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SUMMARY

The utilization of heat recuperators in high-temperature industrial processing facilities to recover the waste heat from flue gas streams and use it to preheat incoming combustion air can result in significant energy savings. Little information concerning the performance characteristics of most commercial alloys in various corrosive flue gas environments is available to guide materials selection for heat recuperators. This paper discusses four principal flue gas environments, i.e. oxidizing, sulfidizing, carburizing, and chlorine-contaminated environments, that are frequently encountered in high-temperature industrial processing systems. A ranking of relative alloy performance in these hostile environments for a variety of commercial alloys is presented in order to help the design engineer select the most appropriate alloys for construction of recuperators. Other materials properties that are of importance in the materials selection, including short-time tensile properties, creep rupture properties, and thermal stability, are also discussed.

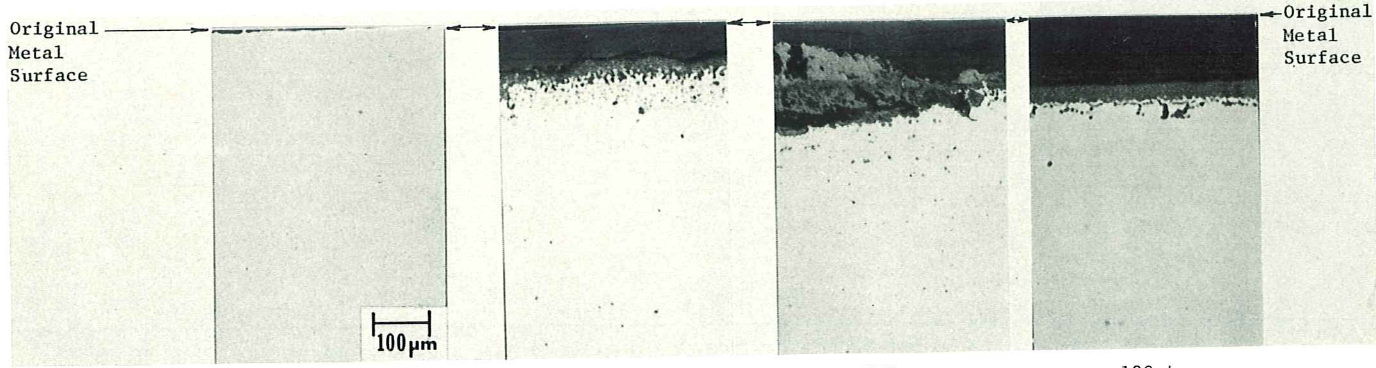
INTRODUCTION

Significant amounts of energy are lost each year from numerous high-temperature industrial processing facilities in the form of high-temperature exhaust gases. Energy can be saved by recovering this lost heat with a recuperator and using it to preheat the combustion air for processing combustion. Increasing the preheated combustion air temperature will increase the thermal efficiency of the process and thus the product yield.

Generally, the material used to construct the heat recuperator determines the temperature limitations on the preheated combustion air. These maximum temperature limits are primarily governed by the creep strength of the materials and their resistance to the corrosive environments usually associated with the flue gas stream. The alloy data pertaining to elevated temperature properties are generally available for a wide variety of alloys, including the stainless steels and nickel- and cobalt-base alloys. As for the material's resistance to corrosion attack by various corrosive flue gas streams, little relevant data and information are available to guide materials selection. Thus, there have been instances involving total failure of a heat recuperator system in service for as little as several months due to severe high-temperature corrosion attack.

In many cases, the corrosive nature of a flue gas environment is not very well characterized or understood. The mode of high-temperature corrosion strongly depends on, among others, the corrosive species present in the environment. Typical modes of high-temperature corrosion in flue gas environments include oxidation, sulfidation, carburization, chlorination, or any combination of these. Understanding the corrosive nature of the flue gas environment and the behavior of the alloy in this type of environment is of paramount importance in making an informed alloy selection. Other factors, including the creep strength and thermal stability of the alloy are also important in the materials selection process.

