

High-Temperature Corrosion in Various Waste Incineration Environments

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ABSTRACT

High-temperature corrosion in waste-incineration imposes a complex set of environmental conditions on the materials of construction. The corrodents in the combustion environment may include sulfur, chlorine, sodium, potassium, zinc, lead and many other species. The paper discusses the modes of corrosion in the combustion environments involving several different types of wastes, such as, liquid hazardous wastes, waste water sludges and municipal wastes. In addition, the performance of various commercial alloys in these environments is discussed.

INTRODUCTION

Increasing scarcity of landfills has accentuated in recent years the trend toward the use of waste incineration as a means for disposal of waste material. The waste incineration system is expensive regardless of any payback from the generation of power and/or process steam, so designers and

operators will find it necessary to improve the integrity and reliability of the system. For this it is necessary to ensure the proper selection of materials for components of a waste incineration system. However, different systems of waste incineration (e.g., mass burning or refuse-derived fuels with or without waste heat recovery systems) and different origin and type of the waste (e.g., municipal wastes or industrial wastes) will impose different environmental conditions on materials of construction.

It is reasonable to assume that the combustion products generated from incineration of wastes will include a variety of corrodents that can cause corrosion problems for structural components in the waste incineration system. These corrodents may include S, Cl, Na, K, Zn, Pb, Sn, and many others. Some of the problems associated with the corrosion at temperatures up to approximately 1200°F (650°C) in municipal waste incineration boilers have been described by Krause.^(1,2) Recently Fluck et al.⁽³⁾ discussed

the performance of the materials at temperatures up to about 1800°F (980°C) in several waste incineration systems. In this paper, we will discuss the mode of corrosion in the combustion environments involving several different types of wastes.

EXPERIMENTAL PROCEDURE

As stated in the introduction, the environment produced in the waste incineration process is generally very complex. Therefore, field testing is considered to be a more reliable method to study the material's corrosion behavior. Typically, a test rack consisting of a set of test coupons of various alloys (Table 1) is assembled for exposure in the operating system. A typical test rack is shown in Figure 1. The coupons are typically 2-inch x 2-inch (5cm x 5cm) or 1-inch x 4-inch (2.5cm x 10.2cm) sheet samples. They are fitted on to a rod and are spaced by alumina spacers. At the conclusion of the exposure, the test rack is subjected to metallurgical evaluation. Each sample was cathodically descaled in a mixture of sodium hydroxide and sodium carbonate at about 1000°F (538°C) to remove the corrosion product. Average metal loss values were determined from the change in weight before and after the exposure and descaling. A cross section of the descaled sample was examined metallographically to determine the depth of internal penetration. The sum of metal loss and internal penetration is referred to as the total depth of attack (mils/side). Prior to descaling, the corrosion products on samples were examined using scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDS) to identify the contaminants and thus determine the mode of attack.

RESULTS AND DISCUSSION

Combustion of Liquid Hazardous Waste

Etching chemicals consisting of HCl, HNO₃, H₂SO₄ and CH₃COOH are used in the manufacture of electronic components. These acids are

normally neutralized by NaOH, KOH, NH₄OH and Ca(OH)₂ to pH of 8 prior to their disposal in a furnace. The liquid chemicals are placed in a barrel which is heated in a furnace to 1400°F (760°C) for approximately eight hours. The furnace off-gas is then incinerated. At the end of each batch operation, ash and other solid residues are discarded. A test rack consisting of coupons of various alloys was placed at the ductwork and exposed to the furnace off-gas at about 1400°F (760°C) for a total of 552 hours.

The results for the total depth of attack for alloys investigated are tabulated in Table 2. Most nickel alloys suffered catastrophic corrosion. The alloy 600 coupon was disintegrated. Sulfidation was found to be the predominant mode of corrosion attack. Stainless steels and nickel-base alloys all suffered breakaway corrosion. Figure 2 illustrates the breakaway corrosion of a nickel-base alloy. The corrosion products consist of numerous nickel-rich sulfides (marked "A") and chromium-rich sulfides (marked "B"). There is absence of any protective oxide film. The evidence of nickel sulfides formed on alloy 214 was confirmed by SEM/EDS analysis (Figure 3). The Fe-Ni-Cr-Co alloy 556 suffered the least attack. More importantly, the alloy still retained its protective oxide scale. Other corrosive contaminants, particularly chlorine, could also play a role in the degradation of materials in this environment.

