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SELECTION OF MATERIALS FOR COMBUSTION ENVIRONMENTS ASSOCIATED WITH WASTE INCINERATION

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ABSTRACT

The paper discusses high-temperature corrosion attack resulting from the incineration of various municipal and industrial waste products. Results of multiple alloy field tests and the failure analyses of incinerator components are used to identify the nature of attack in each type of environment. Laboratory data are also used in order to compare material behavior with various environments associated with incineration.

INTRODUCTION

The high temperature corrosion problems in waste incinerator plants can vary from plant to plant, depending on, among other things, the type of waste to be incinerated, the presence of contaminants in the flue gas, process temperatures and incinerator design. The severity of the corrosion attack upon metallic components in incinerators of similar design can often vary due to the levels of corrosive contaminants such as chlorine and sulfur which could accelerate the oxidation of metals or alloys through the formation of chlorides, oxy-chlorides and sulfides. Corrosion may also be accelerated by the presence of other contaminants such as zinc, lead, potassium and sodium, although the role of these elements is often difficult to quantify.

Laboratory corrosion data may be useful to guide materials selection. However, due to the complex environment generated by the incineration of wastes, field testing is a more reliable method in determining materials performance. Typically, a test rack (or test probe) consiting of coupons of various candidate alloys is installed in the operating plant. After exposure to the environment for a predetermined time, the test rack is then retrieved for metallurgical evaluation. The total depth of attack upon each coupon is determined; the relative performance ranking for the alloys is then obtained.

In cases where field testing is not feasible, an analysis of failed components combined with data generated by laboratory corrosion testing in relevant environments along with prior field experience could yield valuable information needed to make an informed materials selection. This paper will examine several high temperature corrosion problems associated with the incineration of both municipal and industrial wastes. The types of industrial wastes range from waste oil and chemicals to wooden shipping pallets. The chemical compositions of the alloys discussed in this paper are shown in Table 1.

EXPERIMENTAL PROCEDURE

The test racks for the experiments were designed individually based on size and shape requirements identified by the user. Each rack was composed of approximately eight to twelve alloy coupons. The coupon samples, generally 2-inch x 2-inch or 1-inch x 4-inch sheet samples, were fitted onto a rod with each sample separated by an alumina spacer in order to limit reactions between dissimilar metals. The alloy coupons were weighed and measured prior to the assembly of the rack so that metal loss values could be calculated following exposure. The racks are then installed in an industrial facility for a predetermined length of time.

Following exposure, each coupon was cathodically descaled in a salt solution in order to remove the loose corrosion product. Average metal loss values were calculated from the change in weight before and after testing. A cross-section of the descaled sample was examined metallographically to measure the depth of internal penetration. In addition, corrosion scales of each alloy were examined using energy dispersive analysis (SEM/EDS) to determine the mode of internal attack.

RESULTS AND DISCUSSION

MATERIALS PERFORMANCE IN AN ENVIRONMENT GENERATED BY THE INCINERATION OF PAINT SLUDGES

An incinerator incorporating a waste heat boiler was used to treat solvent sludge waste and paints. Its combustion chamber was divided into a boiler section and an incineration section. The wastes were incinerated in the upper incineration section and No. 6 fuel oil was used for combustion in the lower boiler section with a boiler heat exchanger used to produce steam for process applications. The test program was initiated to identify candidate materials for air injection pipes previously made from Type 316 stainless steel.

The test rack was exposed in the boiler side of the unit for a period of six months. The atmosphere was not analyzed but was thought to consist of N_2, O_2, CO_2, H_2O, CO, ash and possibly small amounts of chlorine. In addition, the atmosphere of the boiler side might have contained small amounts of SO_2 since No. 6 fuel oil contains approximately 1-2 percent sulfur. The sulfur, if present, would be in the form of SO_2 instead of H_2S because more than ten percent excess air was used for combustion. The process temperature reportedly ranged from 1800°-2000°F during service. The exposed samples can be seen in Figure 1.

The results of the test in terms of linearly extrapolated corrosion rates are illustrated in Figure 2. All alloys tested, with the exception of alloy 600 which suffered metal loss and internal penetration equivalent to approximately 50 mpy (13 mm/year) based on the corrosion rate, showed rates of corrosion less than 20 mpy (0.45 mm/year). These corrosion rates were found to be of the same order of magnitude as those obtained from oxidation tests performed at 1800°F and 2000°F in air as reported by Lai, et al.(1)

The corrosion products formed on each sample were analyzed using a scanning electron microscope and energy dispersive x-ray analysis (SEM/EDS). The results showed the presence of Zn along with the elements common to the alloy (e.g. Cr, Fe, etc.). An example of the results of a scale analysis using SEM/EDS for MULTIMET alloy is shown in Figure 3. The outer layers of the scale were rich in iron, cobalt, manganese and zinc with small amounts of silicon and titanium also detected. The presence of these elements is not uncommon in this type of application.[2] The inner scale layer (marked as area 3 in Figure 3) was shown to be enriched in chromium.

No sulfur or sulfides were detected in the corrosion products for all alloys on the test rack with the exception of alloy 600 and Type 310 stainless steel. Chlorine was not detected in any samples tested. Figures 4 and 5 illustrate the morphology of corrosion for selected alloys. Chromium-rich sulphide phases were found to form underneath the oxide scale as is shown in Figure 6.

It is believed that oxidation was the dominant mode of attack for most alloys. Alloy 600, which possesses the highest nickel content suffered oxidation and sulfidation attack. The sulfur potential in the present combustion environments may not be very high. The use of greater than 10 percent excess air for combustion might also be instrumental in minimizing the sulfidation attack on the higher-alloyed nickel-base alloys.

MATERIAL PERFORMANCE IN AN ENVIRONMENT GENERATED BY THE INCINERATION OF PACKAGING MATERIALS

The second rack test was performed in a flue gas environment associated with the combustion of paper, cardboard and wooden shipping pallets. The problem in this unit involved the reoccuring failure of the bypass damper made from Type 309 stainless steel which failed after approximately two months of continuous service. Replacing the 309 stainless steel with RA 333 allowed for eighteen months of discontinuous use.

The life of the RA 333 damper was still considered to be unsatisfactory. The use of a field test rack was agreed upon in order to screen a variety of alloys. Alloys chosen for the test include several nickel-base alloys including 600, 214, 617, 601, 230 and X; iron-base alloys 800H, MULTIMET, 310 stainles steel and alloy 556; and cobalt-base alloys including alloys 188 and 6B. Type 309 stainless steel and alloy 333 were included for reference.