Figure 1. Oxidation resistance of several high-temperature alloys. Samples were exposed in still air at 2100°F (1150°C) for times indicated. See Table I for compositions.



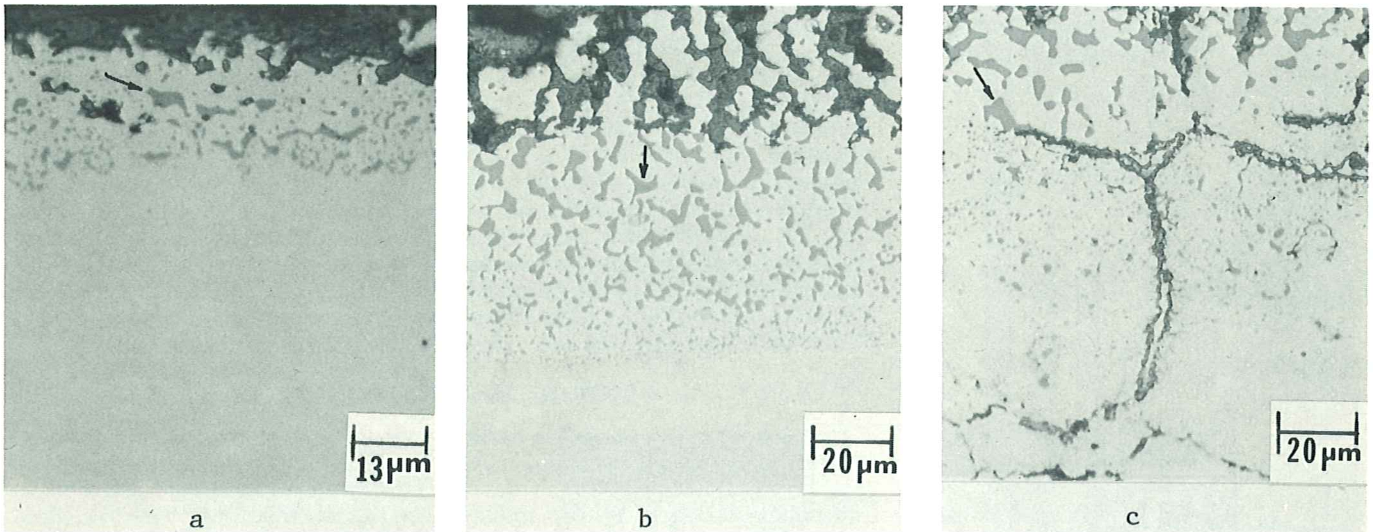


Figure 2. Examples of sulfidation-oxidation attack by various flue gas streams: a) HAYNES alloy No. 25 exposed to the flue gas stream of a glass melting furnace, b) Type 330 stainless steel exposed to the flue gas stream of an oil-fired facility, and c) alloy 800H exposed to the flue gas stream of a refractory manufacturing plant. Arrows indicate sulfide phases formed underneath the oxide scales.

In this paper, we consider the various types of flue gas environments frequently encountered in high-temperature industrial processing systems and the alloys which provide the most resistance to these environments. Also discussed are some additional materials properties that are important in selecting alloys for long-term, elevated temperature service. These include mechanical properties and thermal stability of the alloys. The nominal compositions of the alloys discussed in this paper are listed in Table I.

OXIDIZING ENVIRONMENTS

When the combustion process involves "clean" fuel (e.g., natural gas or low sulfur fuel oil) without the presence of feedstock or chemical additive derived corrosion species such as sulfur, carbon, or halogen, the dominant mode of high-temperature corrosion is typically oxidation. Air oxidation data are readily available in the literature and alloy manufacturer's data brochures for a wide variety of high-temperature alloys.[1-4] The air oxidation data can only be used as a qualitative guide to materials selection. Many factors, including temperature, stress, cyclic conditions, and certain contaminants (e.g., Na, K, Ca) in the combustion atmosphere, can significantly affect the alloy's performance. Thus, the materials selection is best made based on field experience and/or field testing. Lacking field data, laboratory simulation tests are preferred.