Combustion of Waste Water Sludge

Waste water sludge, wood chips and fuel oil are incinerated in a fluidized-bed combustor. A test rack containing various test coupons was placed at the exhaust duct. The rack was exposed to the gas stream at about 1700°F (925°C) with a maximum temperature of 1850°F (1010°C). The system was kept at about 700°F (370°C) during shutdowns. The test rack was exposed to the elevated temperature for 4368 hours with 4824 hours of overall operation.

At the conclusion of exposure the samples were found covered with layers

of fly ash. X-ray diffraction analysis of the fly ash showed Al_2O_3 and possibly $Fe Al_2O_4$ and silicate. The results for metal loss and total depth of attack are summarized in Table 3. It is surprising to find that a Ni-Cr-Mo alloy (alloy C-276) suffered the most severe attack. The sample (about 0.125-inch thick) was partially consumed during the test. The morphology of attack on alloy C-276 is shown in Figure 4. SEM/EDS semi-quantitative analysis of the corrosion products formed on the alloy is shown in Figure 5. No major contaminants were detected in the corrosion products. However, analysis of the scale build up on alloy S indicated presence of several contaminants such as calcium, phosphorus, chlorine, and sulfur, as shown in Figure 6. The outer layer (identified as Area 1 and 2 of Figure 6) appears to be ash deposited on the sample during the exposure. There is some evidence of chlorine in the scale. It is extremely difficult to find chlorine in the corrosion products because of high volatility of metallic chlorides. This is confirmed by the analysis of the corrosion products formed on the samples which were severely chlorinated in the laboratory tests.⁽⁴⁾

It is not clear as to the major mode of corrosion involved in this combustion environment.

Combustion of Municipal Waste

A rack was placed in the superheater area of a municipal waste incineration boiler. The rack was exposed to the flue gas stream for 950 hours at about 1475°F (800°C) with a maximum temperature of 1750°F (925°C). The environment was found to be sulfidizing. Nickel-base alloys such as alloys 690, X, and C-276 suffered severe sulfidation attack. Figure 7 shows the severely sulfidized alloy 690. Sulfide phases were confirmed by the SEM/EDS analysis, as shown in Figure 8. Alloys such as alloys 188 and 556 with good sulfidation resistance were found to perform well in this environment. The corrosion attack of several alloys is summarized in Table 4.

CONCLUSIONS

Three different types of incineration environments were studied. They were the environments generated by burning the liquid hazardous waste containing H_2SO_4 and other acids, the waste water sludges, and municipal wastes. Sulfidation attack was the predominant mode of attack on uncooled specimens in the incineration of both the liquid hazardous wastes and municipal wastes. As a result, the alloys that performed well were those alloys with good sulfidation resistance, such as alloys 188 and 556. In the environment generated by the incineration of waste water sludge, the major mode of corrosion was not clearly understood.

REFERENCES

1. H. H. Krause, "High Temperature Corrosion Problems in Waste Incineration Systems", *J. Mat. for Energy Systems* 7 (4) (1986) 322.
2. H. H. Krause, "Hot Corrosion in Boilers Burning Municipal Solid Waste", to be published in Vol. 13, *Metals Handbook: Corrosion*.
3. D. E. Fluck, G. Y. Lai, and M. F. Rothman, "Selections of Materials for Combustion Environments Associated with Waste Incineration", Paper No. 333, *Corrosion/85*, NACE Meeting, March 1985, Boston, MA.
4. G. Y. Lai, Unpublished results, Cabot Corporation.

