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A NI-CO-CR-SI ALLOY FOR HIGH-TEMPERATURE CORROSION RESISTANCE IN WASTE INCINERATORS

C. M. Antony, S. K. Srivastava, G. Y. Lai

ABSTRACT

A new Ni-Co-Cr-Si base alloy, HAYNES® HR-160™ alloy, has been developed for severely corrosive high-temperature environments typical of waste incineration. The major characteristics of the alloy are 28% chromium and 29% cobalt in conjunction with 2.75% silicon. Silicon and cobalt were found critical in resistance to sulfidation attack. Laboratory corrosion testing in an Ar-5%H_2-5%CO-1%CO_2-0.15%H_2S test gas demonstrate the alloy's performance relative to 601 and RA85H® alloys. Yield strength and thermal stability data are presented for the temperature range 550-1200°C (1000-2200°F). Field test results of HR-160, 601 and RA85H alloy coupons exposed to 870°C (1600°F) for 1,800 hours in the waste heat recovery boiler of an industrial waste incinerator are discussed. Results are analyzed to focus on the resistance of HR-160 alloy to waste incineration environments.

THE WASTE INCINERATION COMBUSTION PROCESS creates environments which are very corrosive. Flue gases typically contain S, Cl, K, Zn, Pb, P and other ash/salt forming constituents which can rapidly corrode materials of construction.

Often the heat produced by incineration is recovered in some type of heat recovery system and transformed into a useful form of energy such as electricity. Heat recovery systems contain various metallic components such as heat exchangers, superheaters, tube supports and shields, soot blowers, and thermowells, among others, all continuously exposed to the combustion or flue gas environment. These are metallic due to higher ductility and better thermal transfer properties in comparison with the more corrosion-resistant ceramics.

The complex and corrosive nature of the incineration environment coupled with high temperatures can lead to premature metallic component failure. Specifying materials solely for service in noncorrosive, high-temperature environments is somewhat straightforward and well understood. However, the effects of corrosion on base metal properties and subsequent life expectancy is not well known and difficult to predict.

Development efforts at Haynes International, Inc. have focused on fundamental understandings of microstructure/property relationships in controlled environments. The resultant data are then used to predict alloy performance in the field. Waste incineration environments tend to be so complex and vary so much over time that laboratory testing in controlled environments is sometimes inadequate to accurately predict field performance. To reduce the uncertainty surrounding applicability of laboratory test results, test racks containing potential candidate alloys are used for in-situ testing. The racks are exposed to actual process gas streams thus minimizing the degree of uncertainty in selecting materials based solely on laboratory testing. Antony, et al. (1, 2) reviewed the correlations between laboratory data and field trial results for soot blowers, dampers, thermowells and feed chutes operating in incineration environments. They found good correlation between laboratory data and the field trial results.

A new Ni-Co-Cr-Si alloy was developed by Haynes International, Inc. to resist the complex and aggressive nature of waste incineration environments. Combustion environments and related incineration performance of this alloy compared to a wide range of alloys has been described by Lai (3). The alloy displays better resistance to sulfidation attack and other ash/salt deposits in comparison with a wide range of commercially available alloys for incineration applications including 601 and RA85H alloys (see Table 1 for elemental compositions).

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HR-160 is a trademark of Haynes International, Inc.
RA85H is a registered trademark of Rolled Alloys, Inc.

Table 1

Nominal Compositions of Alloys Used in Study

	Wt. %							
Alloy	Ni	Fe	Cr	Co	Mo	W	C	Others
HR-160	Bal	2	28	29	-	-	.06	2.75Si
601	Bal	14	23	-	-	-	.05	1.4Al, .5Cu
RA85H	14.5	Bal	18.5	-	-	-	.20	3.5Si, 1Al

Laboratory data in controlled environments, and results of a field trial in an industrial application, will be reviewed. It was found that laboratory findings supported field performance very well in this example, and that this Ni-Co-Cr-Si alloy is well-suited for use in severely corrosive waste incineration applications.

