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A NEW ALLOY FOR SOLVING FIRESIDE CORROSION PROBLEMS IN WASTE INCINERATORS

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ABSTRACT

Combustion environments generated by incineration of household garbage (municipal wastes) as well as industrial wastes are described. Principal corrosion modes in various incinerators are discussed. The corrosion behavior of various alloys in incinerators is presented. The paper focuses on a new commercial alloy based on the Ni-Co-Cr-Si system and its performance capability in various incinerators.

Keywords: municipal wastes, industrial wastes, low level radioactive wastes, incinerators, sulfidation and chloride attack

INTRODUCTION

Waste incineration has become a viable technology for disposal of either household garbage or industrial wastes. Incineration significantly reduces the volume of the wastes, allowing a more effective use of landfills which are becoming increasingly scarce. Many incinerators, such as municipal waste incinerators burning household garbage and some large chemical waste incinerators, frequently recover the heat generated during the combustion of wastes and convert it into useful forms of energy, such as electricity. These incinerators have characteristics similar to coal-or oil-fired boilers. Wastes, in this case, become essentially a fuel for generation of electricity. The most commonly observed impurities that are important in affecting high temperature corrosion for fuel oil, coal and wastes (either household or industrial wastes) are illustrated in Table 1. The wastes generally contain significantly more impurities or contaminants than fuel oil or coal. As a result, the combustion environments generated by incineration of wastes are generally significantly more corrosive than those generated by burning fuel oil or coal.

ENVIRONMENTS AND CORROSION MODES

Daniel[1] of Babcock and Wilcox reported the chemical analysis of a refuse-derived fuel (i.e., segregated wastes) for a municipal waste incinerator (Table 2). These wastes were found to contain sulfur, chlorine, sodium, potassium, zinc, lead and others. Sulfur, in this particular case, was not considered high when compared to fossil fuels such as coal or fuel oil. Chlorine was considered to be high, significantly higher than US coal but at par with British coal which is known to be high in chlorine. Other corrosive impurities include sodium, potassium, zinc and lead. An analysis of the deposits obtained from a superheater tube of a municipal waste incinerator was shown to contain significant amounts of sulfates.[1] Smolik and Dalton[2] of EG&G reported the chemical composition of the deposits formed on the heat exchanger of a low level radioactive waste incinerator, which burned about 10% wood, 5% rubber, 55% plastics and 30% cloth, paper and leather (Table 3). Both sulfur and chlorine were observed. A significant amount of zinc was detected, along with other impurities including, Na, Pb, P, Sb, Cd, etc. The average chlorine content in the wastes was estimated to be about 0.6%. The level of chlorine detected in the deposits was significantly lower. It was probably because many chlorides were highly volatile. Krause[3] indicated that the average chlorine content for the municipal waste was about 0.5%, present as polyvinylchloride (PVC) plastic as well as inorganic (e.g., NaCl).

Two major corrosion modes were most frequently reported. They were sulfidation and chloride attack, and in many cases, combination of both modes. Fluck, et al.[4] and Srivastava et al.[5] observed severe sulfidation attack of Ni-base alloys, such as alloys 690, X and C-276 in municipal waste incinerators at temperatures of 750-980°C (1400-1800°F). Stainless steel "erosion" shields (or tube shields) used to protect the superheater tubing from corrosion attack frequently failed by sulfidation attack in municipal waste incinerators.[6] Harris et al.[7] and Chou et al.[8] also observed sulfidation attack on Ni-base alloys in municipal waste incinerators. Sulfidation attack was also observed in environments generated by burning hospital, chemical and other industrial wastes. Tapping et al.[9] reported sulfidation attack for alloys in a low level radioactive waste incinerator burning combustible solids, waste oils and solvents. Dias and Allegree[10] reported severe sulfidation of high nickel alloy thermowells in an incinerator burning concentrated cooling water wastes generated by a coal gasification plant.