TABLE 1

NOMINAL CHEMICAL COMPOSITIONS OF ALLOYS TESTED

Alloy	Nominal Chemical Composition (Wt. Pct.)							
	C	Fe	Ni	Co	Cr	Mo	W	Others
Type 309	.20+	Bal	12	-	23	-	-	-
Type 310	.25+	Bal	20	-	25	-	-	-
Type 316	.08+	Bal	10	-	17	2.5	-	-
Alloy 800H	.08	Bal	33	-	21	-	-	Al=.38, Ti=.38
HAYNES [®] alloy No. 556	.10	Bal	20	18	22	3	2.5	Al=.2, Ta=.08, La=.02, Nb=.2, Zr=.02
Alloy 600	.08+	8	Bal	-	16	-	-	-
HAYNES alloy No. 214	.04	2.5	Bal	-	16	-	-	Al=4.5, Y (Present)
INCONEL [®] alloy 601	.10+	14.1	Bal	-	23	-	-	Al=1.35, Cu=1.0+
INCONEL alloy 617	.07	1.5	Bal	12.5	22	9	-	Al=1.2, Ti=.3, Cu=.2
INCONEL alloy 690	.03	9.5	Bal	-	30	-	-	-
HASTELLOY [®] alloy S	.02	3+	Bal	2.0+	15.5	14.5	1.0+	Al=.2, La=.02, R=.009
HASTELLOY alloy X	.10	18.5	Bal	1.5	22	9	0.6	-
HASTELLOY alloy C-276	.01+	5.5	Bal	2.5+	15.5	16	4	-
HAYNES alloy No. 188	.10	3+	22	Bal	22	-	14	La=.04

+ Maximum

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TABLE 2

Corrosion of Alloys in The Liquid Hazardous
Waste Combustion Environment

Material	Metal Loss mils (μm)	Total Depth of Attack mils (μm)
556	0.5 (12.7)	4 (101.6)
188	1.4 (35.6)	5 (127.0)
X	0.5 (12.7)	13 (330.2)
310SS	0.8 (20.3)	13 (330.2)
316SS	4.4 (111.8)	15 (381.0)
C-276	21.5 (546.1)	23 (584.2)
214	19.8 (502.1)	> 41 (> 1041.4)
600	> 70.0 (> 1778)	> 70 (> 1778)

TABLE 3

Corrosion of Alloys in The Waste Water Sludge Combustion Environment

<u>Alloy</u>	<u>Metal Loss</u>		<u>Total Depth of Attack</u>	
	mils	(μm)	mils	(μm)
X	0.6	(15.2)	3.5	(88.9)
556	0.7	(17.8)	3.6	(91.4)
601	0.5	(12.7)	4.0	(101.6)
S	0.9	(22.9)	4.4	(111.8)
800H	1.0	(25.4)	5.3	(134.6)
C-276	Partially Destroyed			

TABLE 4

Corrosion of Alloys in The Municipal Waste Combustion Environment

<u>Alloy</u>	<u>Maximum Depth of Attack</u>	
	mils	(μm)
188	7.6	(193.0)
556	8.2	(208.3)
617	13.2	(335.3)
309SS	13.4	(340.4)
X	27.0	(685.8)
690	Partially Destroyed	

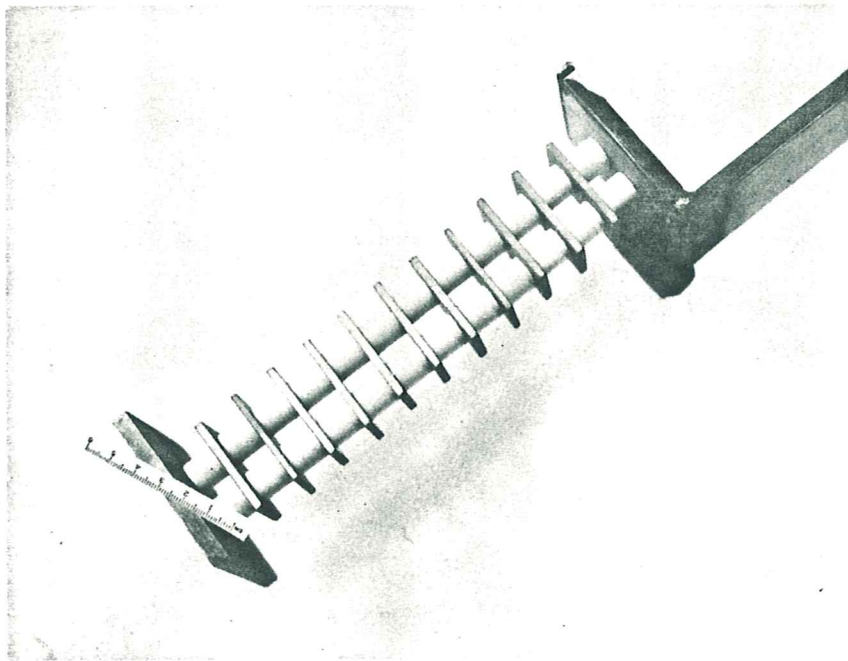


Figure 1 Typical test rack used for field testing.