CORROSION MODES

Sulfidation and chloride attack are the two most frequent modes of corrosion in waste incinerators and the presence of chlorine and/or sulfur is very common for municipal and industrial incinerators (4, 5). Many times they occur in combination by forming metal sulfides and volatile chlorides.

Chloride attack is very prevalent in incineration environments and typically occurs when HCl and Cl_2 are present. Iron forms two types of chlorides, $FeCl_2$ and $FeCl_3$. The melting point of $FeCl_2$ is 676°C (1249°F) while that of $FeCl_3$ is 303°C (577°F), making it very unstable. Nickel, on the other hand, reacts with chlorine to form $NiCl_2$ which has a melting point of 1030°C (1886°F). The addition of nickel as an alloying element improves resistance to chloride attack as illustrated in Figure 1. (6)

The addition of oxygen in a chlorine bearing environment results in the formation of oxychlorides. Cobalt base alloys containing tungsten and nickel base alloys containing molybdenum do not perform well in environments containing chlorine and oxygen due to the formation of oxychlorides of molybdenum and tungsten.

In HCl environments, nickel-base alloys containing molybdenum or tungsten provide relatively good performance. Adding oxygen to HCl environments accelerates the corrosion of iron due to the formation of highly volatile $FeCl_3$. No similar data is available for nickel or cobalt.(7)

Sulfidation is another critical corrosion mode in incineration environments. Sulfur may be present in the forms of SO_2 and SO_3 in combustion processes which utilize excess air for complete combustion. Sulfur is also found in the form of H_2S in reducing environments. Reducing environments are more corrosive than oxidizing environments due to low oxygen activities and increased domination by sulfidation. When oxygen activities are higher, oxidation dominates and sulfidation is less predominant. Nonetheless, when sulfidation and oxidation modes are involved, sulfidation is generally the critical mode.

For high-temperature alloys, the formation of iron, nickel, cobalt and chromium sulfides are the driving forces for determination of long-term performance. Chromium sulfides are more stable than the sulfides of iron, nickel and cobalt. Some metal-metal sulfides have low melting points such as 635°C (1175°F) for Ni-Ni_3S_2, 880°C (1616°F) for Co-Co_4S_3 and 985°C (1805°F) for Fe-FeS.(7)

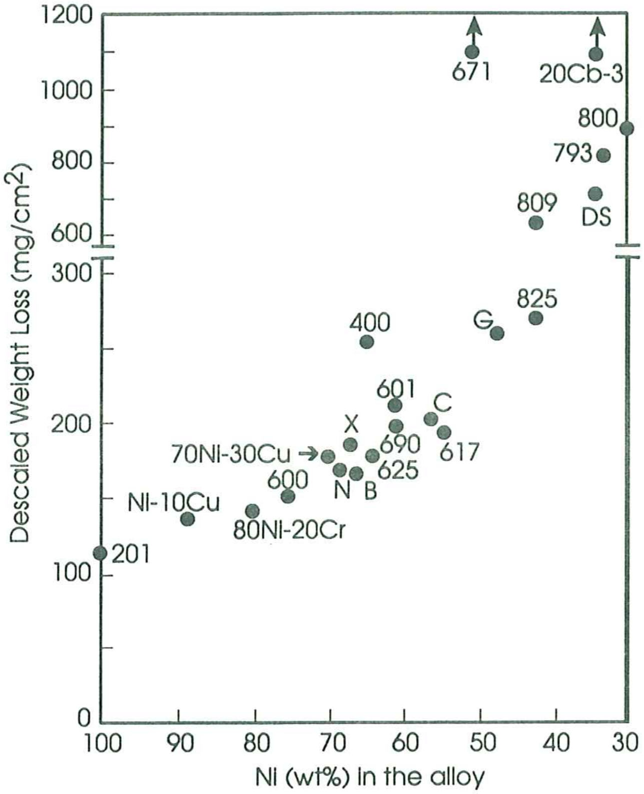


Figure 1: Effect of nickel content on corrosion resistance of a variety of Ni-containing alloys in Ar-$30Cl_2$ at 704°C(1300°F) for 24 hours.(6)

Most high-temperature alloys rely on chromium oxide surface scales for protection from corrosion. Once this scale is broken down, alloys fail very quickly due to breakaway corrosion. Thus, the importance of maintaining a stable and protective scale for prolonged component life.