A recent study[5] by Solar Turbine International (under Gas Research Institute funding) evaluated high-temperature recuperator alloys for industrial waste heat recovery in a system (e.g., forging furnaces) involving combustion of "clean" fuels. The alloys investigated included Type 321 and 310 stainless steels; alloy 800H; alloy 825; INCONEL* alloys 601 and 617; alloy 625; and HASTELLOY** alloy X. Because of its outstanding performance in laboratory simulation tests, HASTELLOY alloy X was selected for field testing in a forging facility. This field testing is currently under way.[6]

A new, wrought, NiCrAlY-type alloy, CABOT† alloy No. 214, will shortly be introduced in the market by Cabot Corporation for applications requiring oxidation resistance at very high temperatures. The alloy, which develops an adherent Al_2O_3 protective scale during high-temperature exposure, has exceptionally good oxidation resistance properties. The oxidation resistance of this alloy as compared to other commonly used high-temperature alloys is demonstrated by the results of laboratory oxidation tests, which are shown in Figure 1.

Figure 3. Results of sulfidation tests conducted at 1400°F (760°C)/215 h for a variety of commercial alloys. See Table I for compositions.

SULFIDIZING ENVIRONMENTS

Sulfur is the most common contaminant in flue gas streams that can pose a potential materials problem to metallic recuperators if the proper alloy is not selected. Sulfur can come from fuel, feedstock, or chemical additives. Examples of sulfidation attack upon alloys caused by the flue gas streams generated in various industrial process facilities are given in Figure 2. In response to a lack of data on the performance characteristics of a wide variety of commercial alloys in high-temperature sulfidizing environments, an investigation was undertaken to develop data as a guide to materials selection.

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**HASTELLOY is a registered trademark of Cabot Corp.

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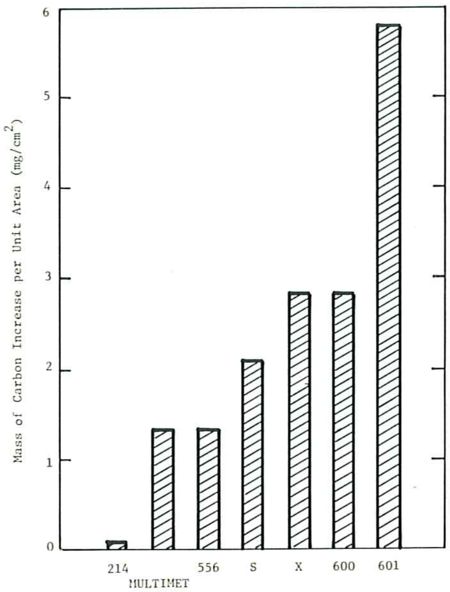

Figure 4. Results of carburization tests conducted at 1800°F (980°C)/55 h for a variety of commercial alloys.

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Laboratory screening tests were performed in a severe sulfidizing environment characterized by a low oxygen potential and a high sulfur potential. Sulfur and oxygen potentials (P_{S_2} and P_{O_2}) at 1400°F (760°C), for example, were 1 x 10^{-7} atm and 5 x 10^{-22} atm, respectively. The test gas environment (i.e., inlet gas mixture) consisted of 5% H_2, 5% CO, 1% CO_2, 0.15% H_2S, and balance Ar (vol. %). The ranking of alloy performance using the test results generated at 1400°F (760°C) is shown in Figure 3. These results suggest that when stainless steels or nickel-base alloys with little or no aluminum and titanium (such as Type 310 stainless steel, alloy 800H, alloy 600, INCONEL alloy 601, HASTELLOY alloy X) fail, due to sulfidation attack, alternate alloys with better sulfidation resistance should be considered. These alloys include HAYNES†† alloy No. 556 and MULTIMET†† alloy (Fe-Ni-Cr-Co alloys); CABOT alloy No. 263 (a nickel-base alloy with aluminum and titanium); and HAYNES alloys No. 25, No. 150, and No. 188 (cobalt-base alloys).