Chloride attack is another important corrosion mode for the fireside corrosion in incinerators. Chlorine has been found in flue gas streams produced in incinerators burning hospital wastes,[11] low level radioactive wastes[2,9] and municipal wastes.[3,12-16] Whitlow et al.[17] concluded that the stainless steels and several high performance alloys tested in a municipal waste incinerator at 650-700°C suffered chloride attack. The severe corrosion attack of Co-Ni-Cr-W alloy 188 observed by Whitlow et al. was indicative of chloride attack. This alloy was found to be susceptible to chlorination presumably due to the formation of volatile tungsten oxychlorides.[18]

In many cases, the fireside corrosion in incinerators is the result of combined sulfidation and chloride attack.[6] This is illustrated in Figure 1 which shows both sulfidation and chloride attack of an Fe-Ni-Co-Cr alloy in an industrial waste incinerator.[6] Because of high temperature (i.e., about 900°C) in this case, chloride attack resulted in the formation of internal voids due to volatile metal chlorides formed.

Another important feature for the fireside corrosion in waste incinerators is the ash/salt deposit. Many components that failed by fireside corrosion contained ash/salt deposits. It is well known that the ash/salt deposit can accelerate high temperature corrosion. The sulfate-rich salt deposit is known to accelerate sulfidation attack, known as "hot corrosion" in gas turbines. Fuel ash corrosion in fossil-fired boilers is another well known example. The formation of low melting-point salts may be responsible for the fireside corrosion of furnace tubes and superheater tubes.[3, 13, 16] A general review of incineration environments and modes of corrosion in waste incinerators can be found elsewhere.[6]

MATERIALS PERFORMANCE

One effective means for generating corrosion data useful in assisting the selection of materials for applications in waste incinerators is to perform rack tests in operating systems. Additionally, the environment and predominant mode of corrosion can be better understood by analyzing the corrosion behavior of different alloy systems in a rack test. The chemical compositions of the alloys discussed in this paper are tabulated in Table 4.

An alloy performance ranking in a waste incinerator where sulfidation dominated the corrosion reaction is illustrated in Table 5.[5] The Co-Ni-Cr-W alloy 188 was the best performer among the alloys tested. In another incinerator where chloride attack was dominating, alloy 188 was severely corroded.[17] The results of this rack test are summarized in Table 6.[17] The Co-Ni-Cr-W alloy (alloy 188) is susceptible to chlorination attack due to the formation of volatile tungsten oxychlorides.[18] Many incineration environments, however, contain both sulfur (sulfates) and chlorine (chlorides). Thus, the alloy that is capable of providing consistent, adequate performance in waste incinerators requires good resistance to both sulfidation and chloride attack.

A new Ni-Co-Cr-Si alloy (HAYNES alloy HR-160), which was originally developed for severely sulfidizing environments, was found to be resistant to both sulfidation and chloride attack. The alloy is a Ni-Co base utilizing high chromium (28%) and relatively high silicon (2.75%) to form a protective oxide scale. This oxide scale is Cr-riched, doped with silicon.[19] The performance of HR-160 alloy in comparison with various commercial alloys in a municipal waste incinerator at 700-760°C (1300-1400°F) was summarized in Table 7. Analyses of corrosion products and scales by scanning electron microscopy with an energy dispersive analyzer (SEM/EDX) showed sulfur, chlorine, potassium, zinc and lead. HR-160 alloy was found to perform nearly ten times better than alloy 188, and more than ten times better than stainless steels. In a hospital waste incinerator at 650-760°C (1200-1400°F), the alloy was also found to be significantly better than a stainless steel (0.5 mm/y or 18 mpy for HR-160 alloy vs. 3.1 mm/y or 121 mpy for Type 316). Major contaminants detected by SEM/EDX in the corrosion products in this case were sulfur, chlorine and zinc.

Field testing of this alloy has also been extensively performed as a weld overlay over existing commercial alloy thermowells, such as stainless steels and alloy 600 thermowells, in municipal and industrial waste incinerators. Typical life extension of more than ten times was achieved with an HR-160 alloy weld overlay at service temperatures up to 1090°C (2000°F).

Smolik and Dalton[2] investigated the corrosion behavior of various alloys in an incinerator burning primarily wood, rubber, plastics, cloth, paper and leather. Their test results are shown in Table 8. HR-160 alloy, again, demonstrated the performance capability significantly better than any of the current commercial alloys tested. A summary of field test results comparing the HR-160 alloy with some of the current commercial alloys is tabulated in Table 9. Also indicated in the table are the contaminants in the corrosion products of the sample detected by SEM/EDX analysis.