The presence of ash/salt deposits can accelerate sulfidation or chloride attack. The impurities needed for ash/salt formation come from the feedstock (i.e., wastes for incineration). These include sodium, potassium, vanadium and chlorine, among others, which may combine to form salt vapors. These vapors deposit at lower temperatures and can accelerate the sulfidation or chloridation attack.

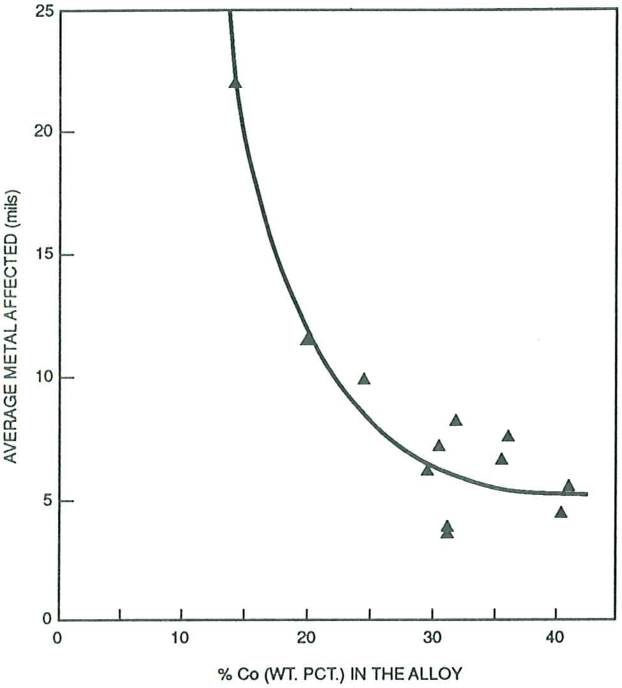
NI-CO-CR-SI ALLOY DEVELOPMENT

Development of a superior alloy system for sulfidizing and other aggressive systems was undertaken at Haynes International, Inc. to meet an important industry need. Besides environmental resistance, other key alloy design criteria included good forgeability, structural and thermal stability, and good weldability.

The overriding criterion was environmental resistance and initial efforts sought to develop the alloy composition based on resistance to sulfidation attack.

The composition was modified to produce the best combination of the aforementioned properties without compromising significantly on sulfidation resistance.

The alloy utilizes high chromium levels (28% by weight) to form a Cr_2O_3 surface oxide scale. The high chromium supply in the matrix continuously feeds the surface and rapidly forms the oxide scale in service. Cobalt is also known to improve resistance to sulfidation. The influence of varying amounts of cobalt in the matrix on sulfidation resistance is shown in Figure 2.



SULFIDATION TESTS
1600°F (870°C)/215 Hours
$Po_2 = 3 \times 10^{-19}$ atm,
$Ps_2 = 0.9 \times 10^{-6}$ atm