CARBURIZING ENVIRONMENTS

Flue gas streams containing carbon monoxide and/or hydrocarbon gaseous components can pose potential materials problems to metallic recuperators as a result of carburization attack. Carburization furnaces and petrochemical plants are some of the industrial facilities that can generate these types of flue gas streams. Here, too, there is a lack of data concerning relative alloy performance in carburizing environments for a wide variety of commercial alloys. Therefore, an investigation was performed to generate such data as a guide to material selection.

Laboratory screening tests were performed in a severely carburizing environment, with unity carbon activity and low oxygen potentials (i.e. P_{O_2} = 4 x 10^{-22} atm at 1600°F [871°C]). The tests were performed in a gas mixture with the inlet gas composition being 5% H_2, 5% CO, 5% CH_4, and balance Ar (vol. %). Figure 4 summarizes the test results generated at 1800°F (980°C). 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:

$$\Delta M = \Delta C \left(\frac{W}{A}\right) \tag{1}$$

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 unexposed specimen (mg), and
A = surface area of the specimen exposed to test environment (cm^2).

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 method commonly used to present carburization results).

Several alloys, such as CABOT alloy No. 214, MULTIMET alloy, HAYNES alloy No. 556, and HASTELLOY alloy S, were found to exhibit excellent carburization resistance.

Table I: Nominal Chemical Composition of High-Temperature Alloys, Wt.%

Alloy	C	Fe	Ni	Co	Cr	Mo	W	Si	Mn	Al	Ti	Others
Type 446 stainless steel	0.20+	Bal	—	—	25	—	—	1.5+	1.5+	—	—	N=0.25+
Type 304 stainless steel	0.08	Bal	9.3	—	19	—	—	1.0+	2.0+	—	—	—
Type 310 stainless steel	0.25+	Bal	20	—	25	—	—	1.5+	2.0+	—	—	—
CABOT* alloy No. 800	0.10+	Bal	33	—	21	—	—	1.0+	1.5+	0.38	0.38	Cu=0.75+
CABOT alloy No. 800H	0.08	Bal	33	—	21	—	—	1.0+	1.5+	0.38	0.38	Cu=0.75+
MULTIMET* alloy	0.10	Bal	20	20	21	3	2.5	1.0+	1.5+	—	—	Cb+Ta=1,Cu=0.5+,N=0.15
HAYNES* alloy No. 556	0.10	Bal	20	18	22	3	2.5	0.4	1.0	0.2	—	Cb+Ta=0.8,La=0.02, N=0.2,Zr=0.02
CABOT alloy No. 600	0.08+	8	Bal	—	16	—	—	0.5+	1.0+	0.35+	0.3+	Cu=0.5+
CABOT alloy No. 214	0.04	4	Bal	—	16	—	—	—	—	4.5	—	Y=0.01
INCONEL** alloy 601	0.10+	14.1	Bal	—	23	—	—	0.5+	1.0+	1.35	—	Cu=1.0+
INCONEL alloy 617	0.07	1.5	Bal	12.5	22	9	—	0.5	0.5	1.2	0.3	Cu=0.20
CABOT alloy No. 263	0.06	0.7+	Bal	20	20	6	—	0.4+	0.6+	0.5	2	Cu=0.20+
HASTELLOY* alloy S	0.02	3+	Bal	2.0+	15.5	14.5	1.0+	0.4	0.5	0.2	—	La=0.02,B=0.009
HASTELLOY alloy X	0.10	18.5	Bal	1.5	22	9	0.6	1.0+	1.0+	—	—	—
CABOT alloy No. 625	0.10+	5+	Bal	—	21.5	9	—	0.5+	0.5+	0.4+	0.4+	Cb+Ta=3.5
HAYNES alloy No. 188	0.10	3+	22	Bal	22	—	14	0.35	1.25+	—	—	La=0.04
HAYNES alloy No. 25	0.10	3+	10	Bal	20	—	15	1.0+	1.5	—	—	—
HAYNES alloy No. 150	0.06	18	1.0	Bal	27	—	—	0.3	0.4	—	—	—

