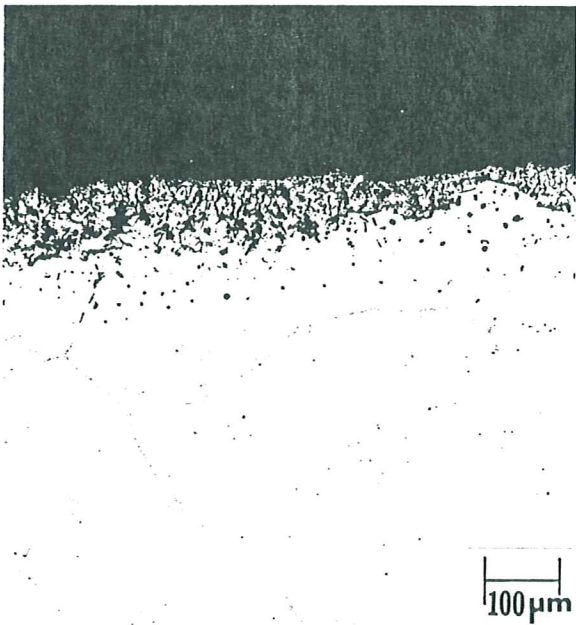


Fig. 15 Results of carburization tests conducted at 1700°F (927°C) for 215 hours.





(a) Type 310SS



(b) Alloy 214

Fig. 17 - Optical photomicrographs showing (a) oxidation/carburization attack upon the Type 310SS component which failed in 2 to 3 months in an environment produced by carbon regeneration, and (b) oxidation attack upon the alloy 214 component after service for 3 months in a similar environment produced by carbon regeneration.

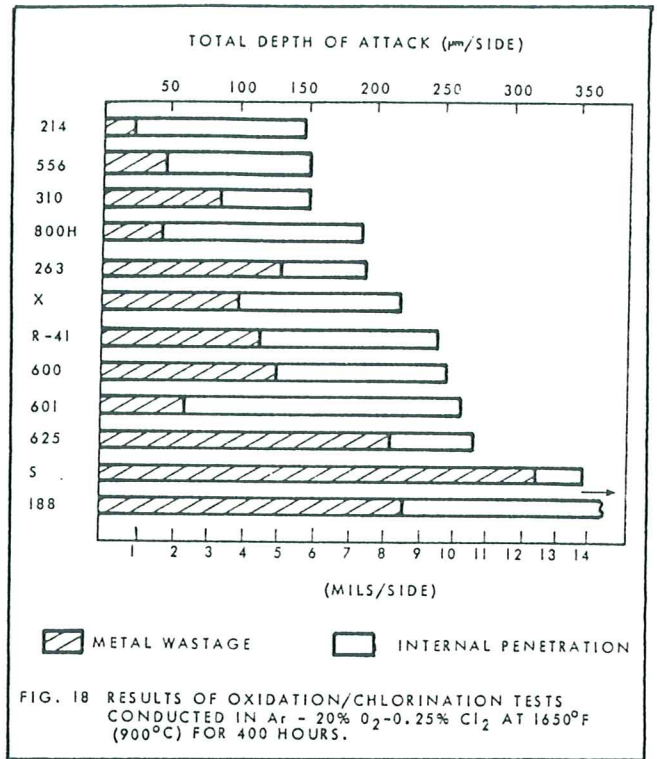


FIG. 18 RESULTS OF OXIDATION/CHLORINATION TESTS CONDUCTED IN Ar - 20% O<sub>2</sub>-0.25% Cl<sub>2</sub> AT 1650°F (900°C) FOR 400 HOURS.

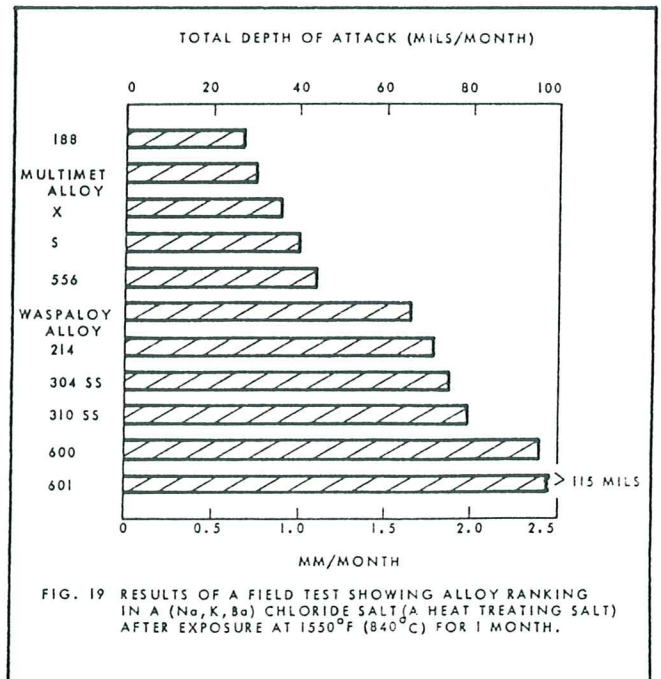


FIG. 19 RESULTS OF A FIELD TEST SHOWING ALLOY RANKING IN A (Na, K, Ba) CHLORIDE SALT (A HEAT TREATING SALT) AFTER EXPOSURE AT 1550°F (840°C) FOR 1 MONTH.