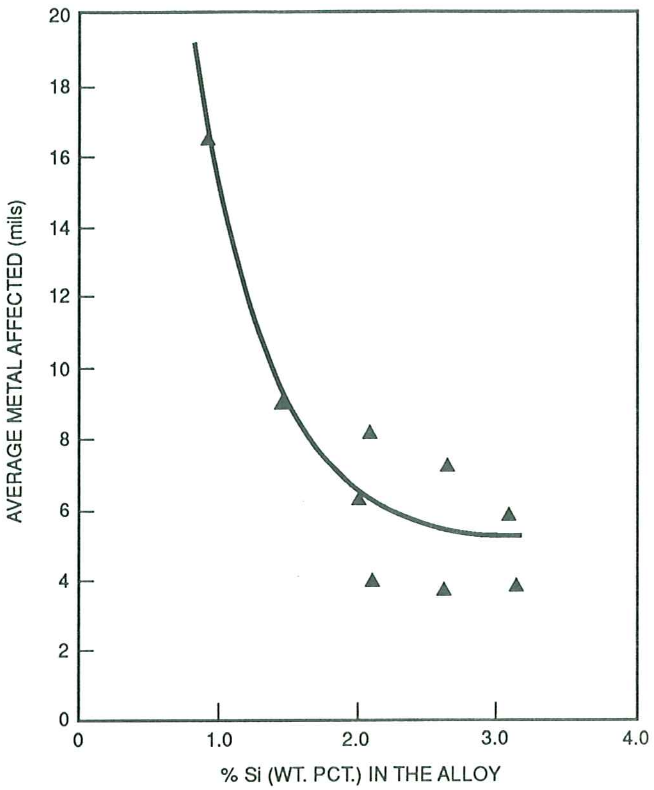
Figure 2: Influence of Co content on sulfidation resistance for HR-160 alloy.

Resistance is maximized at approximately 29 percent by weight. Similarly, silicon is known to be beneficial in resistance to sulfidation attack by improving the chromium oxide surface scale. The influence of varying amounts of silicon on the matrix composition is shown in Figure 3. As seen, at approximately 2.75 percent by weight, the metal affected by sulfidation is minimized.

Nickel is added to impart structural and thermal stability at levels which did not compromise the alloy's sulfidation resistance. Iron was kept low to improve weldability and forgeability.

HIGH TEMPERATURE CORROSION RESISTANCE

Comparative laboratory sulfidation tests were carried out in a test gas of $Ar\text{-}5\%H_2\text{-}5\%CO\text{-}1\%CO_2\text{-}0.15\%H_2S$ with a $Po_2 = 3 \times 10^{-19}$ atm and $Ps_2 = 0.9 \times 10^{-6}$ atm.



SULFIDATION TESTS
1600°F (870°C)/215 Hours
$Po_2 = 3 \times 10^{-19}$ atm,
$Ps_2 = 0.9 \times 10^{-6}$ atm

Figure 3: Silicon contribution to the chromium oxide scale protection against sulfidation attack for HR-160 alloy.

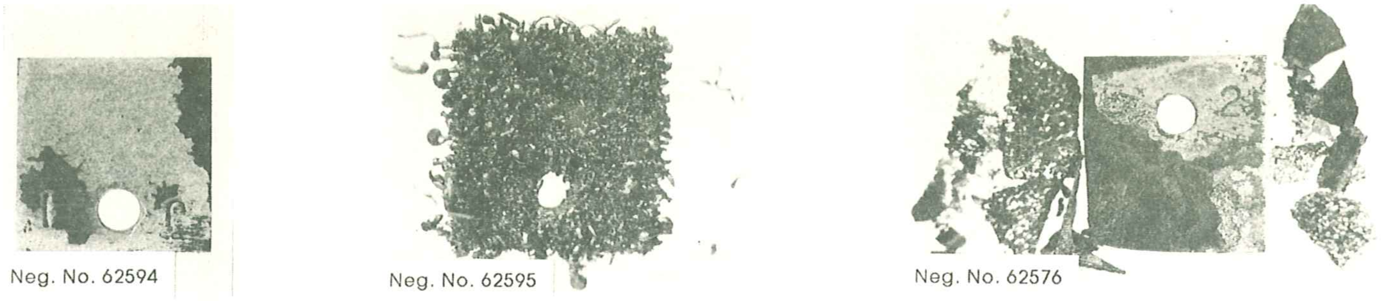
This gas is a reducing environment and the sulfur potential is such that nickel sulfides will form.