The discussion so far has focused on the fireside corrosion at temperatures about 650°C (1200°F) and higher. Severe fireside corrosion has also been encountered for furnace tubes and superheater tubes where the temperatures were below 650°C (1200°F) in municipal waste incinerators.[16,20,21] The temperatures were low, generally from 150 to 650°C (300 to 1200°F). Corrosion rates of 0.8-1.3 mm/y (30-50 mpy) for carbon steel furnace tubes in refuse-fired boilers,[21] and of 6 mm/y (232 mpy) for a 1Cr-0.6Mo steel superheater tubing [20] have been observed. Formation of low melting-point salts in ash deposits may be responsible for the corrosion of furnace tubes and superheater tubes.[3,13,16]

The corrosion behavior of HR-160 alloy at temperatures below 650°C (1200°F)has not been studied as extensively as that at high temperatures (i.e., 650°C and higher). One test was carried out in a chemical waste incinerator at about 480°C (900°F). After exposure for about 5800 hours, HR-160 alloy showed little corrosion in contrast to alloy 600 and carbon steel, which suffered significant corrosion attack, as illustrated in Figure 2. SEM/EDX analyses of the scales or corrosion products for these three alloys are tabulated in Table 10. Significant amounts of sulfur was detected for all three alloys. Other contaminants detected were Zn, K, Pb and Ca.

SUMMARY

The environments and principal modes of corrosion in waste incinerators are discussed. The combustion environments generated by incineration of municipal, hospital, chemical and other industrial wastes contain common corrosive contaminants which typically include sulfur, chlorine, sodium, potassium, zinc and lead. In general, at temperatures higher than 650°C (1200°F), sulfidation and/or chloride attack are frequently responsible for the corrosion reaction. For service temperatures below 650°C (1200°F), the corrosion reaction is far from clear. A new Ni-Co-Cr-Si alloy (HAYNES alloy HR-160) with high chromium (28%) and relatively high silicon (2.75%) was found to be extremely resistant to both sulfidation and chloride attack in incinerators burning municipal, hospital, low level radioactive and other industrial wastes. The alloy has outperformed many existing commercial alloys by more than tenfold.

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TABLE 1
SOME CORROSIVE IMPURITIES IN OIL, COAL AND WASTES

Oil	Coal	Wastes
S	Cl	Cl
Na	S	S
(V)	Na	Na
	K	K
		Zn
		Pb
		P
		Sb
		Cd

TABLE 2
CHEMICAL ANALYSIS OF A REFUSE-DERIVED FUEL*
FOR A MUNICIPAL WASTE INCINERATOR (From Daniel[1])

Element	Weight Percent
S	0.29
Cl	0.62
Na	1.08
K	0.77
Zn	0.02
Pb	0.05
Ca	3.88
Mg	0.28
Si	6.40
Al	0.72
C	41.5
H	9.0
O and other elements	34.6

* Includes moistures.

TABLE 3
CHEMICAL ANALYSIS OF DEPOSITS FORMED ON THE HEAT EXCHANGER OF A LOW LEVEL RADIOACTIVE WASTE INCINERATOR BURNING 10% WOOD, 5% RUBBER, 55% PLASTICS AND 30% CLOTH, PAPER AND LEATHER
(From Smolik and Dalton[2])

Element	Weight Percent
Cl*	0.02
S	8.0
Na	0.04
Zn	15.2
Pb	1.4
P	0.17
Sb	0.18
Cd	0.37
Ca	21.0
Cr	0.05
Cu	0.26
Fe	1.2
Ni	0.16
C	0.07

* The average chlorine content of the waste was estimated to be about 0.6%.

