

OXIDATION OF IRON-BASE ALLOYS IN ENVIRONMENTS

WITH AND WITHOUT SO<sub>2</sub>

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ABSTRACT

Sulfur dioxide is present at low levels in many industrial environments and can cause serious high temperature corrosion problems. In general, the presence of SO<sub>2</sub> accelerates the overall rate of corrosion, due to the simultaneous formation of oxide and sulfide. In the present work, alloy 556 and Type 304 stainless steel were exposed in environments with and without SO<sub>2</sub> to determine the effect of the contaminant on corrosion. Exposure in an Ar-O<sub>2</sub>-CO<sub>2</sub> environment at 1800°F (982°C) showed that Type 304SS suffered breakaway oxidation, whereas alloy 556 formed a thin, compact oxide scale. In the SO<sub>2</sub>-bearing environment (Ar-10%SO<sub>2</sub>-5%O<sub>2</sub>-5%CO<sub>2</sub>), the stainless steel was severely attacked while the compact oxide scale on alloy 556 served to retard the ingress of sulfur from the environment. It is clear from the results that oxidation resistance is a reasonable criterion to use in selecting materials for SO<sub>2</sub>-bearing environments.

Keywords: Oxidation/Sulfidation, Iron-base alloys, alloy 556, Type 304 Stainless Steel, Oxide scale formation

INTRODUCTION

The corrosion of metals and alloys in SO<sub>2</sub>-bearing environments at elevated temperatures is a major problem in many industrial applications, including various energy conversion processes and processing plants in the petrochemical industry. Most industrial environments contain quite low levels of SO<sub>2</sub>. In the combustion of coal, for example, a typical SO<sub>2</sub> level in the flue gas is 1% or less. By contrast, SO<sub>2</sub> levels in sulfur furnaces for sulfuric acid production may reach

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10%. In many cases, both oxide and sulfide are formed as a result of exposure in this type of environment. Sulfidation is particularly detrimental to a material due to the rapid growth rates of sulfides and the existence of low-melting nickel sulfides. The formation of a liquid sulfide can lead to catastrophic failure of a component.

The principal alloys used under conditions favoring oxidation/sulfidation are iron-base with chromium as a major constituent. The behavior of Fe-Ni-Cr alloys in oxidizing/sulfidizing environments is usually characterized by the initial formation of a chromia scale. Although the sulfides of Fe and Ni may be thermodynamically stable in the environment, chromia nucleation is, apparently, more rapid. A protective scale requires that only chromium be incorporated in the growing oxide. Duplex scales rich in Mn, Fe or Ni have to be avoided because sulfide formation will occur if the concentration of these elements is high enough. Perkins<sup>1</sup> has proposed that Mn should be excluded from alloys for applications in coal gasification environments. Wild<sup>2</sup> found that Mn diffused about 100 times faster than Cr in chromium oxide and thus may become concentrated at the scale/gas interface. This can lead to the formation of channels of MnS through the oxide scale, providing easy access of sulfur to the alloy. The detrimental effect of Mn was confirmed by Grabke and Papaiacovou<sup>3</sup>, who showed that the sulfur content and overall corrosion of Fe-32Ni-20Cr alloys exposed in an oxidizing/sulfidizing environment increased with the Mn content of the alloy.

It is clear from several studies that the nature of the oxide scale is of primary importance in determining the behavior of an alloy in a oxidizing/sulfidizing environment. Danielewski and Natesan<sup>4</sup> found that the preferential formation of sulfide scales on Fe-Ni-Cr alloys that contained 4 and 12 wt% Cr could be explained on the basis of the oxidation behavior of these alloys. It is well known that in Fe-Cr and Ni-Cr alloys with 18 wt% Cr or less the oxide layers which form are discontinuous and the mode of interaction is internal oxidation. In alloys with > 20 wt% Cr a continuous layer of oxide has been observed, which retards sulfide formation.

