134

Advanced Alloys for Industrial Heating Equipment Subject to Severe Service Conditions

By M. F. ROTHMAN and G. Y. LAI
Cabot Corporation
Kokomo, Indiana

Reprinted from
INDUSTRIAL HEATING
August, 1986

Advanced Alloys for Industrial Heating Equipment Subject to Severe Service Conditions

By M. F. ROTHMAN and G. Y LAI
Cabot Corporation
Kokomo, Indiana

Selection of materials for construction is more often a matter of picking an alloy that will provide the desired service life rather than choosing one "that will work".

A number of different materials will work in a given application. However, the most "inexpensive" choice for high-temperature service might not be a plain carbon steel; it will very often be a stainless steel. "More Expensive" alternatives will certainly be available in the form of nickel-chromium alloys, iron-nickel-chromium alloys, and more advanced heat-resistant materials. But the real issue is whether the initial higher cost will be justified when one considers increased maintenance, lost time or premature replacement requirements that would be associated with a less serviceable material.

A case in point is the heat treating operation illustrated in Fig. 1. It involves the use of Hastelloy® alloy X baskets in a 1740°F (949°C) carburizing furnace. In this service alloy X baskets have resisted warping and are still in service after more than seven years! Furthermore, from their appearance in Fig. 1, even longer service can be expected. Thus in this case, an initially more expensive material was justified in that baskets fabricated from a high Ni-Cr alloy, initially costing about ½ less, had to be discarded after one year because of distortion.

The message is not that all heat treating baskets should be made of alloy X. Clearly, there are many applications where stainless steels and nickel alloys are the right choices based upon desired service life considerations. There are also applications where advanced alloys seem to be economically justified, but their potential for longer service life is not realized because of an unintentional, but predictable, premature demise under the wheels of an errant forklift truck. The more understanding of the factors which control the service life of a particular component, and the more that is known about the performance characteristics of various materials of construction, the easier it is to select the right alloy to provide the most economical service over the desired life of the equipment.

Compositions of various materials to be considered are given in Table I. Many of the advanced alloys were developed for highly demanding applications in the aerospace industry. There, key attributes are superior high-temperature strength, environment-resistance, and fabricability. These alloys possess performance capabilities which justify their initial expense in these aerospace applications, and have similar applicability in the industrial heating industry. For perspective, a rough guide to the relative initial

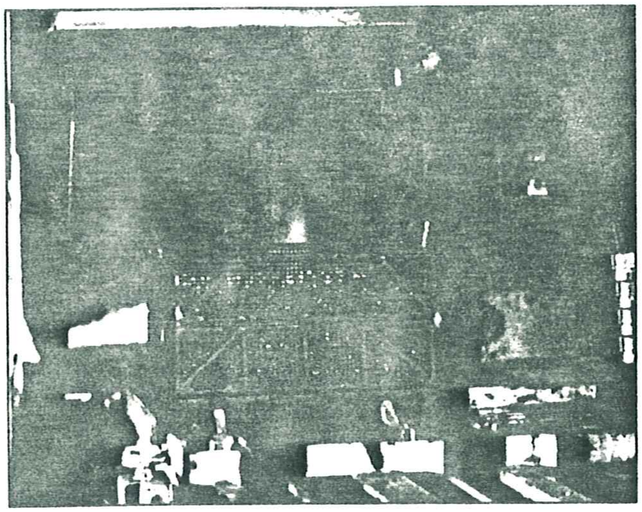

Fig. 1 Heat treat baskets made from Hastelloy alloy X in service in a carburizing furnace facility for over seven years.