The test rack was placed inside a refractory-lined breeching which connects the incinerator to the boiler in which the flue gas was vented (see Figure 7). The rack was exposed for 417 hours of operation over a thirty day period. The temperature of the flue gas was estimated to be 1700°-1800°F. The components of the flue gas were reported to be CO, CO_2, H_2O, N_2, O_2 and ash. In addition, small amounts of sulfur and chlorine were determined to be present based on the composition of typical samples routinely incinerated in this facility.

Samples which were removed from the test rack after exposure are shown in Figure 8. Visual examination revealed pitting attack for some alloys. The morphology of corrosion attack for selected alloys is illustrated in Figure 9. An SEM/EDS analysis of the corrosion products formed on selected alloys (e.g., alloy 800H and alloy 214) indicate the presence of sulfur and, in some cases, Zn and Ca.

The relative performance in mils per month based on a linear extrapolation, is shown in Figure 10. The results are presented in terms of the total depth of attack. As indicated by this figure, high nickel alloys such as alloys 600, 601 and 214 and iron-base alloys (e.g. alloy 800H) suffered severe corrosion attack. The severe corrosion attack suffered by nickel alloys is indicative of sulfidation. The predominant mode of corrosion in this environment is believed to be oxidation in combination with sulfidation.

MATERIALS PERFORMANCE IN AN ENVIRONMENT GENERATED BY INCINERATION OF MUNICIPAL WASTES

The third test program was performed to identify suitable materials for a rapper system used in a water-wall boiler which is used for the incineration of municipal waste. The purpose of the rapper system is to remove slag and soot and other particulates which accumulate on tubes and walls by hammering on the end of a rapper bar. In addition to high-temperature corrosion resistance, the selected material must also possess good high-temperature strength.

Two test racks were constructed using a reversed sample sequence to identify the effect of sample location for control purposes. The racks were placed at opposite walls of the boiler for 950 hours. The average temperature in this area was reported to be 1475°F with a maximum temperature of approximately 1750°F. A variable was introduced during the test when tubes on one side of the boiler became partially plugged during operation, effectively increasing the gas velocity on one side of the boiler. These conditions resulted in a slightly greater degree of attack on one test rack. At the conclusion of the test, the samples were inadvertantly sandblasted thus limiting the evaluation of scale on the samples.

The results of the evaluation performed on two test racks are shown in Table 2. The rankings obtained from both racks were found to be in reasonable agreement. The alloys which suffered the worst attack were some of the nickel-base alloys including alloys C-4, X, C-276 and 690. Some of the nickel-base alloys, particularly those containing Al and Ti such as WASPALOY alloy, alloys R-41 and 263, suffered less attack. Alloy 188 (Co-base alloy) and alloy 556 (Fe-Ni-Cr-Co alloy) were most resistant to attack.

The morphology of corrosion attack for selected alloys is illustrated in Figure 11. An SEM/EDS analysis was performed on selected samples. Sulfides were found to form on some alloys. Figure 12 (a) shows a coupon of alloy 690 which was partially destroyed after the exposure. Examination of the cross section of the coupon revealed severe sulfidation attack. The sulfides formed on the alloy 690 sample are illustrated in Figure 12 (b and c) and were determined to be Cr-rich sulfides. The severe, localized attack was probably due to the formation of molten, Ni-rich and Cr-rich sulfides.

Other contaminants detected by SEM/EDS analysis of the corrosion products included traces of Zn, K and Ca. Chlorine was not detected. However, due to the volatile nature of metallic chlorides or oxychlorides, the presence of Cl may have been limited to the outer scale which could not be analyzed.

The predominate mode of attack in this environment is believed to be oxidation and sulfidation. The role of sulfidation is more dominant in this case than previous cases. The alloy performance ranking was found to be in general agreement with the laboratory sulfidation test results reported by Lai.[3]

Similar to his findings, those alloys containing titanium (e.g. alloy R-41 and WASPALOY alloy) were found to be the best performers among the nickel-base alloys tested, although the corrosion rate was still relatively high. Among all the alloys tested, alloy 188 (a Co-base alloy) was found to perform the best followed by alloy 556 (an Fe-Ni-Cr-Co alloy).

The heavy pitting attack and localized metal loss seen on several samples may have been partially caused by erosion/corrosion from the particulate matter in the gas stream. This type of corrosion results in the wearing away of metal, especially where gas velocities are high.[4] This effect might have been evident in Test No. 4 (see Table 2) where plugged tubes effectively increased the gas velocity in the boiler. The exact gas velocity was not determined. The particulate matter in the gas stream was also high as was in evidence by the complete coating of the test racks by ash.

SUMMARY

The performance of various alloys in environments generated by incineration of various wastes was investigated by performing field tests in various industrial facilities. Tests were performed in incinerators burning paint sludges, package materials, and municipal wastes, respectively.

Sulfur appears to be present in the environments produced by burning three different types of wastes. For the environment generated by incinerating paint sludges, the level of sulfur appears to be high enough to cause oxidation/sulfidation for a high nickel alloy, Alloy 600. Other alloys tested suffered mainly oxidation attack with the oxidation rates in the same order of magnitude as those obtained from laboratory oxidation tests in air at comparable temperatures. Sulfidation attack, where identified, was minimal for this application.

In the environments generated by burning either packaging materials or municipal wastes, the predominant mode of corrosion attack was found to be oxidation accelerated by sulfidation. In both of these environments, alloys containing high levels of cobalt were found to perform best.

REFERENCES

1. G. Y. Lai, M. F. Rothman and D. E. Fluck, "High Temperature Corrosion and Selection of Materials for Various Industrial Processing Equipment," presented at NACE Corrosion/85 meeting in Boston, MA, March 1985.

2. H. H. Krause, P. W. Cover, and W. E. Berry, "Materials for Power Generation from Refuse Combustion," Symposium on Advanced Materials for Alternative-Fuel-Capable-Directly-Fired Heat Engines, presented at Castine, Maine, July 31-August 3, 1979, p. 490

3. G. Y. Lai, "Sulfidation Resistance of Various High Temperature Alloys in Low Oxygen Potential Atmospheres," presented at TMS-AIME Fall Meeting, Detroit, MI, September 17-20, 1984.

4. W. D. Turner, "Technical Status Report on the Mass Burning of Solid Waste in Waterwalled Incinerators, "Argonne National Laboratory Report, 31-109-38-6807, December 1982.