Figure 4 shows individual coupons of HR-160, 601 and RA85H alloys after exposure at 870°C (1600°F) for 500 hours. As seen, both RA85H and 601 show evidence of severe surface scaling. The HR-160 alloy sample shows no evidence of scaling and maintains sharp corners.

Table 2 lists metal loss and maximum attack for HR-160 and 601 alloys following 215 hours in the same test gas. HR-160 alloy had 0.13 mm of attack and 601 alloy suffered complete coupon attack in 215 hours. The 601 alloy did not perform well in this environment possibly due to its very high nickel content. No RA85H alloy results are available at this time.

MECHANICAL PROPERTIES

The HR-160 alloy possesses very good high-temperature mechanical strength. This is due in part to its high nickel and cobalt contents. Figure 5 shows the 0.2% yield strengths for HR-160, 601 and RA85H alloys. HR-160 alloy behaves very similar to 601 alloy at temperatures above 900°C and is stronger than RA85H alloy at temperatures above 800°C.



HR-160 601 RA85H

Figure 4: Test coupons of HR-160, 601 and RA85H alloys following 500 hours exposure in $Ar-5\%H_2-5\%CO_2-0.15\%H_2$ at 870°C(1600°F) .

Table 2

Sulfidation Tests at 871°C (1600°F) for 215 Hours in
$Ar-5\%H_2-5\%CO_2-0.15\%H_2S$ (Vol %)
($Po_2 = 3 \times 10^{-19}$ atm, $Ps_2 = 0.9 \times 10^{-6}$ atm)

Alloy	Metal Loss mm (mils)	Maximum Metal Affected mm (mils)
HR-160	.01 (0.4)	.13 (5.1)
601	1.1 (43.3)	sample consumed in 215 hours

Table 3 lists the stress to cause rupture in 1000 hours at 760, 870 and 980°C. Again, HR-160 alloy is shown to be appreciably stronger than RA85H alloy. In contrast to tensile properties, HR-160 alloy displays strength levels 15-25% higher than 601 alloy at all three temperatures.

Thermal stability is critical for extended high-temperature service. Table 4 shows tensile properties for HR-160 alloy following 1,000-hour aging at intermediate temperatures. The alloy retains reasonable ductility following prolonged exposure at temperature and is considered stable for extended service conditions.

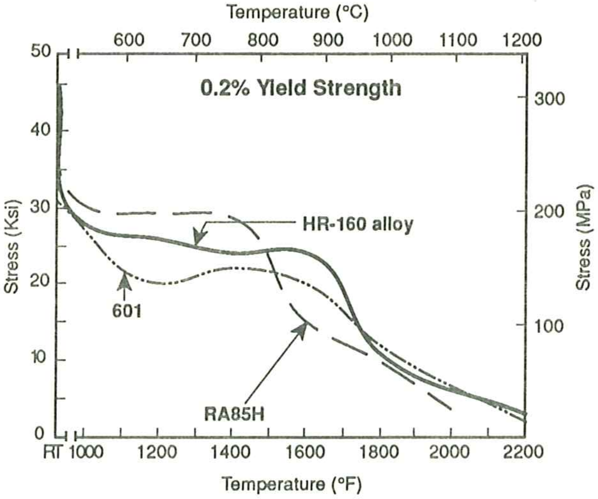


Figure 5: Comparison of the 0.2% yield strengths for HR-160, 601 and RA85H alloys.

Table 3

1,000 Hour Stress-Rupture Strength
Stress, MPa (Ksi)

Alloy	760° (1400°F)	870°C (1600°)	980°C (1800°F)
HR-160	76 (11.0)	40 (5.8)	19 (2.7)
601	64 (9.3)	30 (4.3)	14 (2.1)
RA85H	52 (7.6)	21 (3.0)	6 (0.9)

FIELD TEST

A large chemical producing company operates an industrial waste-to-energy incinerator to dispose of its industrial wastes, principally flammable materials. Each year, approximately 11.5 million gallons of wastes are incinerated. The incinerator provides process steam for on-site requirements along with electricity for general consumption.