Table I Nominal Chemical Compositions of Alloys Included in Studies

	Nominal Chemical Composition (Wt. Pct.)									
Alloy	C	Fe	Ni	Co	Cr	Mo	W	Si	Mn	Others
Type 304	.08+	Bal	8	-	18	-	-	1.0+	2.0+	-
Type 309	.20+	Bal	12	-	23	-	-	1.0+	2.0+	-
253MA alloy	.08	Bal	11	-	21	-	-	1.7	0.8+	N=.17, Ce=.05
Type 310	.25+	Bal	20	-	25	-	-	1.5+	2.0+	-
Type 316	.08+	Bal	10	-	17	2.5	-	1.0+	2.0+	-
Type 446	.20+	Bal	-	-	25	-	-	1.0+	1.5+	N=.25
Alloy 800H	.08	Bal	33	-	21	-	-	1.0+	1.5+	Al=.38, Ti=.38
RA®330 alloy	.05	Bal	35	-	19	-	-	1.3	1.5	-
HAYNES® alloy No. 556	.10	Bal	20	18	22	3.0	2.5	0.4	1.0	Al=.2, Ta=0.8, La=.02, N=.2, Zr=.02
Alloy 825	.05+	29	Bal	-	22	3.0	-	0.5+	1.0+	Cu=2.0, Ti=1.0
Alloy 600	.08+	8	Bal	-	16	-	-	0.5+	1.0+	Al=.35+, Ti=.3+, Cu=.5+
HAYNES® alloy No. 214	.04	4	Bal	-	16	-	-	-	-	Al=4.5, Y=.01
INCONEL® alloy 601	.10+	14.1	Bal	-	23	-	-	0.5+	1.0+	Al=1.35, CU=1.0+
INCONEL® alloy 617	.07	1.5	Bal	12.5	22	9	-	0.5	0.5	Al=1.2, Ti=.3, Cu=.20
HASTELLOY® alloy S	.02	3+	Bal	2.0+	15.5	14.5	1.0+	0.4	0.5	Al=.2, La=.02, B=.009
HASTELLOY® alloy X	.10	18.5	Bal	1.5	22	9	0.6	1.0+	1.0+	-
Alloy 625	.10+	5+	Bal	-	21.5	9	-	0.5+	0.5+	Al=.4+, Ti=.4+, Cb+Ta=3.5
HAYNES® alloy No. 230	.1	3+	Bal	3+	22	2	14	0.4	0.5	Al=.3, B=.005, La=.03
RA333® alloy	.05	18	Bal	3	25	3	3	1.25	1.5	-
HASTELLOY® alloy N	.06	5+	Bal	-	7	16.5	0.5+	1.0+	0.8+	Cu=.35+
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 AND HASTELLOY are registered trademarks of Cabot Corporation.
INCONEL is a registered trademark of the Inco Family of Companies.
RA330 and RA333 are registered trademarks of Rolled Alloys, Inc.
253MA is a registered trademark of Avesta Jernverks Aktiebolag

cost of these and other materials is presented in Table II.

Factors Governing Materials Performance

In operation of most industrial heating equipment, the limiting factors which govern service life of a material are either its strength, its ductility, or its resistance to high-temperature corrosion. In actual practice, these all can be interactive. Thinning due to corrosion can lead to accelerated mechanical failure, or the application of stresses can accelerate corrosion. Another possibility is that exposure to the environment can cause mechanical embrittlement (such as from carburization).

Strength and Ductility

The strength of a material at elevated temperatures may be considered in a number of ways. There is its ability to resist deformation under load for long periods — its resistance to creep or stress rupture. There is also its ability to withstand very high stresses for short exposures. This is measured by tensile properties. Resistance to deformation, cracking and failure under the imposition of cyclic stress or repeated thermal cycles is governed by a material's mechanical or thermal fatigue strength. all are relevant to industrial heating applications, although not in every case.

Data describing the elevated temperature mechanical properties of stainless steels, nickel-chromium alloys, iron-nickel-chromium alloys and advanced heat-resistant materials are generally available, but seldom in a single comparison. Typical data from the literature combined with detailed test results have been used to establish the comparisons of stress-rupture strengths/lives presented in Tables III, IV and V.

As might be expected, advanced materials such as Haynes alloy No. 230, Haynes alloy No. 556, and alloy X exhibit significant strength advantages. The data in Table III are useful for examining the load-bearing capability of these alloys at a given temperature. For example, alloy No. 230 exhibits three times the load-bearing capability of 304 stainless at 1600°F (871°C), and more than twice that for alloys 601 and 253 MA. Such data are very relevant if section thicknesses are subject to size constraints, and a component cannot be made stronger simply by using thicker material.