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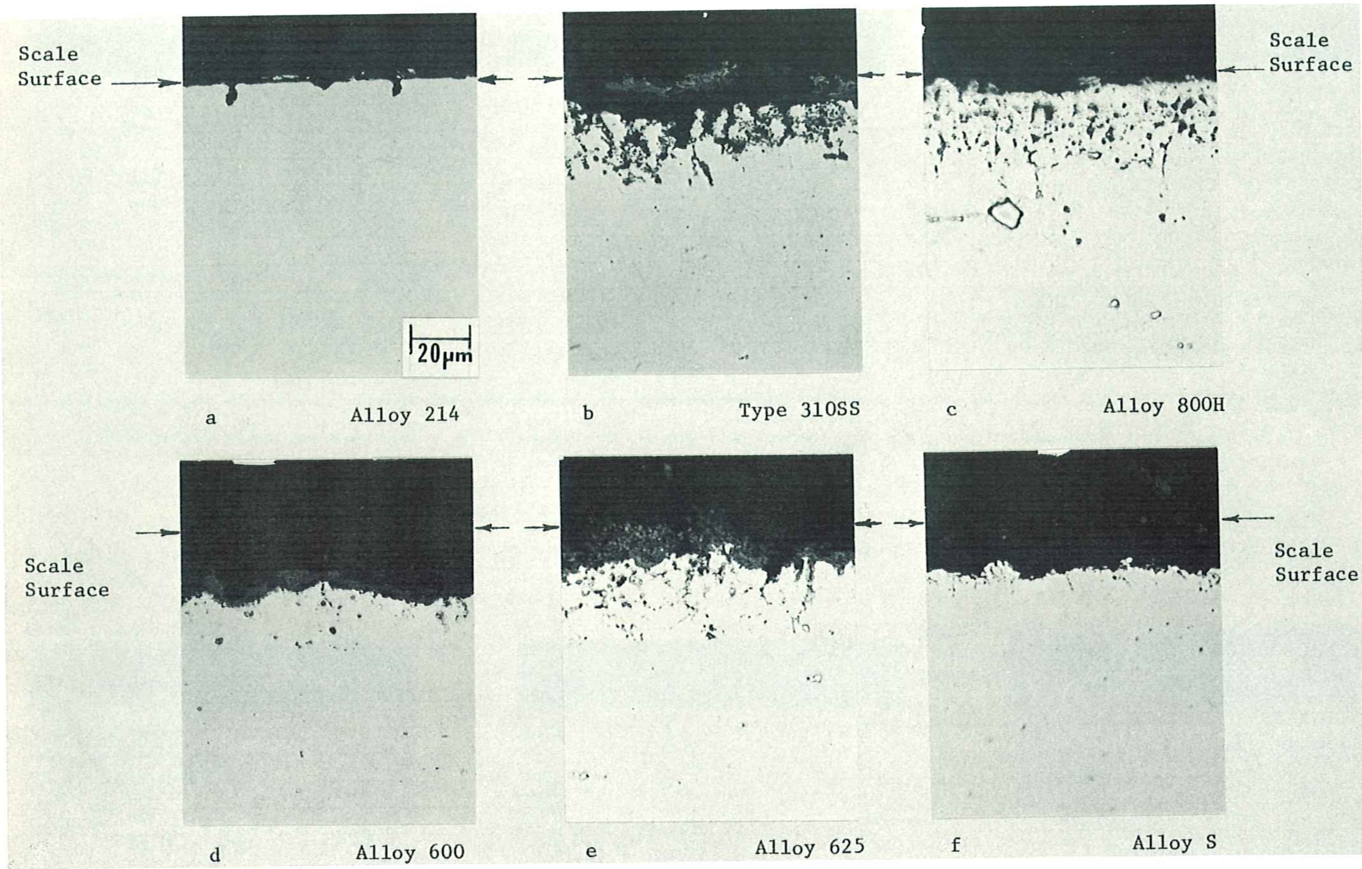