After combustion in a large rotary kiln, flue gases enter a waste heat recovery boiler at temperatures in excess of 870°C (1600°F) and exit at 550°C (1025°F). The composition of the flue gas varies with the type of materials being incinerated, but one analysis showed evidence of CO_2, H_2O, N_2, CO, F, Cl and SO_2.

First row superheater tube shields were a chronic maintenance problem. No cost-effective material solutions emerged after substitution of various high-performance alloys. Substitutions were made based on laboratory corrosion data and field experience, but none were made with HR-160 or RA85H alloys. A field test rack trial encompassing a wide variety of alloys was suggested to ascertain the most suitable alloy. The rack contained HR-160, 601 and RA85H alloys, among others, and was exposed for 1,800 hours at 870°C (1600°F) at the bottom of the flue gas entry to the waste heat boiler. Actual heat shields were exposed to the middle of the flue gas stream.

The appearances of the HR-160, 601 and RA85H alloy coupons following exposure are shown in Figure 6. The rack was disassembled and depth of attack (metal loss + internal penetration) was determined metallographically. The metal loss was calculated from the changes in weight before exposure, and after exposure and descaling.

Table 4

HR-160 Alloy Thermal Stability

	RT Tensile Properties				
	0.2% YS		UTS		
Condition	MPa	Ksi	MPa	Ksi	% El*
annealed	317	46	738	107	73
aged 650°C(1200°F)/1000 hrs	352	51	814	118	35
aged 760°C(1400°F)/1000 hrs	365	53	924	134	31
aged 870°C(1600°F)/1000 hrs	310	45	696	101	19

*elongation in 1.4 inches

HR-160 601 RA85H

Figure 6: Appearance of individual coupons following 1,800-hour exposure in a waste heat boiler.

Results are presented in Table 5. The HR-160 alloy suffered the least amount of maximum attack, 0.50 mm (19.8 mils). The 601 and RA85H alloys suffered 0.72 mm (28.5 mils) and 0.95 mm (37.4 mils) of maximum attack, respectively.

The corrosion products were determined for each coupon using scanning electron microscopy/energy dispersive x-ray spectroscopy (SEM/EDX). The contaminants consisted of S, K, Zn, Ca, Si, etc. Chlorine was not detected, but in earlier trials, Cl was observed using SEM/EDX. Additionally, Cl was detected in a flue gas sample analysis.

Figure 7 shows the analysis of surface contaminants on the HR-160 alloy coupon. All areas showed evidence of S, K and Zn, although the S is relatively low compared with other coupons. The RA85H alloy coupon exhibited a S intensity reading as high as 36% and 601 alloy had levels up to 22%.

The sample cross-sections were also examined. Figure 8 shows the cross-section of the HR-160 alloy coupon. Evidence of S is seen in locations 1 and 5 from area A, and location 6 from area B. Location 6 had the highest S content at 7.7% relative intensity.