Most applications call for design lives based upon fixed temperature and loading conditions. In this case, the data in Tables IV and V are more useful. Table IV shows that, under fixed conditions, the advanced materials can last up to more than 100 times longer than such materials as type 304 stainless steel. In Table V the rupture lives are expressed as a multiple of that expected from alloy 800H under the same service conditions. The magnitude of the potential performance advantages to be gained with the stronger materials warrants their consideration in spite of their relatively higher initial cost.

Indeed, the stress rupture strength advantages of these materials are so large as to suggest using thinner sections to save on the initial cost. This is an important concept, as illustrated by the data in Table VI. Comparing alloy No. 230 to alloy 800H at 1600°F (871°C), for example, it should be possible to use a section size only 5/8's as thick as that for alloy 800H and still have a rupture life advantage of as much as 5 X. Similar considerations apply to the other materials.

The tensile properties of this same range of materials are summarized in Fig. 2 and 3. Once again, the advanced heat-resistant alloys exhibit significant advantages over the stainless steels and the other materials shown. This is particularly evident at temperatures above 1400°F (760°C). However, high tensile and yield strength must be matched by good room and elevated temperature ductility if complex parts are to be fabricat-

Table II Relative Costs of Materials

Relative Cost	Materials
1	Type 310 Stainless
2 - 3	Alloy 800H Alloy 601 Alloy 600
4 - 5	Alloy X Alloy 214
6 - 7	Alloy 230 Alloy 556
10 - 12	Alloy 188

Table III Stress Rupture Strengths of Various Materials in Bar or Plate Form

Alloy	Stress to Produce Rupture in 1000 Hours (000's psi) 1400°F	1600°F	1800°F
230	20.0	9.0	3.0
556	18.0	7.8	3.3
214	16.0	4.9	1.5
X	15.0	6.2	2.4
800H	10.5	4.6	2.0
253MA	9.6	4.3	1.9
601	9.3	4.3	2.1
316 Stainless	8.8	3.4	1.3
304 Stainless	7.4	3.0	1.2
RA 330	7.0	3.1	1.3
600	5.8	3.5	1.8

Table IV Stress Rupture Lives Under Fixed Conditions for Various Materials in Bar or Plate Form

Alloy	Hours to Produce Rupture 1600°F and 4500 psi	1800°F and 2000 psi
230	41,000	8,700
556	29,000	10,600
X	5,900	2,800
601	1,200	1,000
800H	1,200	920
214	800	330
253MA	730	750
600	280	580
316 Stainless	240	130
304 Stainless	100	70
RA 330	80	80

Table V Relative Stress Rupture Life Under Fixed Conditions

Alloy	Relative Rupture Life (800 H = 1.0) 1600°F and 4500 psi	1800°F and 2000 psi
230	34.2	9.5
556	24.2	11.5
X	4.9	3.0
601	1.0	1.1
800H	1.0	1.0
214	0.7	0.4
253MA	0.6	0.8
600	0.2	0.6
316 Stainless	0.2	0.14
304 Stainless	0.08	0.08
RA 330	0.07	0.09

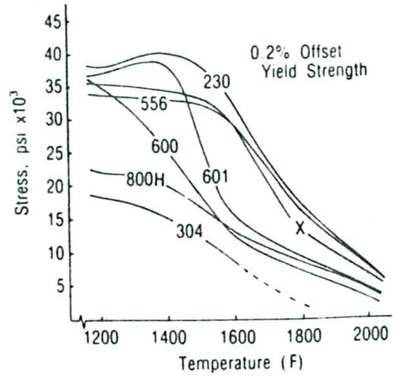

Fig. 2 0.2% offset yield strength for various sheet materials as a function of temperature.