Neg. No. 52769

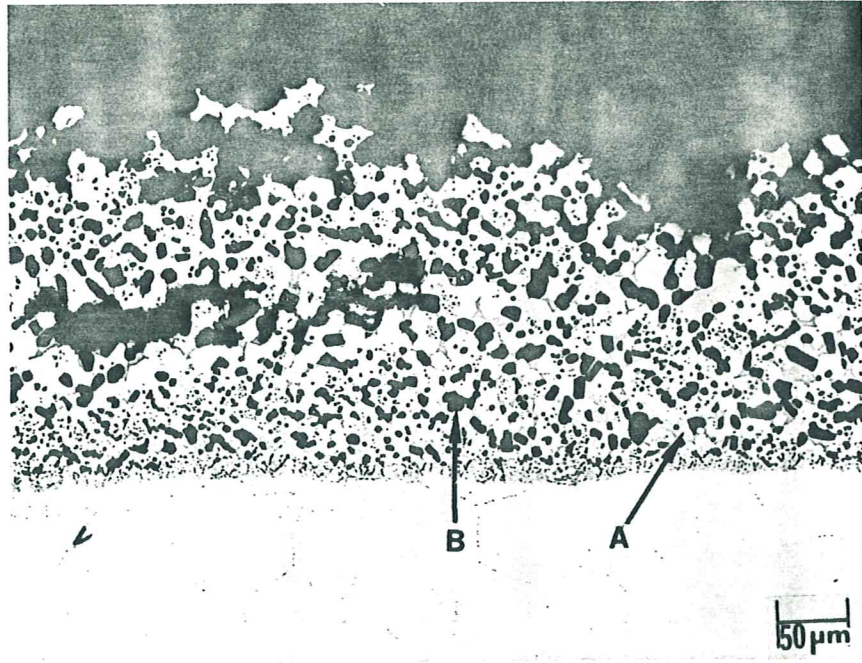
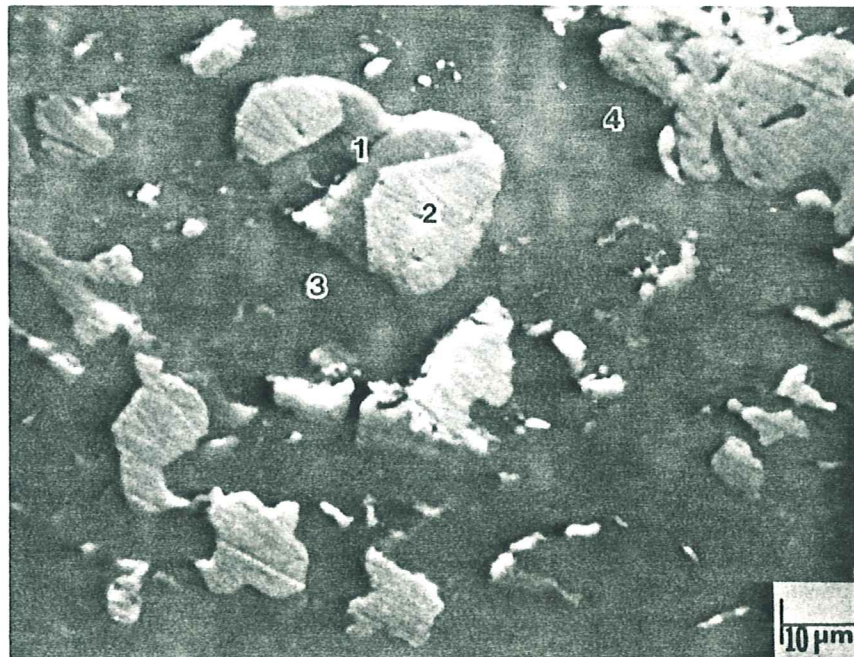