Table 1
NOMINAL COMPOSITIONS OF ALLOYS TESTED

Nickel-Base Alloys	Nominal Composition (Wt. %) Ni	Fe	Co	Cr	Mo	W	Al	Ti	C	Others
HASTELLOY® alloy X	47	18.5	1.5	22	9.0	0.6	-	-	0.1	
CABOT® alloy No. 214	75	3.5	2.0*	16	0.5*	0.5*	4.5	-	0.05	Y Present
CABOT alloy No. 600	72	8.0	1.0	15.5	-	-	0.35*	0.3*	0.08	
HAYNES® alloy No. 230	57	3.0*	-	22	2.0	14.0	0.3	-	0.1	.03 La
CABOT alloy No. 625	62	5.0*	1.0*	21.5	9.0	-	0.4*	0.4*	0.1	3.5 Cb + Ta
INCONEL® alloy No. 601	60.5	14.1	-	23	-	-	1.4	-	0.05	
INCONEL alloy 617	54.0	-	12.5	22.0	9.0	-	1.0	-	0.07	
RA® 333	45.0	18.0	3.0	25.0	3.0	3.0	-	-	0.05	1.25 Si
INCONEL alloy 690	60.0	9.5	-	30.0	-	-	-	-	0.03	
WASPALOY® alloy	58.0	2.0*	13.5	19.0	4.3	-	1.5	3.0	0.08	0.05 Zr
CABOT alloy No. R-41	52.0	5.0*	11.0	19.0	10.0	-	1.5	3.1	0.09	
CABOT alloy No. 263	50.0	0.7*	20.0	20.0	6.0	-	0.4	2.2	0.06	
HASTELLOY alloy C-276	57.0	5.5	2.5*	15.5	16.0	4.0	-	-	0.01*	0.35 V*
HASTELLOY alloy C-4	65.0	3.0*	2.0*	16.0	15.5	-	-	0.7*	0.01*	
HASTELLOY alloy C-22	56.0	3.0	2.5*	21.5	13.5	3.0	-	-	0.015*	0.35 V*
Iron-Base Alloys										
HAYNES alloy No. 556	20	29	18.0	22.0	3.0	2.5	0.2	-	0.1	0.8 Ta,0.02La,0.15N
MULTIMET® alloy	20	30	20.0	21.0	3.0	2.5	-	-	0.12	1.0Cb+Ta, 0.15N,0.4Si
CABOT alloy 800H	32.5	44	2.0*	21.0	-	-	0.38	0.38	1.0*	
Type 309 Stainless Steel	13	BAL	-	23	-	-	-	-	0.2	
Type 310 Stainless Steel	20	BAL	-	25	-	-	-	-	0.25	
Cobalt-Base Alloys										
HAYNES STELLITE® alloy No. 6B	2.5	3.0*	58	30	1.5*	4.0	-	-	1.0	
HAYNES alloy No. 188	22.0	3.0*	39	22	-	14.0	-	-	0.1	0.04La, 0.4Si
HAYNES alloy No. 25	10.0	3.0*	51	20	-	15.0	-	-	0.1	

* Maximum

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RA is a registered trademark of Rolled Alloys Inc.
INCONEL is a trademark of the Inco Family of Companies
WASPALOY is a trademark of United Technologies Co.

TABLE 2: Maximum Depths of Internal Attack For Alloys Tested in a Municipal Waste Incinerator

A. Test Rack No. 4

Alloy	Max. Depth of Internal Attack (mils)	Description
HAYNES alloy No. 188	7.6	Very slight attack
CABOT alloy No. 625	8.2	Heavy pitting
HAYNES alloy No. 556	8.2	Slight pitting
CABOT alloy R-41	10.0	Moderate attack
HASTELLOY alloy C-22	10.0	Moderate attack
CABOT alloy C-263	10.4	Mainly intergranular attack
INCONEL alloy 617	13.2	Moderate attack
Type 309 Stainless Steel	13.4	Moderate attack
HASTELLOY alloy C-4	23.4	Heavy attack
HASTELLOY alloy X	27.0	Heavy attack
HASTELLOY alloy C-276	Slight internal attack but severe metal loss (approximately 20 mils per side of metal loss)	
INCONEL alloy 690	Partially destroyed	

B. Test Rack No. 5

Alloy	Max. Depth of Internal Attack (mils)	Description
WASPALOY alloy	3.0	One side very clean
CABOT alloy C-263	5.4	One side very clean
HAYNES alloy No. 188	5.6	Slight pitting
HAYNES alloy No. 556	8.0	Slight attack
HASTELLOY alloy C-22	8.0	Heavy pitting
HASTELLOY alloy C-276	12.0	Moderate attack
CABOT alloy No. R-41	12.6	Moderate attack
HASTELLOY alloy X	16.0	Heavy pitting
HASTELLOY alloy C-4	18.0	Heavy attack
CABOT alloy No. 625	19.0	Heavy pitting