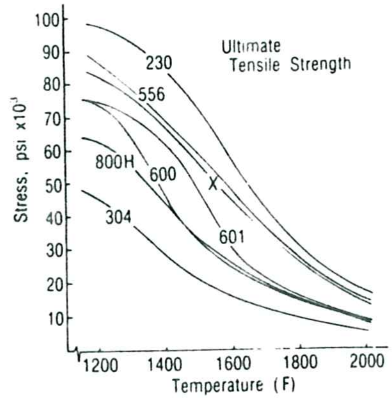

Fig. 3 Ultimate tensile strength for various sheet materials as a function of temperature.

Table VI Relative 1600°F (871°C) Stress Rupture Life for Various Alloys if Alloy 800H 1-Inch Plate = 1.0

Alloy	Ratio to Alloy 800H 1-Inch Plate Life for Decreasing Alloy Plate Thicknesses — Thickness (in): 1.00	.875	.750	.625	.500
230	34	25	13	5	1.3
556	24	11	4	1.5	-
X	5	2	-	-	-

ed. In Table VII the tensile elongation data for all materials shown indicate excellent ductility over the entire temperature range of interest.

Resistance to Environment

There are undoubtedly hundreds of different environments that are relevant to industrial heating applications. Many are unique, and many are so complex as to defy analysis. In these cases, the only way to judge the capabilities of different materials is to perform field tests involving either actual components or multiple-alloy test rack assemblies. In many cases, however, service environments can be sufficiently characterized as to allow the use of laboratory test data to guide material selection. Although less definitive than field tests, such data already exist, and can be applied with reasonable confidence in most cases. Both types of information will be utilized in an examination of various application service conditions.

Clean Combustion Environments

Clean combustion environments are defined as those in which the fuels burned do not contain appreciable amounts of complicating contaminants. These contaminants include sulfur, salts, and chlorine, among others. Some typical materials applications might be forging or heat-treating furnace hardware such as burners, recuperators, thermocouple protection tubes, or radiant heating tubes. There also is the entire range of accessory items, such as belts, baskets, trays and fixtures.

Fuels burned usually include natural gas or high quality fuel oil. The major environment-resistance issue under these circumstances is oxidation by the combustion gases. Resistance to combustion gases can be evaluated in laboratory combustion test rigs. Some typical data for a variety of materials are presented in Figs. 4 and 5. The exposures were to combustion gas produced by burning No. 2 fuel oil at 50:1 air:fuel ratio. Samples were cycled to less than 400°F (204°C) every half hour by removal from gas stream and application of forced-air cooling.

As measured by the average metal affected during the exposure, which includes metal loss plus average internal penetration, Figs 4 and 5 show that HAYNES alloy No. 214 is by far the best of the materials tested. Alloy No. 230 is also quite good, exhibiting more than a 2:1

Table VII Tensile Elongation for various Alloys as a Function of Temperature* (%)

Alloy	Test Temperature (°F) 70	1200	1400	1600	1800	2000
230	48	54	43	64	71	41
556	47	52	50	53	64	59
X	44	54	53	58	65	60
601	47	50	41	65	86	67
600	38	42	52	55	68	102
800H	46	45	62	56	83	65

*Sheet

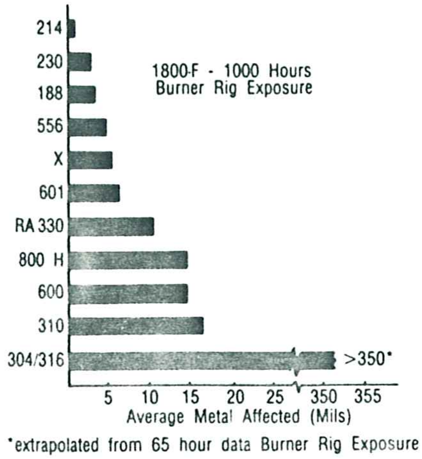

Fig. 4 Oxidation damage sustained by various alloys exposed for 1000 hours in a burner rig running at 1800°F (982°C), burning No. 2 fuel oil.