Figure 2. Optical photomicrograph showing severe sulfidation attack upon alloy 214 after exposure to the liquid hazardous waste combustion environment at 1400°F for 552 hours.
Neg. No. 51309



Area	Semi-Quantitative Analysis (Relative Intensity)					
	Ni	Fe	Cr	S	Al	Ca
1	76.0	-	-	23.0	1.0	-
2	97.8	-	1.0	0.8	0.4	-
3	62.9	5.3	20.6	2.5	5.7	3.0
4	63.4	1.5	29.9	0.8	2.9	1.5

Figure 3. SEM/EDS analysis of the corrosion products formed on alloy 214 after exposure to the liquid hazardous waste combustion environment at 1400°F for 552 hours.

Neg. No. 52795

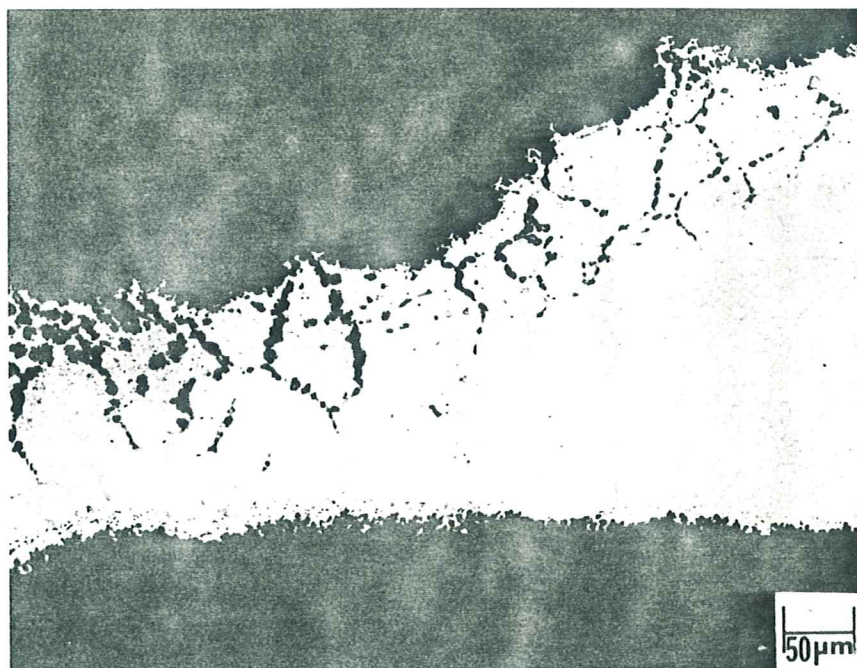
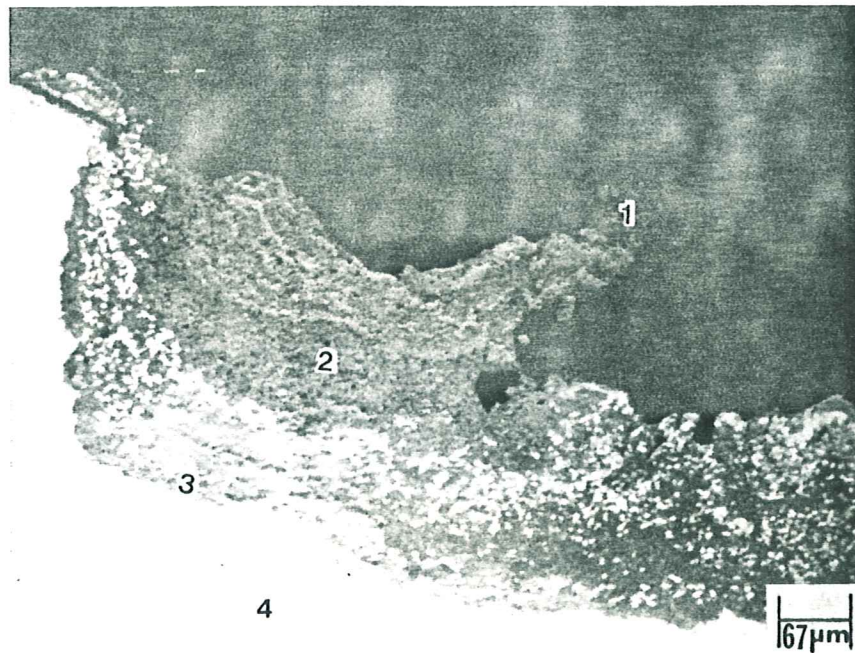