Rack #456

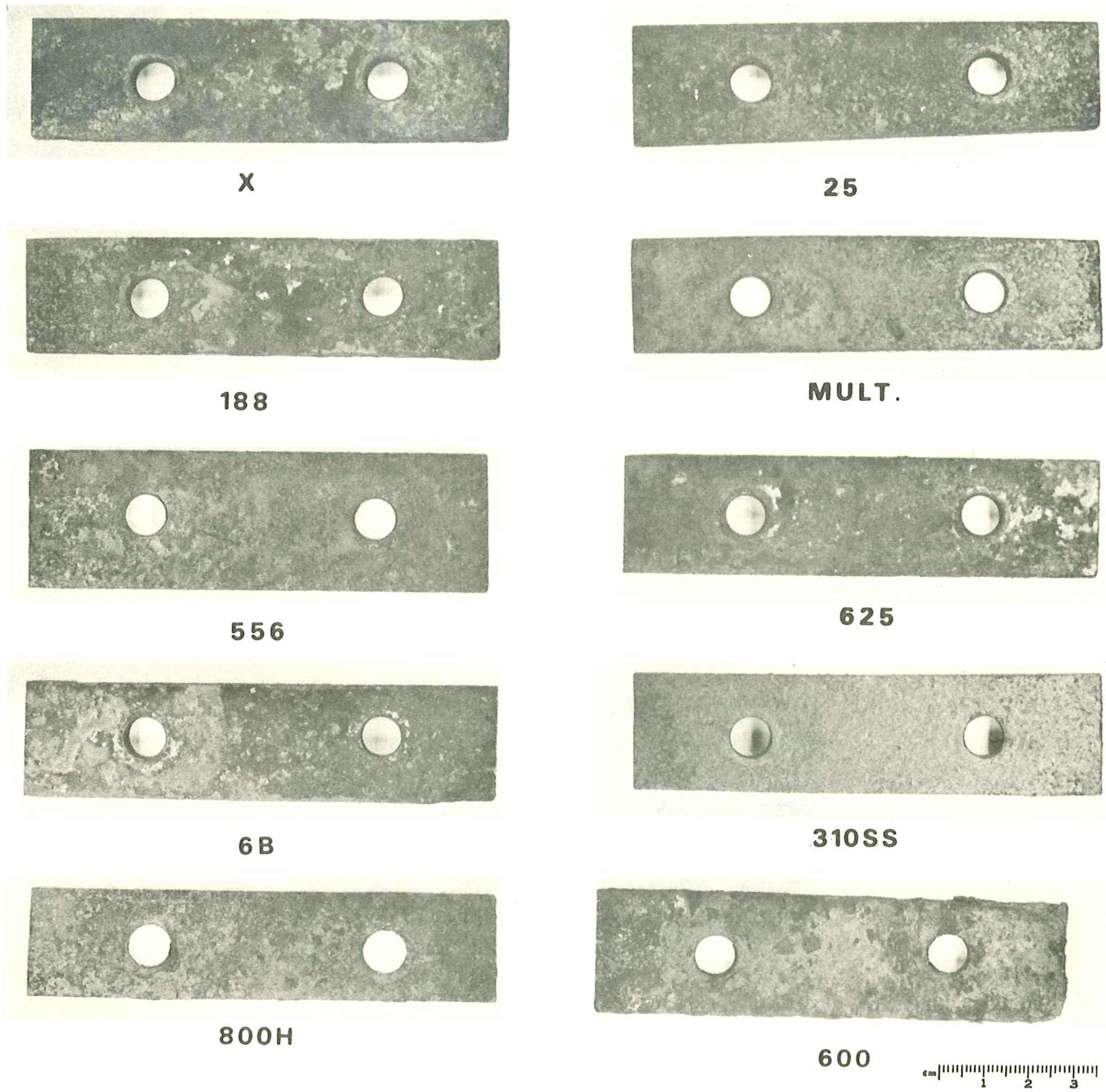


FIGURE 1: SAMPLES FROM TEST RACK EXPOSED IN A COMBUSTION ENVIRONMENT GENERATED BY THE INCINERATION OF PAINT AND SOLVENT SLUDGE WASTE.

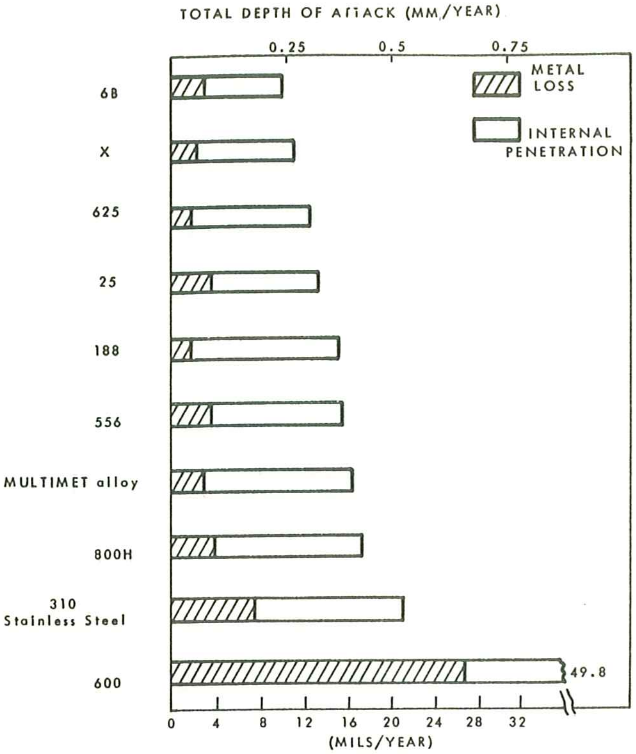
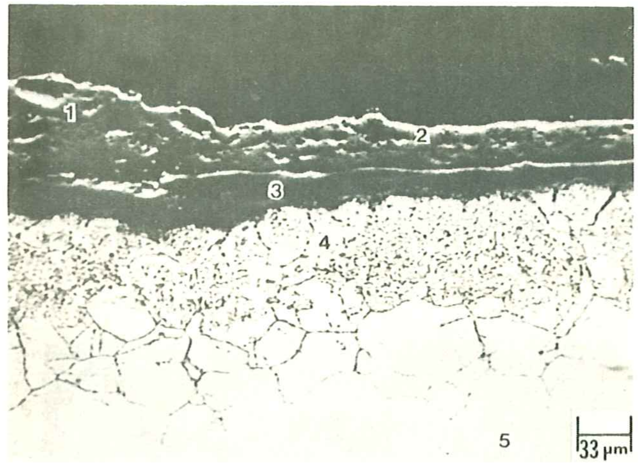
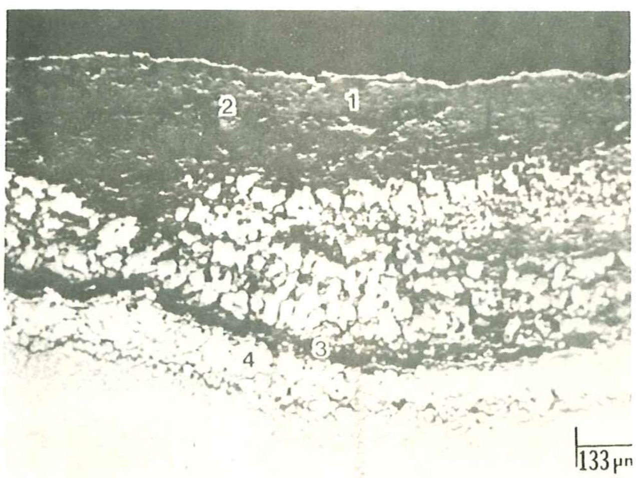


FIGURE 2: CORROSION RATES OF ALLOYS TESTED IN AN ENVIRONMENT GENERATED BY THE INCINERATION OF PAINT AND SOLVENT SLUDGE.