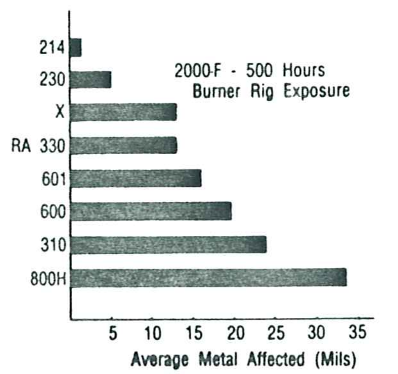

Fig. 5 Oxidation damage sustained by various alloys exposed for 500 hours in a burner rig running at 2000°F, burning No. 2 fuel oil.

advantage over the best of the nickel-chromium or iron-nickel-chromium alloys. Austenitic stainless steels such as types 304 and 316 are "blown away" in this type of cyclic environment. These results are in close agreement with results obtained from the field.

Carburizing & Nitriding Environments

The focus for carburizing and nitriding environments is, of course, the heat treating field, although there are certainly other areas where such environments are encountered. The use of laboratory data to gauge material performance in the well-characterized heat-treating operations is a reasonable approach.

Table VIII Carburization - Resistance of Various Materials Exposed to Severe Carburizing Environment at 2000°F (1093°C) for 24 Hours

Alloy	Carbon Absorption (mg/cm²)
214	3.4
600	9.9
625	9.9
230	10.3
X	10.6
S	10.6
304	10.6
617	11.5
316	12.0
RA333	12.4
800H	12.6
RA330	12.7
25	14.4

Results of carburization-resistance tests performed in the laboratory at 1700 and 1800°F (927 and 982°C) have been previously reported[1]. These tests indicated that advanced materials, such as alloy No. 214, could provide about 2X to 5X the resistance to carburization of more common materials. Recent tests have been performed at 2000°F (1093°C) to gauge the potential resistance to carburization of materials being considered for higher temperature carburizing facility components. Results of these tests, performed for 24 hours in Ar-5%H_2-5%CO-5%CH_4, are given in Table VIII

These results once again demonstrate a significant advantage for alloy No. 214, which is three times better than the next best materials, alloys No. 600 and No. 625. Alloy No. 230 is near the top of the list of the remaining materials, but there is some question of the significance of differences within the range of 9.9 to 14.4 mg/cm² carbon absorption displayed by the full group of alloys excluding alloy No. 214. Perhaps shorter or less severe tests are required to suitably separate the capabilities of these materials.

Nitriding test results were also reported previously[1]; however, additional alloys have been characterized in these 1200°F (649°C) test in ammonia for 168 hours. The updated full results are shown in Fig. 6. In terms of the amount of nitrogen absorbed per unit area of sample, alloy No. 230 displays the most resistance to nitriding, absorbing slightly less than alloy No. 600. As expected, the largest nitrogen absorptions are displayed by iron-base materials, with the level of nitrogen ingress decreasing roughly with increasing nickel content.

The somewhat less dramatic trend among the nickel- and cobalt-base alloys is not explainable simply as

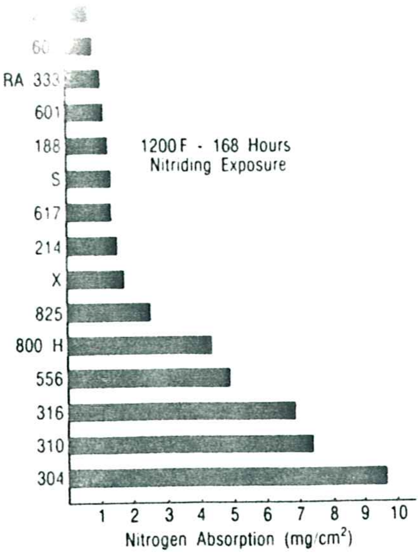

Fig. 6 Nitrogen absorption per unit area observed for various alloys exposed 168 hours to ammonia gas at 1200°F (1093°C).