TABLE 4
CHEMICAL COMPOSITIONS (WT.%) OF THE ALLOYS DISCUSSED IN THE PAPER

Alloy	C	Cr	Ni	Co	Fe	Mo	W	Others
HAYNES®alloy HR-160	0.05	28.0	Bal.	29.0	2.0	-	-	Si 2.75
HAYNES alloy 230	0.1	22.0	Bal.	-	3.0*	2.0	14.0	La 0.02
HAYNES alloy 214	0.04	16.0	Bal.	-	3.0	-	-	Al 4.5, Y
HASTELLOY® alloy X	0.1	22.0	Bal.	1.5	19.0	9.0	0.6	
INCONEL® alloy 600	0.08*	15.5	Bal.	-	8.0	-	-	
INCONEL alloy 617	0.07	22.0	Bal.	12.5	1.5	9.0	-	Al 1.2
INCONEL alloy 625	0.1*	21.5	Bal.	-	2.5	9.0	-	Cb 3.6
INCOLOY® alloy 825	0.03	21.0	Bal.	-	30.0	3.0	-	Cu 2.2
HAYNES alloy 556	0.1	22.0	20.0	18.0	Bal.	3.0	2.5	Ta 0.6, La 0.02, N 0.2
INCOLOY alloy 800H	0.08	21.0	32.5	-	Bal.	-	-	Al 0.4, Ti 0.4
Type 304	0.08*	19.0	10.0	-	Bal.	-	-	
Type 316	0.08*	17.0	12.0	-	Bal.	-	-	Mo 2.5
Type 309	0.2*	23.0	13.0	-	Bal.	-	-	
Type 310	0.25*	25.0	20.0	-	Bal.	-	-	
Type 446	0.2*	25.0	-	-	Bal.	-	-	N 0.25*
HAYNES alloy 188	0.1	22.0	22.0	Bal.	3.0*	-	14.0	La 0.07

* Maximum

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TABLE 5
ALLOY RANKING OBTAINED FROM A RACK TEST AT 800°C WITH 954°C MAX. (1475°F WITH 1750°F MAX.) FOR 950 HOURS IN A MUNICIPAL WASTE INCINERATOR
(From Srivastava[5])

Alloy	Corrosion Rate mm/y (mpy)
188	1.8 (70)
556 alloy	1.9 (76)
617	3.1 (122)
Type 309	3.1 (124)
X	6.3 (249)
690	Partially destroyed in 950 hours

TABLE 6
ALLOY RANKING OBTAINED FROM A RACK TEST AT 650-700°C (1200-1400°F) FOR 6750 HOURS IN A MUNICIPAL WASTE INCINERATOR
(From Whitlow et al.[17])

Alloy	Corrosion Rate mm/y (mpy)
X	0.25 (10)
625	0.33 (13)
556 alloy	1.0 (41)
Type 310	2.3 (89)
188	Destroyed in 6750 hours
Type 316	Destroyed in 6750 hours
825	Destroyed in 6750 hours

TABLE 7
PERFORMANCE OF HR-160 ALLOY IN COMPARISON WITH EXISTING COMMERCIAL ALLOYS IN A MUNICIPAL WASTE INCINERATOR AT 700-760°C (1300-1400°F) FOR 1440 HOURS

Alloy	Corrosion Rate mm/y (mpy)
HR-160 alloy	0.3 (12)
556 alloy	1.7 (67)
625	2.7 (106)
188	2.9 (113)
214 alloy	3.3 (131)
825	3.8 (149)
Type 304	4.5 (179)
Type 446	>3.6 (143)
Carbon Steel	4.6 (183)

TABLE 8
RESULTS OF A FIELD TEST AT 590-750°C (1100-1380°F) FOR 1803 HOURS IN AN INCINERATOR BURNING 10% WOOD, 5% RUBBER, 55% PLASTICS AND 30% CLOTH, PAPER AND LEATHER
(From Smolik and Dalton[2])

Alloy	Corrosion Rate mm/y (mpy)
HR-160 alloy	0.18 (7)
800H	0.94 (37)
230 alloy	1.3 (50)
Type 310	1.6 (63)
556 alloy	2.7 (107)
Type 316	2.8 (109)
188	2.9 (112)
X	3.1 (124)
214 alloy	3.2 (124)
600	3.3 (129)

TABLE 9
HR-160® ALLOY PERFORMANCE CAPABILITY IN VARIOUS WASTE INCINERATORS

Incinerator Type	Field Test Conditions	Performance as Compared to Current Materials: Improvement Factor	Performance as Compared to Current Materials: 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 Radio-active Waste Incinerators (from Smolik & Dalton[2])	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

TABLE 10
SEM/EDX ANALYSES OF THE SCALES OR CORROSION PRODUCTS FORMED ON HR-160 ALLOY, ALLOY 600 AND CARBON STEEL AFTER 5800 HOURS OF EXPOSURE AT ABOUT 480°C (900°F) IN A CHEMICAL WASTE INCINERATOR