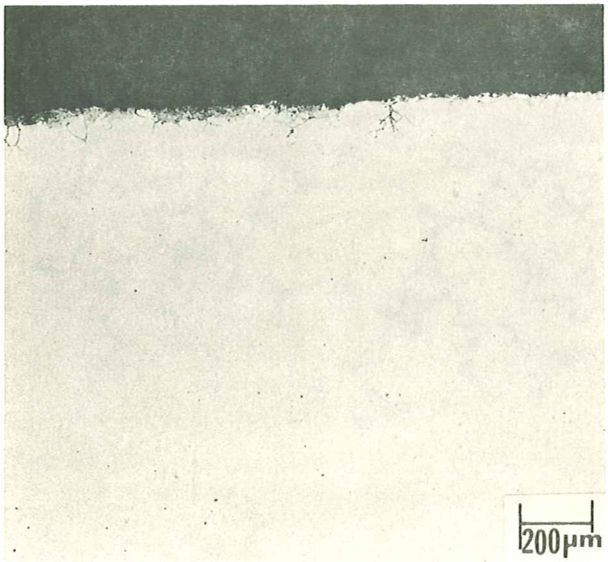
	Ni	Cr	Fe	Co	Al	Mo	Mn	Zn	S
AREA 1	2.9	0.9	67.3	11.7	1.1	-	10.8	5.3	-
AREA 2	0.3	9.0	77.1	5.5	-	-	-	3.1	-
AREA 3	0.5	97.0	0.6	-	-	-	-	-	0.5
AREA 4	14.7	35.8	32.0	13.1	-	1.7	-	-	-
AREA 5	13.8	36.0	31.0	13.9	-	1.7	-	-	-

FIGURE 3: SEM/EDS SEMI-QUANTITATIVE ANALYSIS OF MULTIMET alloy IS SHOWN AFTER EXPOSURE IN AN INDUSTRIAL INCINERATOR BURNING PAINTS AND SOLVENT SLUDGE. IMPURITIES INCLUDING ZINC, MANGANESE AND SILICON WERE PRESENT IN THE OUTER LAYER OF SCALE. (BSE)
NOTE: SEMI-QUANTITATIVE VALUES ARE NORMALIZED ON THE BASIS OF RELATIVE INTENSITY. THEY ARE NOT WEIGHT PERCENTAGE VALUES.

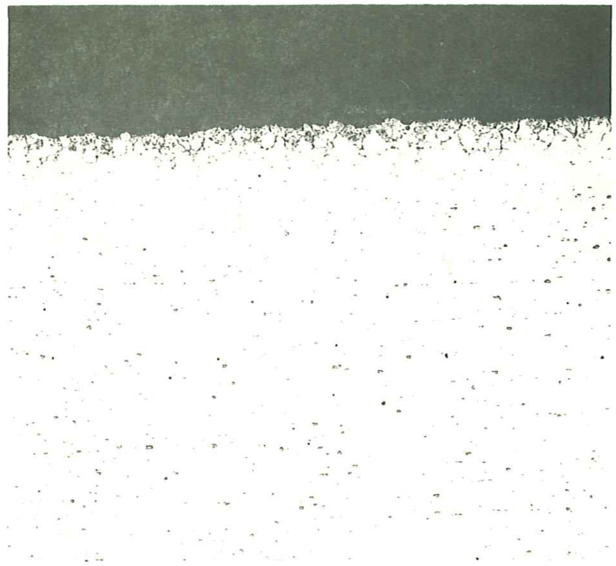


	Ni	Cr	Fe	S
AREA 1	90.7	0.7	8.6	-
AREA 2	14.1	79.9	5.9	-
AREA 3	13.6	76.1	1.0	9.3
AREA 4	87.0	2.6	10.5	-
AREA 5	65.2	22.9	11.7	-

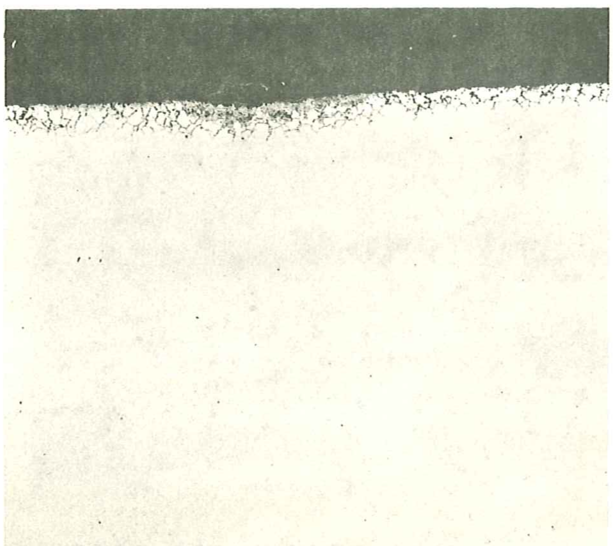
FIGURE 4: THE SEM/EDS SEMI-QUANTITATIVE ANALYSIS OF ALLOY 600 SHOWS THAT Cr-RICH SULFIDES CONTRIBUTED TO THE HIGH CORROSION RATE ON ALLOY 600.