Figure 4. Optical photomicrograph showing severe high temperature corrosion upon alloy C-276 after exposure to the waste water sludge combustion environment at about 1700°F for 4368 hours.

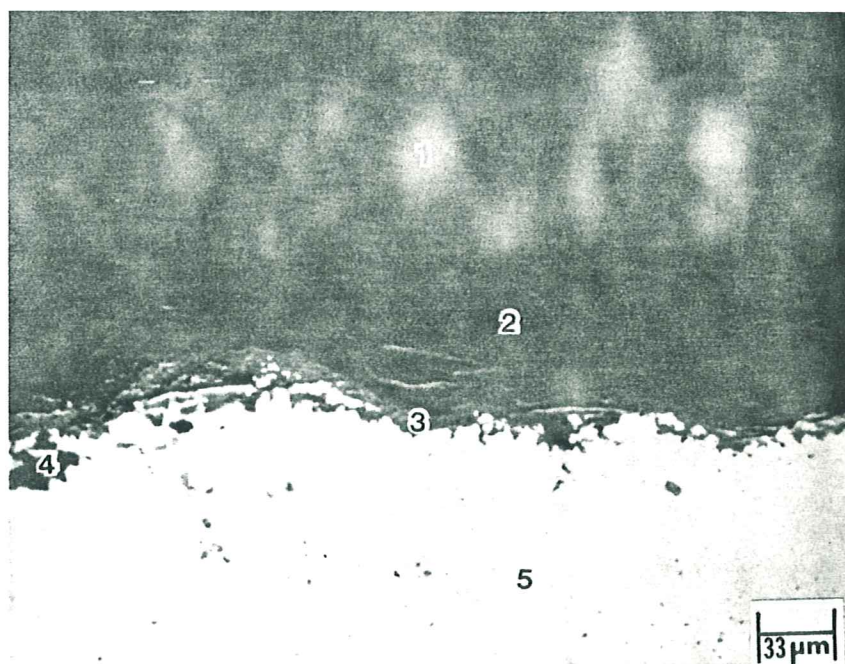
Neg. No. 49348



Area	Semi-Quantitative Analysis (Relative Intensity)					
	Ni	Cr	Mo	Fe	Al	W
1	51.2	35.0	-	11.3	0.2	1.5
2	68.5	19.2	-	9.9	0.6	1.6
3	40.2	26.6	21.7	7.8	0.8	2.5
4	55.3	23.7	9.5	9.3	-	1.8

Figure 5. SEM/EDS analysis of the corrosion products formed on alloy C-276 after exposure to the waste water sludge combustion environment at about 1700°F for 4368 hours.

Neg. No. 52794



Area	Semi-Quantitative Analysis (Relative Intensity)									
	Ni	Cr	Mo	Al	Ca	Fe	P	S	Cl	Ti
1	0.4	0.7	--	1.1	83.5	3.7	4.6	1.4	1.4	2.9
2	0.6	1.4	--	0.4	82.2	4.1	5.4	4.1	0.2	1.4
3	1.7	86.2	--	0.1	1.0	0.2	0.1	0.1	0.2	--
4	11.4	83.5	--	0.1	2.1	0.4	--	--	--	--
5	74.4	12.9	8.1	--	2.4	1.3	--	--	--	--

Figure 6. SEM/EDS analysis of the scale and corrosion products on alloy S after exposure to the waste water sludge combustion environment at about 1700°F for 4368 hours.