Table 5

Corrosion Attack of Field Test Coupons
1600°F/1800 hours

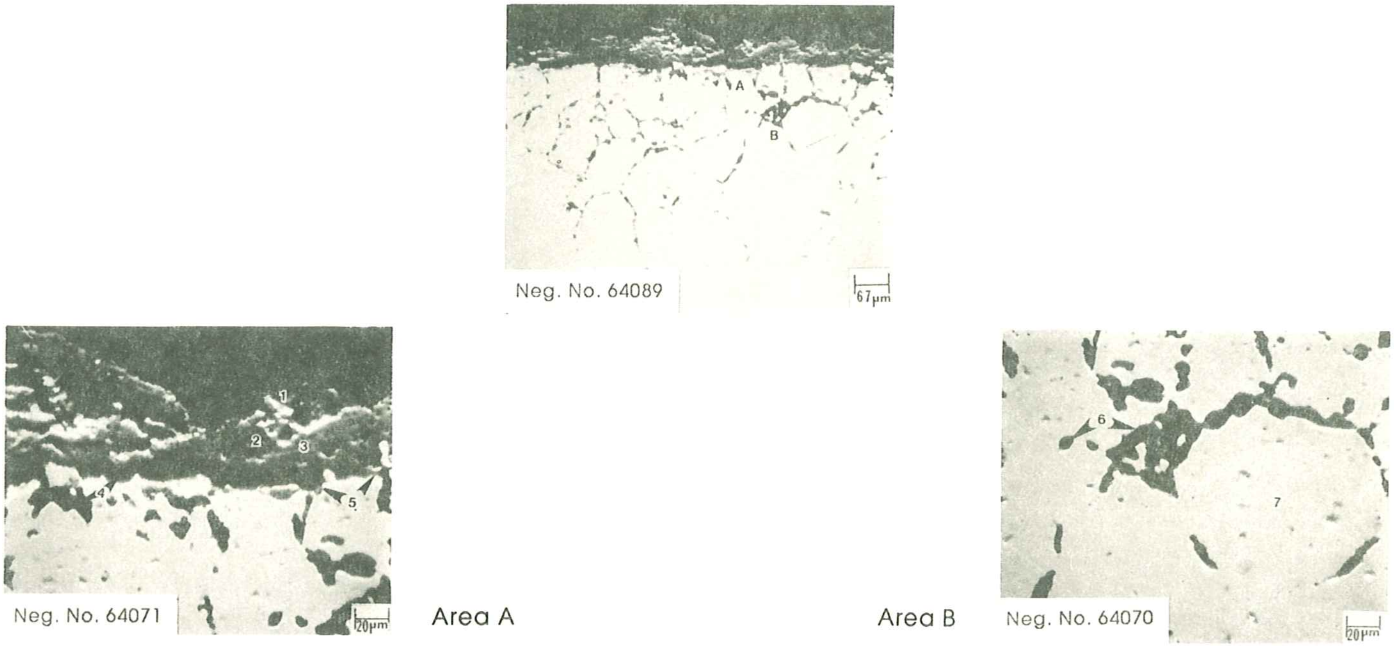
			Total Metal Affected			
	Metal Loss		Average		Maximum	
Alloy	mm/side	mils/side	mm/side	mils/side	mm/side	mils/side
HR-160	0.05	1.8	0.44	17.3	0.50	19.8
601	0.04	1.5	0.56	22.2	0.72	28.5
RA85H	0.16	6.4	0.64	25.3	0.95	37.4

Total Metal Affected = metal loss + internal attack

Semi-Quantitative Analysis Relative Intensity, %

Area	Al	S	Cr	Fe	Ni	Ti	Zn	K	Ca
1	-	2.1	63	5.3	4.0	5.6	14	2.0	3.1
2	.2	5	92	-	2.1	2.8	.2	.6	1.5
3	-	3.0	78	1.5	1.5	3.1	1.7	1.6	11
4	-	1.5	48	5.6	33	2.9	2	.1	10

Figure 7: EDAX analysis of surface corrosion products on HR-160 alloy coupon following 1,800-hour exposure test.



Area A

Area B

Semi-Quantitative Analysis Relative Intensity, %

Area	Al	S	Cr	Fe	Ni	Ti	Zn	K	Ca	Si	Co
A1	.8	2.1	64	6.1	1.3	3.2	19	1.3	2.2	-	-
A2	.4	-	37	-	-	1.1	1.8	17	-	42	.5
A3	.2	-	72	-	-	1.2	15	3.0	-	5.4	2.7
A4	-	-	7.6	.8	8.4	-	-	-	-	78	4.9
A5	-	3.4	67	.6	1.3	4.4	-	.7	1.0	21	1.5
B6	-	7.7	31	1.0	19	-	-	-	-	27	14
B7	-	-	40	.9	35	-	-	-	-	1.0	23

Figure 8: Cross-section EDAX analysis of HR-160 alloy coupon following 1,800-hour exposure test.