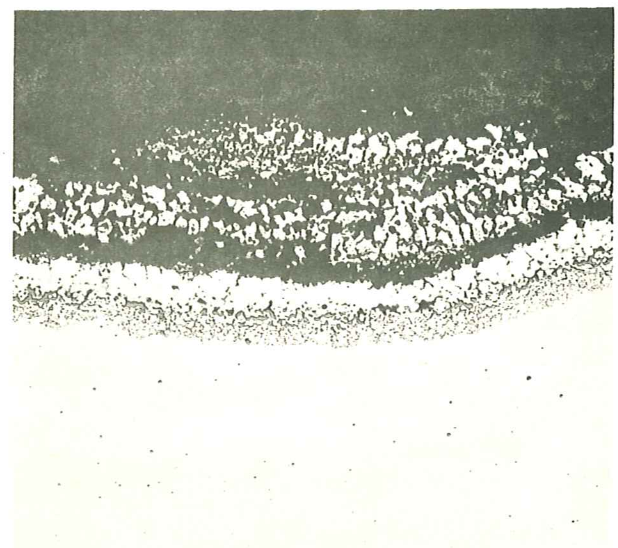
HAYNES alloy No. 188



MULTIMET alloy



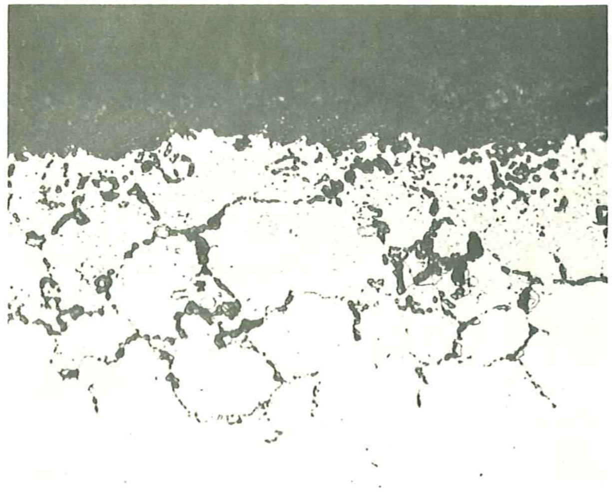
HASTELLOY alloy X



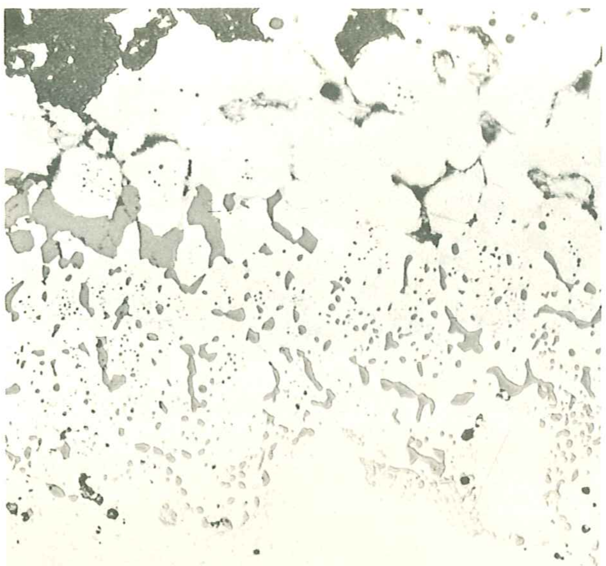
CABOT alloy No. 600

FIGURE 5: OPTICAL PHOTOMICROGRAPHS SHOW THE MORPHOLOGY OF ATTACK UPON SELECTED ALLOYS AFTER EXPOSURE IN A COMBUSTION ENVIRONMENT GENERATED BY INCINERATED PAINT SLUDGE. AS-POLISHED

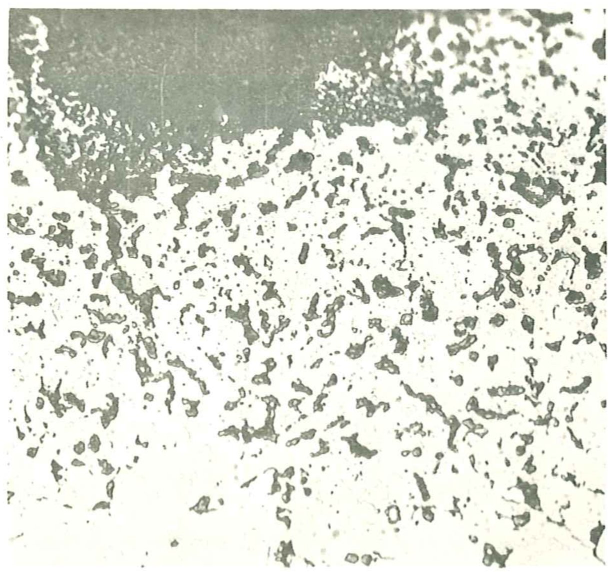
HAYNES alloy No. 188



HASTELLOY alloy X



CABOT alloy No. 600



TYPE 310 STAINLESS STEEL

FIGURE 6: THE HIGH MAGNIFICATION PHOTOMICROGRAPHS OF ALLOYS EXPOSED IN THE INDUSTRIAL INCINERATOR SHOW THAT THE ATTACK INVOLVED THE PENETRATION OF SULFIDE PARTICLES IN THE HEAVILY ATTACKED SAMPLES SUCH AS 310 STAINLESS STEEL AND CABOT alloy NO. 600. AS-POLISHED

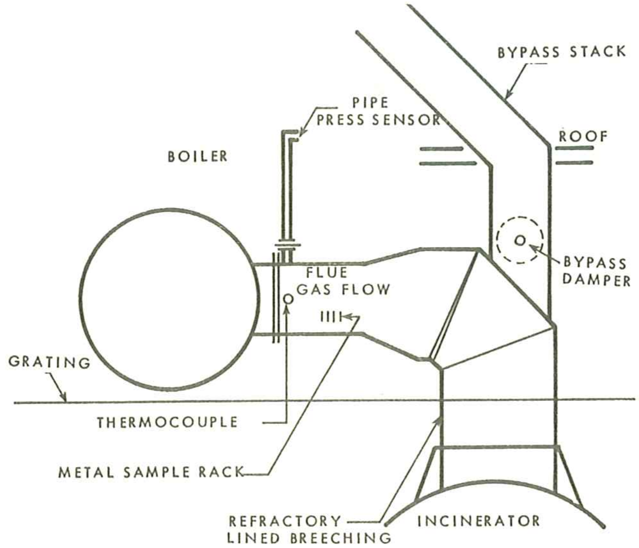


FIGURE 7: THE DRAWING SHOWS THE LOCATION OF THE TEST RACK IN THE INCINERATOR BREECHING.