Compared with studies in H<sub>2</sub>S-bearing environments, relatively few studies have been performed on the behavior of commercial alloys in SO<sub>2</sub>/O<sub>2</sub> environments. A recent impetus for this type of study is the possible use of a thermochemical transport system involving SO<sub>2</sub>, O<sub>2</sub> and SO<sub>3</sub> for distributed solar receivers. Studies of materials for use in this application have been carried out by Cerchiara et al<sup>5</sup> and Weirick.<sup>6</sup> Cerchiara et al concluded that, in SO<sub>2</sub>/O<sub>2</sub> environments at 1292 and 1652°F (700 and 900°C), alumina and silica scale formers are the most resistant to attack. Sulfur penetration of the scale was detected in all of the alloys studied. These authors proposed the use of aluminide or silicide coatings to retard attack in SO<sub>2</sub>/O<sub>2</sub> environments. The work of Weirick similarly concluded that sulfur penetration of the oxide was inevitable, even for highly oxidation-resistant materials. Alloys which formed scales of both alumina and chromia were found to be most effective in retarding the ingress of sulfur.

In the present study, the oxidation behavior of two iron-base alloys, Type 304 stainless steel and alloy 556 are considered. These alloys were exposed in environments with and without SO<sub>2</sub> at 1800°F (982°C). The level of SO<sub>2</sub> used was 10%, which is considerably higher than the level present in many combustion environments. Thus, this environment is expected to be more corrosive than the typical combustion environment. The influence of SO<sub>2</sub> on the oxidation behavior of the alloys is described. The nature of the oxide scales is described and related to the behavior of the alloys in oxidizing environments with and without SO<sub>2</sub>.

## THERMODYNAMIC CONSIDERATIONS

In a gas mixture containing SO<sub>2</sub> and O<sub>2</sub>, involving the equilibrium:



the sulfur activity,  $a_S$  is defined as:

$$a_S = \left( P_{\text{S}_2} \right)^{1/2} = \left( \frac{P_{\text{SO}_2}}{P_{\text{O}_2}} \right) K_1 \quad (2)$$

where  $K_1$  is the equilibrium constant for reaction (1) above.

Thus, the sulfur activity is very strongly dependent on the partial pressure of oxygen. The species SO<sub>3</sub> is formed in SO<sub>2</sub>/O<sub>2</sub> mixtures, through the equilibrium:



Both SO<sub>2</sub> and SO<sub>3</sub> may participate in reactions with metal or oxide to form sulfides or sulfates.

In many cases, both oxide and sulfide are formed on materials exposed in SO<sub>2</sub>/O<sub>2</sub> environments. Sulfide is generally formed beneath the oxide scale. Pettit et al<sup>7</sup> and Birks<sup>8</sup> have reviewed the thermodynamic aspects of metal corrosion in the bi-oxidant situation and have shown that the simultaneous formation of oxide and sulfide is unlikely, on thermodynamic grounds. However, sulfides are often observed when the thermodynamic phase stability diagram predicts they may not be formed. Thus, it is clear that kinetic aspects must be considered in order to explain the phenomenon of simultaneous oxide and sulfide formation. Rahmel<sup>9</sup> has provided six sets of conditions for this behavior. His experimental work, together with that of Birks et al<sup>10,11</sup> and Strafford et al<sup>12</sup>, have shown that the two most likely mechanisms are:

- (i) ionic diffusion of sulfur through the oxide to the metal/scale phase boundary
- (ii) penetration of the scale by the gas through fine cracks.