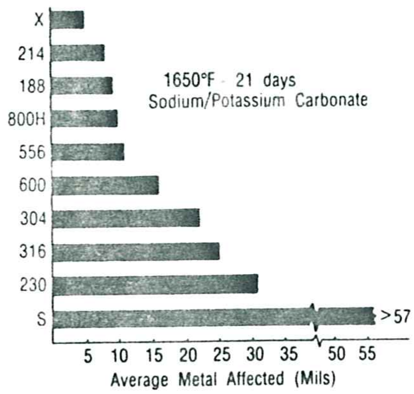

Fig. 8 Corrosion damage sustained by various materials exposed for 21 days in eutectic sodium/potassium carbonate salt at 1650°F (899°C). After Coyle et al.[3]

a function of increasing nickel content or nickel+cobalt content, as demonstrated by chemistries in Table I. The factor of two difference in absorption between alloy No. 230 and alloy No. 214 is contrary to their 60% and 75% nickel contents, respectively. Nitrogen solubility and diffusion kinetics are markedly affected by other elements, such as aluminum, silicon, titanium and columbium, commonly present in nickel-base alloys.

Molten Salt Environments

Used as a medium for heat processing or storage, molten salts are commonly encountered under controlled conditions in the heat treating field where relevant components of concern include pots, covers, fixtures, electrodes, etc. Molten salts can also play a role in complex processes, not as a bulk molten mass in a container, but as a deposit or film on process components.

Field test results in neutral NaCl-KCl-$BaCl_2$ salt baths at 1550°F (843°C) have been previously reported[1]. These indicated that a number of advanced

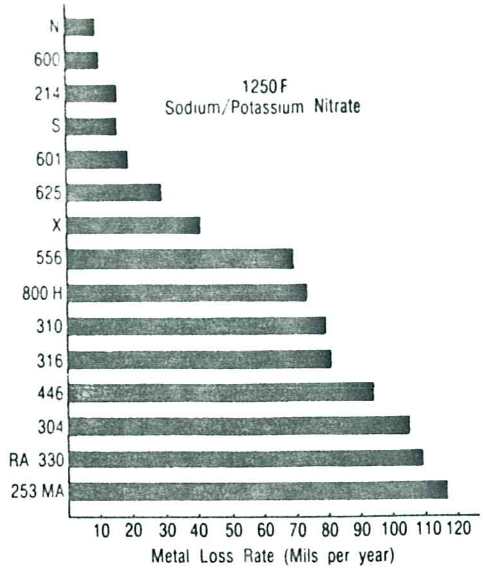

Fig. 7 Corrosion rate of various materials exposed in equimolar sodium/potassium nitrate salts at 1250°F (677°C). After Slusser et al[2].

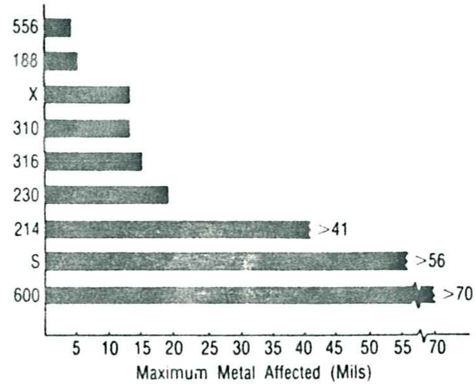

Fig. 9 Corrosion damage sustained by various materials exposed to 1400°F (804°C) flue gases from a chemical waste incinerator for 550 hours. (Average metal affected = metal loss + internal penetration.)

alloys, in particular HAYNES alloy No. 188, exhibit significantly better corrosion resistance than austenitic stainless steels and nickel-chromium alloys. Somewhat similar results have been obtained in laboratory tests conducted for 100 hours in pure NaCl at 1550°F (843°C). These data are given in Table IX. Again in these tests, alloy No. 188 performed best. Alloy No. 556 was also somewhat better than the stainless steels; however, the margin of improvement in this short exposure was not very large. Longer tests may be necessary to separate performance capabilities accurately.