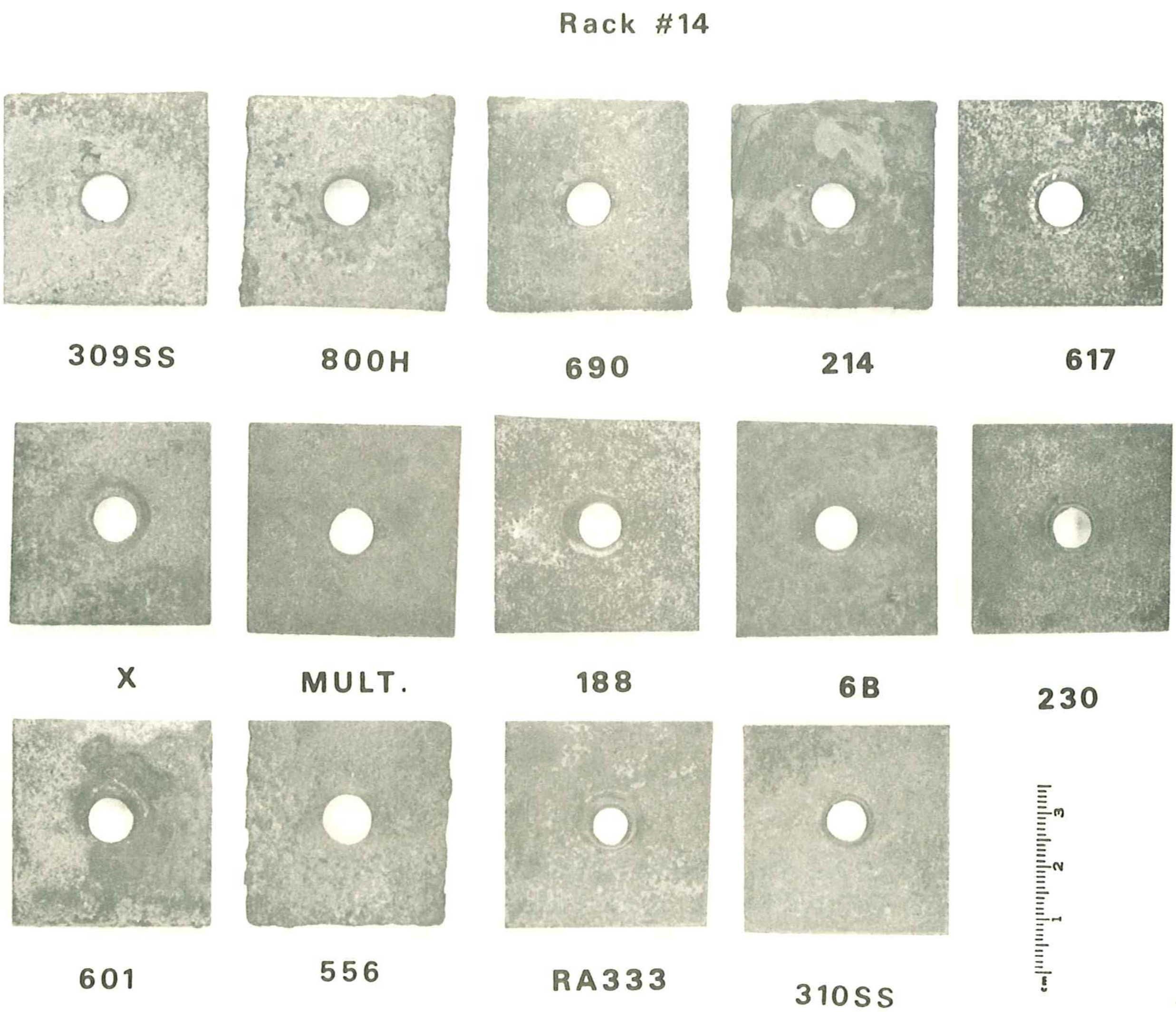
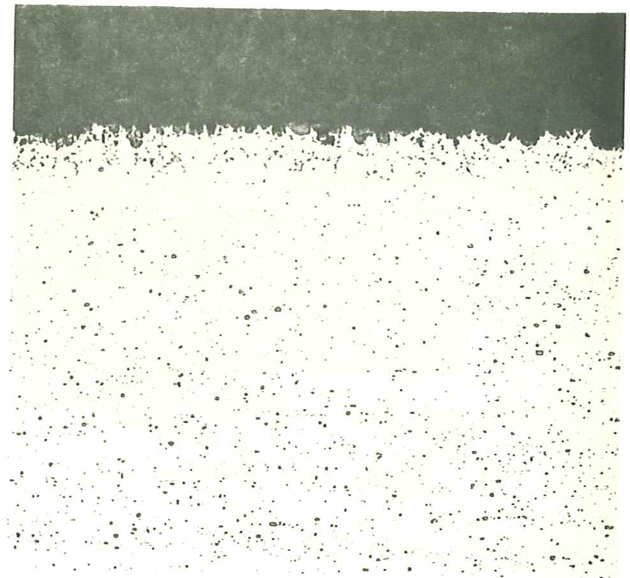
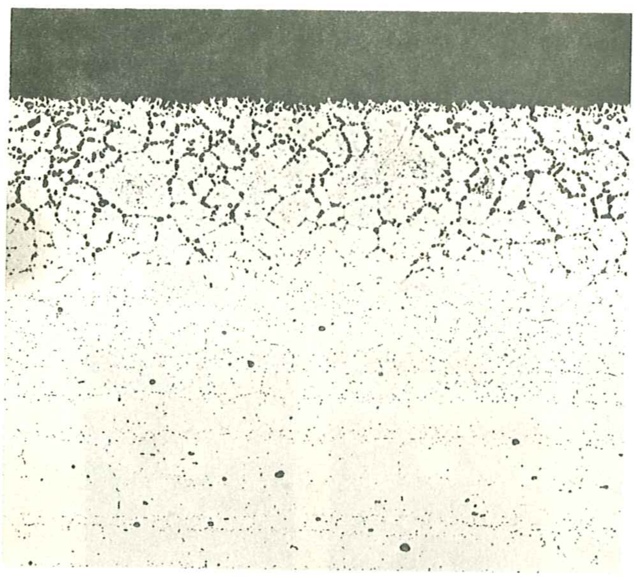


FIGURE 8: SAMPLES AFTER 417 HOUR EXPOSURE IN THE INCINERATION OF WOOD AND PACKAGING MATERIAL AT 1700°-1800°F.

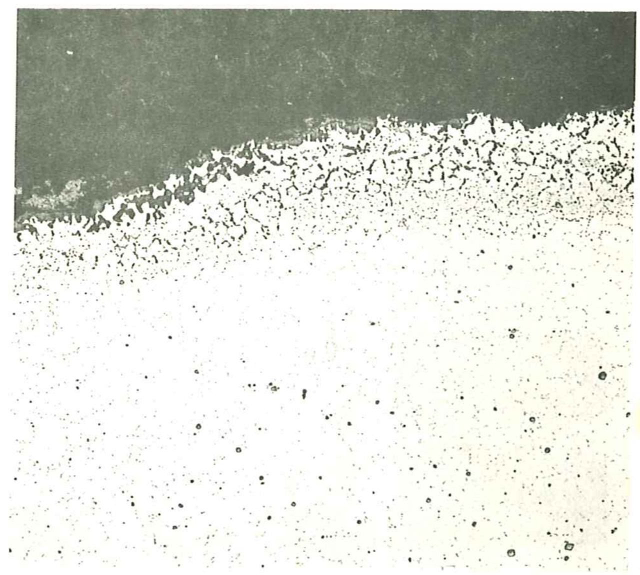
HAYNES alloy No. 188



MULTIMET alloy



INCONEL 601



CABOT alloy No. 800H

FIGURE 9: THE OPTICAL PHOTOMICROGRAPHS SHOW THE DEGREE OF ATTACK ON SAMPLES AFTER 417 HOURS OF ATTACK IN THE INCINERATION OF WOOD AND PACKAGING MATERIALS. AS-POLISHED