		SEM/EDX Semi-Quantitative Analyses (wt.%)										
Alloy	Area	Cr	Fe	Ni	Co	Ti	Si	S	K	Zn	Ca	Pb
HR-160	1	60.1	16.5	1.3	-	2.8	2.0	2.2	0.6	14.5	-	-
	2	62.8	3.3	0.4	-	1.0	23.3	1.0	1.2	7.0	-	-
	3	27.6	12.3	1.9	-	0.2	1.7	28.9	16.8	8.9	1.7	-
	4	19.5	6.3	0.8	-	0.9	13.4	32.5	20.9	1.8	3.9	-
	5	63.5	12.6	1.2	-	2.1	2.6	2.6	1.2	13.8	0.4	-
	6	91.7	1.0	1.3	1.0	0.7	3.7	-	-	0.6	-	-
600	1	-	-	13.2	-	-	-	66.8	9.2	0.2	1.7	8.9
	2	-	-	97.7	-	-	-	2.3	-	-	-	-
	3	-	-	60.8	-	-	-	37.1	-	2.1	-	-
	4	-	0.6	92.5	-	-	-	6.9	-	-	-	-
	5	-	3.1	58.4	-	-	-	37.9	-	0.6	-	-
	6	48.9	7.5	38.2	-	-	-	5.4	-	-	-	-
	7	3.5	0.4	67.7	-	-	-	28.4	-	-	-	-
	8	44.6	24.7	21.0	-	-	-	8.6	-	1.1	-	-
Carbon Steel	1	0.8	86.2	-	-	-	0.8	0.4	2.6	2.3	-	6.9
	2	-	34.3	-	-	-	-	29.1	-	-	35.5	1.1
	3	-	95.5	-	-	-	-	4.5	-	-	-	-
	4	-	77.2	-	-	-	-	22.0	-	-	0.8	-
	5	-	95.9	-	-	-	-	4.1	-	-	-	-

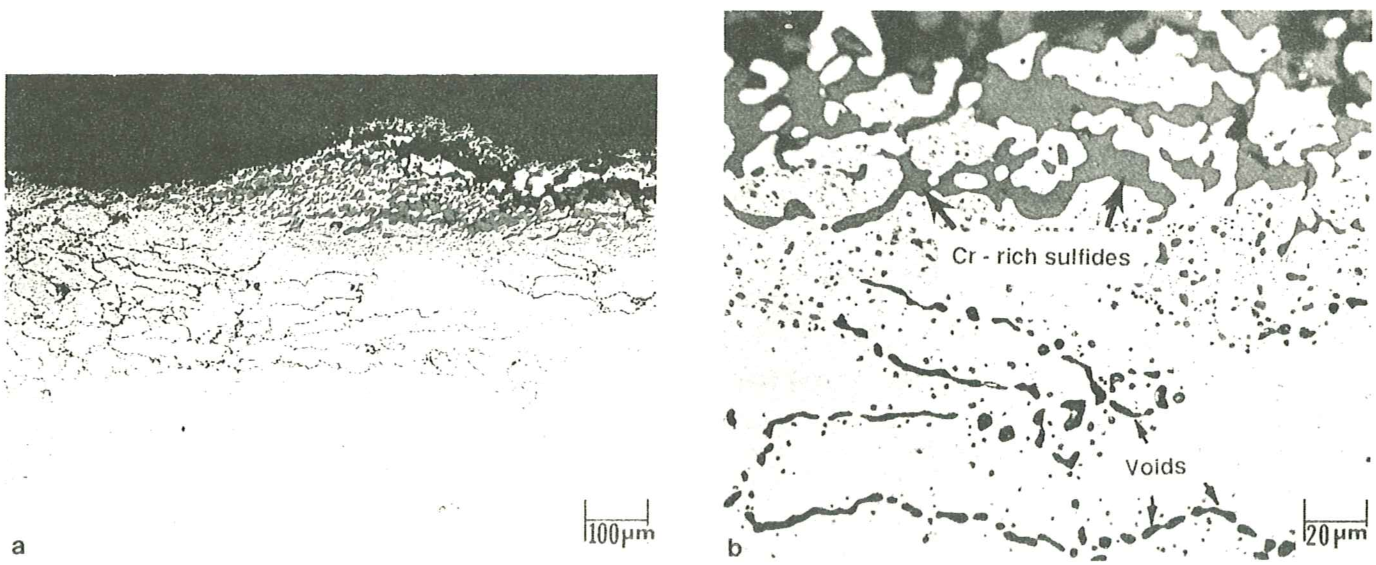

FIGURE 1: Fe-base alloy showing both sulfidation and chloride attack in an industrial waste incinerator at 900°C (1650°F).