Figure 5. Optical photomicrographs showing corrosion attack upon various alloys in Ar-20% O_2-2% Cl_2 at 1650°F (900°C)/8 h.

CHLORINE-CONTAMINATED ENVIRONMENTS

Aluminum melting, fiberglass manufacturing, waste incineration, calcination, and chlorination processing are some industrial processes that can generate flue gases containing Cl_2, HCl, and metal chlorides. Incineration of chemical wastes or wastes containing plastic materials can produce flue gas contaminated with chlorine or chlorides. Chlorine can also come from the additives used for a particular processing reaction. In an aluminum melting facility, for example, chlorine gas is injected into the molten aluminum to remove some of the impurities, e.g. magnesium.

Little materials information concerning high-temperature corrosion of commercial alloys at temperatures over 1400°F (760°C) in chlorine-contaminated environments is available to guide materials selection. A study was begun to evaluate oxidation/chlorination attack upon a representative number of high-temperature alloys. Figure 5 illustrates corrosion attack upon these alloys exposed in Ar-20% O_2-2% Cl_2 (vol. %) at 1650°F (900°C)/8 h.[7] The nature of the corrosion attack upon these alloys in a reducing environment is shown in Figure 6.[8] The alloys in this case were exposed in argon containing 4% H_2 and 4% HCl (vol. %) at 1650°F (900°C)/8 h. CABOT alloy No. 214 was found to be the best alloy among the alloys tested in both oxidizing and reducing environments. HASTELLOY alloy S, while suffering oxidation/chlorination attack in the oxidizing environment, exhibits good corrosion resistance in the reducing environment. More studies, particularly long-term tests, are needed to characterize the behavior of alloys in this type of environment. Such long-term tests on a variety of commercial alloys are currently under way.

MECHANICAL PROPERTIES AND THERMAL STABILITY

In addition to resistance to aggressive high-temperature environments, materials selection for the construction of heat recovery units also depends on the need to maintain structural integrity over the course of long-term service. Thus, properties such as resistance to creep damage, high tensile stresses, and the debilitating effects of long-term thermal exposures on the ductility of materials all must be considered in determining the most appropriate construction materials. Also of considerable importance is the degree of formability and weldability, as the construction of heat recovery equipment often involves complex fabrication operations.