The mode of attack was believed to be high-temperature corrosion involving salts. The primary mode is believed to be sulfidation, but chlorine may also be a contributing factor. As a result of this field trial, HR-160 was selected for the shields and has performed satisfactorily since installation. To date, the HR-160 alloy shields have outlasted original shields by 2-1/2 times and they are still in service.

Extensive field tests in other waste incineration environments have been performed with HR-160 alloy. Results are summarized in Table 6.

CONCLUSIONS

1. A Ni-Co-Cr-Si alloy system, HAYNES HR-160 alloy, is shown to resist high-temperature corrosion attack typical of waste incineration environments.
2. Controlled laboratory sulfidation testing in Ar-5%H_2-5%CO-1%CO_2-0.15%H_2S showed HR-160 alloy displays better resistance to attack compared to RA85H and 601 alloys.
3. The elevated-temperature mechanical strength of HR-160 alloy is comparable to 601 alloy and better than RA85H alloy.
4. A field test rack trial in an industrial waste-to-energy facility showed HR-160, 601 and RA85H alloys in relative order of corrosion resistance. Based on this trial, HR-160 alloy was successfully substituted in the incineration plant.

REFERENCES

1. C. M. Antony, S. K. Srivastava and G. Y. Lai, "A Review of Two High-Temperature Alloys For Waste Incineration Applications", in Proceeding of incineration Conference 1990, San Diego, CA, p. 7.6.1.
2. C. M. Antony, S. K. Srivastava and G. Y. Lai, "Solving a Waste Incinerator Soot Blower Element Material Problem", UK Corrosion Conference 90, Corrosion Engineering Association, October 1990, Manchester, U.K.
3. G. Y. Lai, "A New Alloy For Solving Fireside Corrosion Problems in Waste Incinerators", Paper No. 249, Corrosion/91, NACE, Houston, TX.
4. N. Bolt, A. S. DeClercq and E. J. A. Vogelaar, "Fireside Corrosion in Dutch Waste Incinerations", Materials and Corrosion, Vol. 40, No. 2., March 1989, p. 142.
5. O. Forsen and S. Ylasaari, "Comparison of Different Boiler Tube Materials and the Corrosion Resistance in Burning of Municipal Waste", Materials and Corrosion, Vol. 40, No. 3, March 1989, p. 147.
6. R. H. Kane, in "Process Industries Corrosion", B. J. Moritz and W. I. Pollock, Ed., National Association of Corrosion Engineers, Houston, 1986, p. 45.
7. G. Y. Lai, High Temperature Corrosion of Engineering Alloys, ASM International, Materials Park, OH (1990), p. 94-102 and p. 119-123.
8. G. R. Smolik and J. D. Dalton, Paper No. 207, Corrosion 189, NACE, Houston, TX.

Table 6

HR-160 alloy Performance Capability in Various Waste Incinerators

		Performance as Compared to Current Materials	
Incinerator Type	Field Test Conditions	Improvement Factor	Materials Compared
Municipal Waste Incinerators	980-1090°C(1800-2000°F) S, Cl, K, Zn, Pb	17	Stainless Steels
	700-760°C (1300-1400°F) S, Cl, K, Zn, Pb	6	556
		9	625
		12	825
		15	304
		12	446
Industrial Waste Incinerators	870-930°C (1600-1700°F) S, Cl, K, etc.	5	556
		20	Stainless Steels
Hospital Waste Incinerators	650-760°C (1200-1400°F) S, Cl, Zn, etc.	7	304 and 316
Low Level Radioactive Waste Incinerators (from Smolik & Dalton(8))	590-760°C (1100-1400°F) S, Cl, Zn, P, Pb, etc.	9	310
		16	316
		18	600
Chemical Waste Incinerator	480°C (900°F), Pb, K, S, P, Zn and Ca	15	Carbon Steel