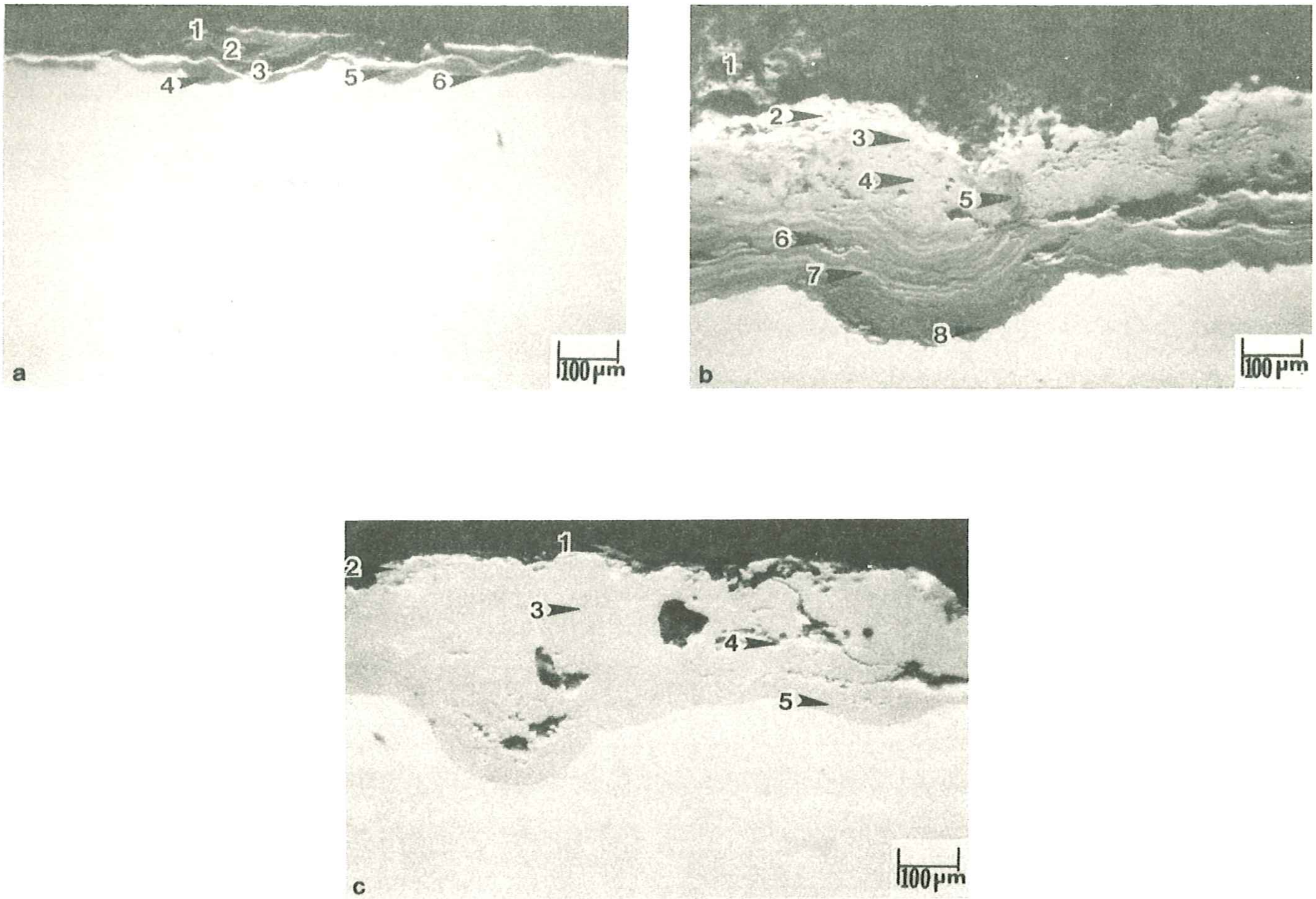

FIGURE 2: SEM photomicrographs showing (a) HR-160 alloy, (b) alloy 600 and (c) carbon steel after 5800 hours of exposure at about 480°C (900°F) in a chemical waste incinerator. The results of SEM/EDX analysis of the scales are tabulated in Table 10.