Neg. No. 52793

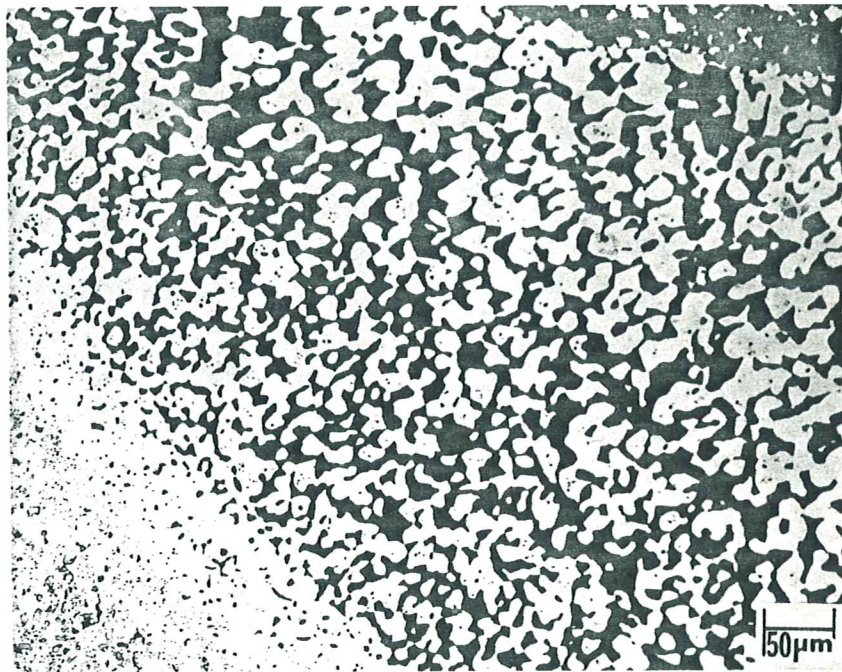
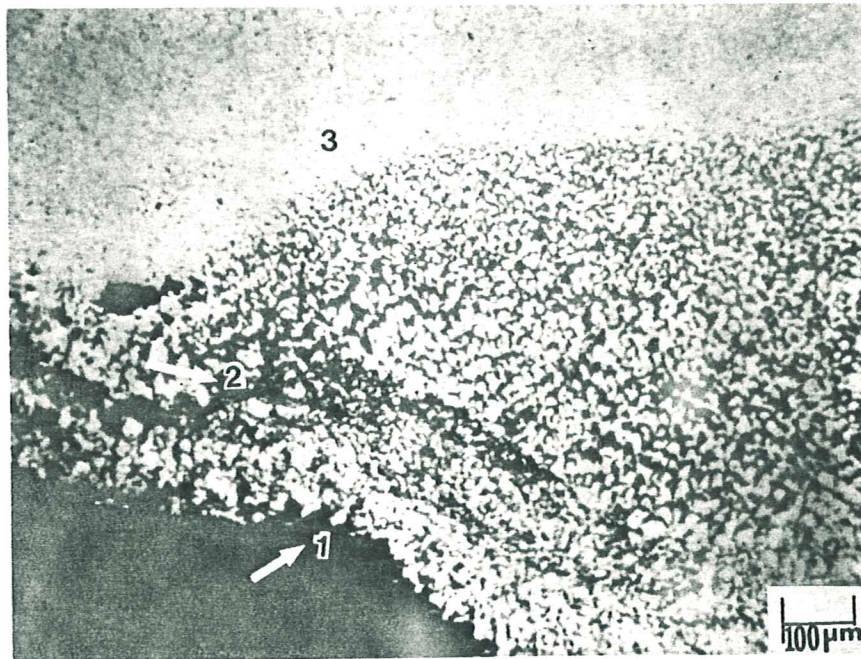


Figure 7. Optical photomicrograph showing severe sulfidation attack upon alloy 690 after exposure to the municipal waste combustion environment at about 1475°F for 950 hours.
Neg. No. 52840



Area	Semi-Quantitative Analysis (Relative Intensity)					
	Ni	Cr	Fe	Ti	S	P
1	8.5	84.3	1.9	-	-	5.4
2	0.6	58.5	-	-	40.9	-
3	54.3	26.9	13.4	0.4	-	-

Figure 8. SEM/EDS analysis of the corrosion products formed on alloy 690 after exposure to the municipal waste combustion environment at about 1475°F for 950 hours.

Neg. No. 52792