Additional data have appeared in the literature for other significant salt systems. Data from Slusser et. al.[2] on corrosion in equimolar sodium/potassium nitrate salts at 1250°F (677°C) are summarized in Fig. 7 using results from their 14- to 18-day exposures, annualized to a yearly corrosion rate. The data seem to follow the same basic rankings as for nitriding in ammonia, with the iron-base alloys showing significantly

Table IX Corrosion of Various Alloys in Pure NaCl at 1550°F (843°C) for 100 Hours

Alloy	Average Metal Affected (Mils)
188	2.0
556	2.6
214	3.1
304	3.2
446	3.2
316	3.2
X	3.8
310	4.2
800H	4.3
625	4.4
RA330	4.6
617	4.8
230	5.5
S	6.6
RA333	7.5
600	7.7

greater attack.

Data from Coyle et al.[3] are available to compare alloy performance in eutectic sodium/potassium carbonate salts at 1650°F (899°C). A candidate thermal storage medium, this salt produced the various corrosion results shown in Fig. 8. These results were obtained by exposing the various materials for a period of 21 days. No clear compositional trend emerges from the data, which show alloy X to be the best performer, with alloys No. 214, No. 188, No. 800H and No. 556 grouped closely behind.

Complex Process Environments

Complex process environments can be defined as those exhibiting the potential for several forms of high-temperature corrosion to take place. Clearly, it is very difficult to judge which, if any, laboratory test results to utilize in attempting to recommend materials for such environments. Results such as those discussed here, or those presented previously for one-dimensional phenomena such as sulfidation or chlorination[1], can be useful in a general sense. The selection of appropriate materials to use, however, can only be performed with confidence in the light of actual field test data when it is known that multi-dimensional corrosion phenomena are potentially involved.

A good example of this is the selection of materials for waste incineration facility components. Fig. 9 shows the results of field tests performed for 550 hours in a chemical waste incinerator burning acid wastes generated from the production of electronic circuit boards. The acids included CH_3COOH, HCl, HNO_3 and H_2SO_4, all partially neutralized with additions of various alkali hydroxides. Obviously, this 1400°F environment could involve sulfur chlorine and various salts, so laboratory data

Table X Corrosion of Various Materials Exposed to 1250°F (677°C) Flue Gases from a Scrap Aluminum Remelting Furnace for 1150 Hours.

Alloy	Average Metal Affected (Mils)
556	2.0
625	5.0
X	10.0
310	12.0
309	17.0
316	20.0
304	24.0

cannot easily predict alloy performance.

Alloys No. 556 and No. 188 were particularly good performers in the field tests in this environment, as they were in the municipal incineration environment reviewed previously[1]. Here materials of construction such as type 316 stainless or alloy No. 600 exhibited 3X to 10X the amount of corrosion attack shown by alloy No. 556.

A different application with perhaps similar environment aspects is waste heat recuperation in the aluminum melting industry. Table X contains the results of field component tests conducted in the 1250°F (677°C) flue gases of a scrap aluminum can recycling furnace. Various ingredients in the environment included sulfur, chlorine and molten salts. Once again, alloy No. 556 was the best of the materials subjected to this 1150-hr test, out-performing the austenitic stainless steels and nickel-chromium alloys by over five to one.

Summary

It has been shown that there are advanced materials available to the industrial heating industry which, despite their higher relative initial costs, can offer significant performance advantages and life-cycle cost savings over the full term of a component's useful life. These advanced materials possess generally superior resistance to corrosion in elevated temperature environments, and in some cases combine that resistance with outstanding strength at very high temperatures. Programs continue to generate field and laboratory test data to help qualify these materials for use in an increasing number of applications which exhibit severe service conditions.

References

1. G.Y. Lai, M.F. Rothman and D.E. Fluck, INDUSTRIAL HEATING, August, 1985, pp. 18-22.
2. J.W. Slusser, J.B. Titcomb, M.T. Heffelfinger and D.R. Dunbobbin, JOURNAL OF METALS, July, 1985, pp. 24-27.
3. R.T. Coyle, T.M. Thomas and G.Y. Lai, JOURNAL OF MATERIALS FOR ENERGY SYSTEMS, March, 1986, pp. 345-352.