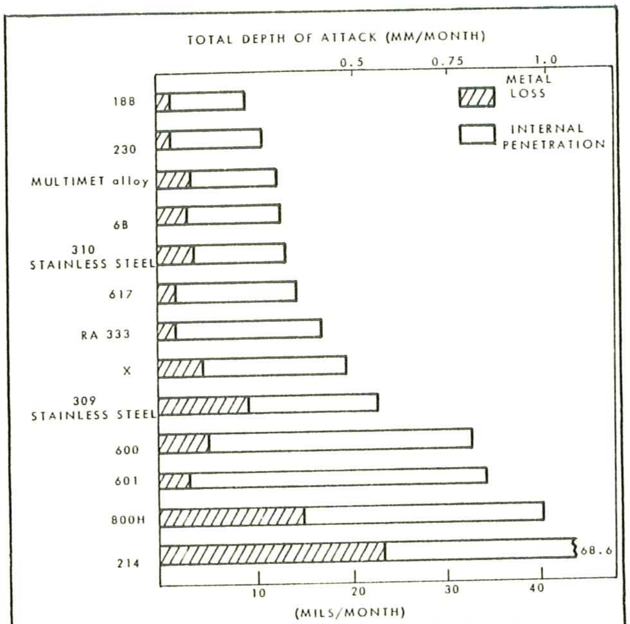
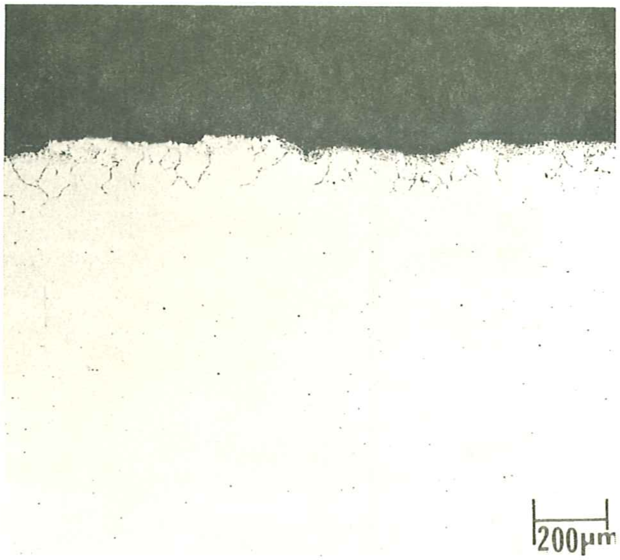
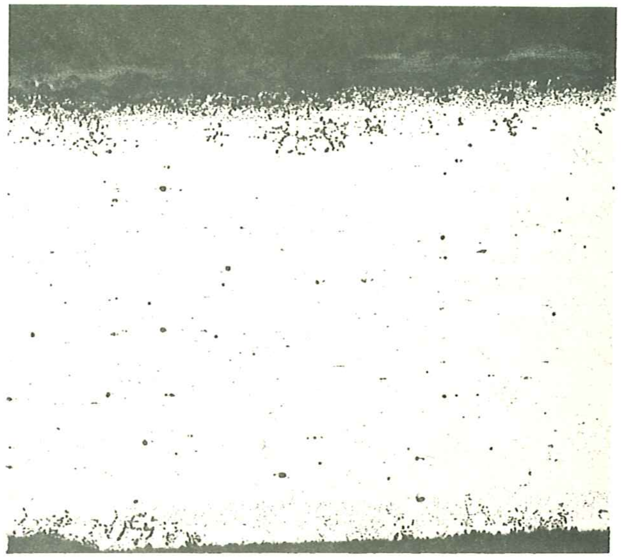


FIGURE 10: CORROSION RATES OF ALLOYS TESTED IN AN ENVIRONMENT GENERATED BY THE INCINERATION OF PACKING MATERIALS.

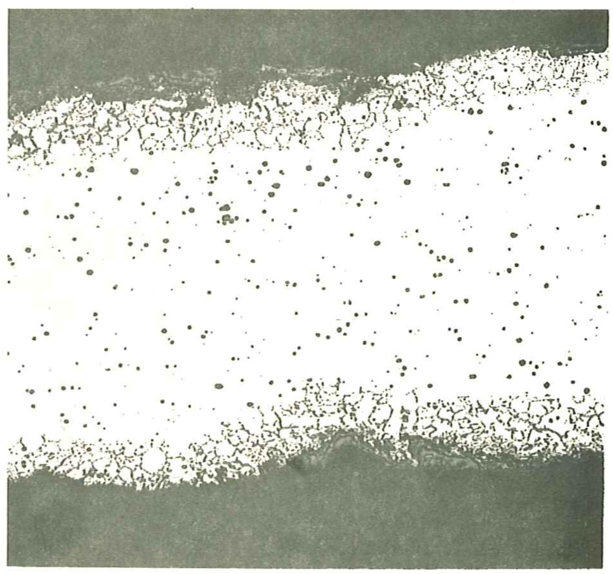


HAYNES alloy No. 188



HAYNES alloy No. 556

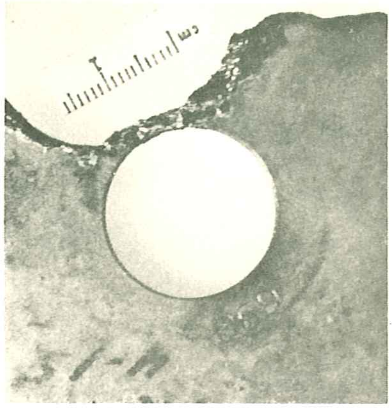
HASTELLOY alloy C-4



CABOT alloy No. R-41

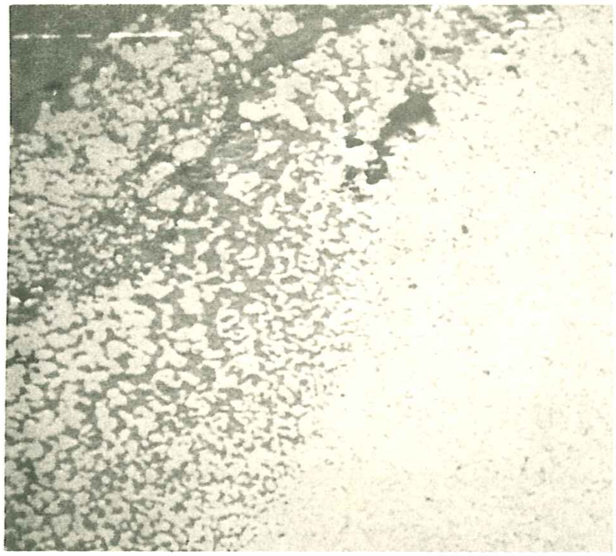
FIGURE 11:

THE OPTICAL PHOTOMICROGRAPHS SHOW THE MORPHOLOGY OF ATTACK ON SAMPLES EXPOSED IN A COMBUSTION ENVIRONMENT ASSOCIATED WITH MUNICIPAL WASTE INCINERATION AT 1450°-1750°F FOR 950 HOURS (AS-POLISHED)



IN 690

(a)



(b) BSE

(c) $(K_\alpha)_S$

FIGURE 12: THE PHOTOGRAPH SHOWS THE HEAVY LOCALIZED ATTACK ON INCONEL alloy 690. THE PRIMARY CAUSE OF ATTACK WAS DETERMINED TO BE SULFIDATION AS IS SHOWN BY THE SULFUR DOT MAP. MAGNIFICATION: 100X; BSE