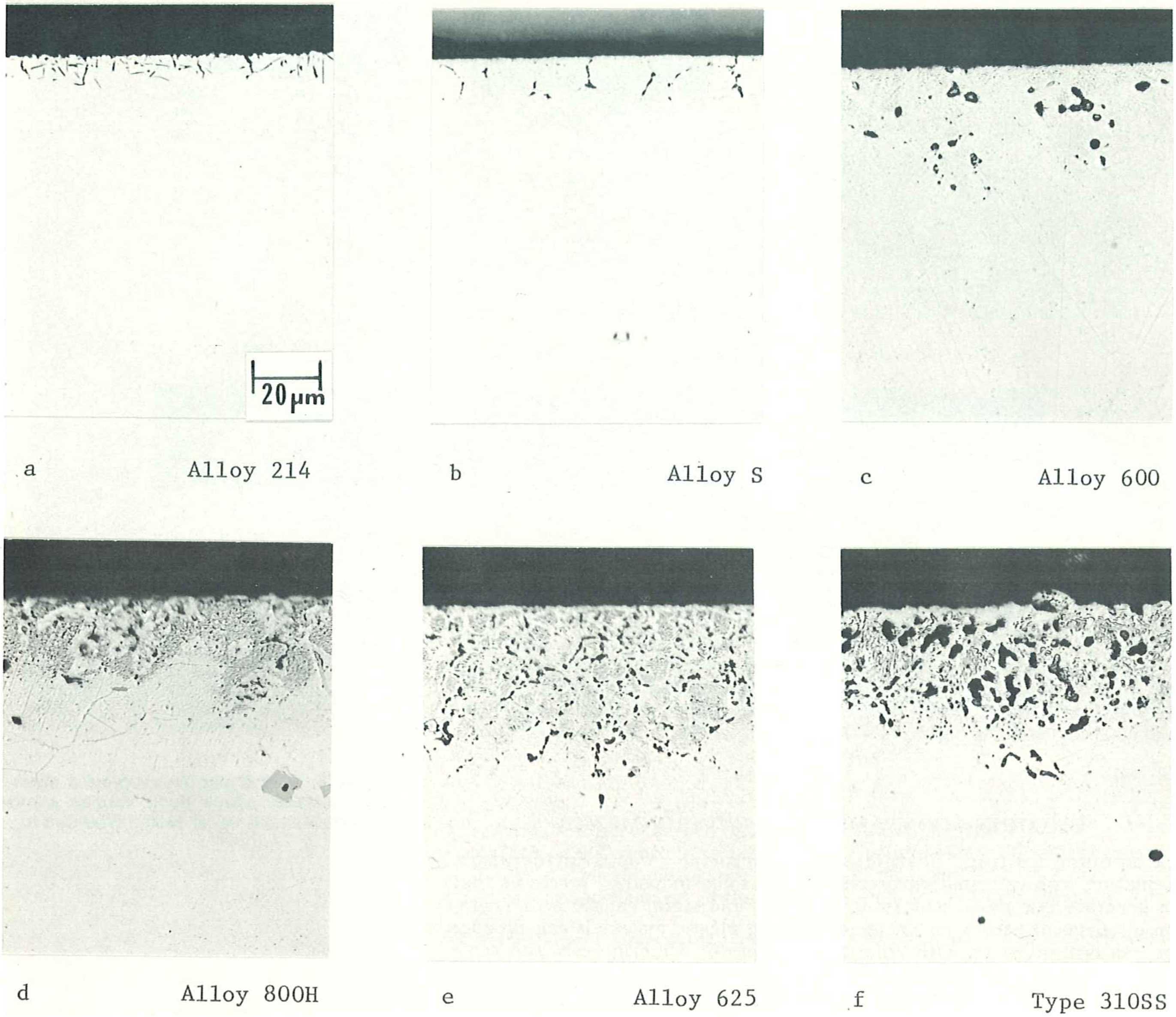

Figure 6. Optical photomicrographs showing corrosion attack upon various alloys in Ar-4% H_2-4% HCl at 1650°F (900°C)/8 h.

Typical short-time tensile yield strength properties for a variety of materials are exhibited in Figure 7.[3,4,9,10] Clearly, a substantial range of yield strengths is available. Beginning with the relatively low strength levels afforded by the austenitic stainless steels, such as Type 310 stainless steel, and the well known nickel and iron-nickel alloys, such as alloy 600 and alloy 800, progressively higher yield strength behavior is available as one considers the family of high-performance, solid-solution-strengthened alloys such as HASTELLOY alloy X, MULTIMET alloy, HAYNES alloy No. 188, and HASTELLOY alloy S. Even higher strength levels up to the 1600°-1700°F range are available through the use of precipitation-strengthened, high-performance alloys such as CABOT alloys No. 263 or No. 214.

Similarly, the design engineer can choose from a broad spectrum of material creep strength capabilities. This is quite evident from the typical stress-to-rupture strength data at 1600°F (870°C) presented for a variety of materials in Figure 8.[3,4,10,11] Once again, a substantial range of strengths is available as one progresses from the austenitic stainless steels and nickel alloys to the high-performance, solid-solution-strengthened, and precipitation-strengthened alloys.

Thermal stability is defined as a measure of a material's ability to resist impairment of structural integrity, principally through the ductility loss that often results from long exposures at high temperature. For applications such as heat recuperators, such considerations are very important to the long service life desired from such equipment. Thermal stability may be characterized in a host of different fashions. For example, impact strength following long thermal exposures is considered a good measure of resist-

Table II: Effect of Exposure at 1200°F (650°C)/10,000 h on the Room-Temperature Impact Properties of Various Materials

Alloy	70°F Charpy V-Notch Impact Strength, ft-lb (joules)	
	Unexposed	Exposed
Alloy 800H	260 (354)	45 (61)
HASTELLOY alloy S	140 (190)	53 (72)
Type 310 stainless steel	75 (102)*	2 (3) *
Alloy 625	81 (110)	5 (7)

*Charpy Keyhole Data

Table III: Effect of Exposure at 1200°F (650°C)/8,000 h on Room-Temperature Tensile Elongation of Various Alloys

Alloy	Room-Temperature Tensile Elongation, %	
	Unexposed	Exposed
Alloy 800	58	35
MULTIMET alloy	57	23
Alloy 600	56	41*
HASTELLOY alloy S	54	50
Alloy 625	46	18

*Exposed 8,700 hours

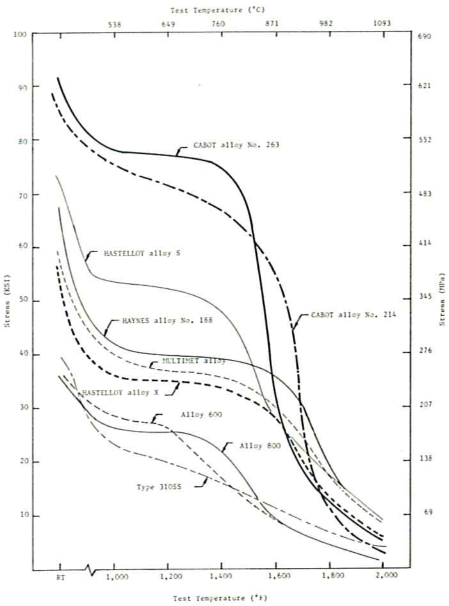

Figure 7. 0.2% yield strength as a function of temperature for various commercial alloys.[3,4,9,10]

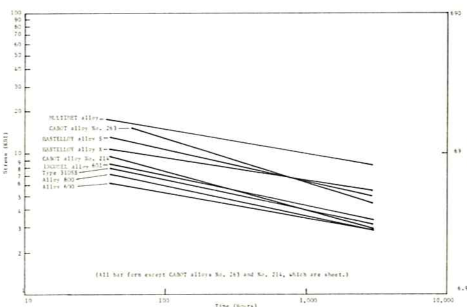

Figure 8. Stress rupture properties of various commercial alloys at 1600°F (870°C).[3,4,10,11]

ance to structural degradation. Typical data are given in Table II for several alloys exposed at 1200°F (650°C)/10,000 h.[3,12,13] Here, the excellent thermal stabilities of materials such as alloy 800H and HASTELLOY alloy S are illustrated, while the sensitivity of materials such as Type 310 stainless steel to embrittling sigma phase precipitation and materials such as alloy 625 to embrittlement by precipitation of copious amounts of Ni_3Cb is clearly revealed.

Another measure of thermal stability is the amount of room-temperature tensile ductility remaining for a material subjected to a long-time thermal exposure. Some typical data of this type are presented in Table III after exposures at 1200°F (650°C)/8,000 h.[14,15] Once again, HASTELLOY alloy S looks very good for these conditions, while materials such as alloy 625, while not totally embrittled, still show marked sensitivity to the exposure.

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