Mechanism (ii) can lead to sulfide formation over a wider range of sulfur partial pressures than mechanism (i) because a relatively high partial pressure of sulfur is developed by the dissociation of SO<sub>2</sub> molecules at the oxide/metal interface. The local oxygen activity decreases with increasing depth in the oxide scale and consequently the dissociation of SO<sub>2</sub> becomes more favored. Mrowec<sup>10</sup> lists the minimum SO<sub>2</sub> partial pressure in the environment required to form sulfide at the oxide/metal interface for a number of pure metals. It is clear that quite low pressures of SO<sub>2</sub> in the environment are sufficient to cause sulfidation. An interesting point made by Mrowec, with regard to sulfide formation, is that the more thermodynamically stable the oxide the more sensitive it is to SO<sub>2</sub> attack. This is due to the fact that the SO<sub>2</sub> molecule will be more readily dissociated at the lower oxygen activity at the metal/oxide interface of the more stable oxide. Thus, it appears that alumina scale formers would be more sensitive to SO<sub>2</sub> attack than chromia scale formers.

## EXPERIMENTAL PROCEDURE

The compositions of the alloys investigated, alloy 556 and Type 304 stainless steel, are listed in Table 1. Two coupons of each alloy were exposed in two different environments, Ar-10%SO<sub>2</sub>-5%O<sub>2</sub>-5%CO<sub>2</sub>, Ar-5%CO<sub>2</sub>-5%O<sub>2</sub> (all volume %) at 1800°F (982°C) for 550 hours. The equilibrium partial pressures of the various species at 1800°F (982°C) are given in Table 2. Thermodynamics predict that the sulfides of the major alloying elements will not be stable in the SO<sub>2</sub>-bearing environment.

Mechanically polished specimens of dimensions 2.5 cm x 2.5 cm x 0.13 cm (1 in. x 1 in. x 0.050 in.) were placed in a tube furnace and the gas mixture flowed through the tube at a rate of about 150 cc/min. A platinum-coated honeycomb alumina catalyst placed upstream of the specimens ensured equilibration of reaction (3) above. The samples were furnace-cooled in the gas mixture after the exposure period.

The exposed specimens were analyzed by x-ray diffraction to determine the identity of the surface phases. SEM/EDAX was used to determine chemical compositions, and metal loss and internal attack were measured by optical metallography.

## RESULTS

Exposure in the sulfur-free O<sub>2</sub>/CO<sub>2</sub> environment resulted in extensive oxidation of the Type 304 sample. The measurements of metal loss and internal attack are given in Table 3. X-ray diffraction analysis of the oxide scale identified it as Fe<sub>2</sub>O<sub>3</sub>. However, SEM/EDAX analysis of the surface of the scale and in cross section revealed the presence of Mn, Cr and Ni in the scale (Figure 1). It appears that the composition of the oxide varies through the thickness. A high level of Cr was detected in the oxide near the scale/metal interface but was not found near the scale/gas interface. In contrast, Mn was present near the scale/gas interface but absent from the scale/metal interface. The scale was also quite porous, which would obviously facilitate access of gas to the metal surface.

Corrosion of Type 304 in the SO<sub>2</sub>-bearing environment was non-uniform. The overall corrosion was severe and in some areas the specimen was corroded through the thickness. X-ray diffraction of the surface scale identified mixed Fe-Cr and Fe-Mn oxides and Fe<sub>2</sub>S. An area of the metal which was not completely consumed was examined by SEM/EDAX. The phases in the grain boundaries (Figure 2) were mostly Fe-Cr oxide. Low levels of sulfur were detected, indicating that sulfur was dissolved in the oxide. Discrete Fe-Cr sulfides were detected in the matrix beneath the oxide, indicating that sulfur may have been displaced by incoming oxygen, forcing sulfur deeper into the alloy to form new sulfides.

Alloy 556 showed little oxidation attack in the sulfur-free oxidizing environment. The metal loss and internal oxidation measurements are given in Table 3. The specimen surface was analyzed by x-ray diffraction and found to consist of MnFe<sub>2</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub>. SEM/EDAX analysis of a spalled area of the scale indicated that there were two layers present - an outer Mn-rich layer and an inner Cr-rich layer (Figure 3). The scale in cross-section was found to be about 10 μm thick and compact (Figure 4). EDAX analysis confirmed that it was chromium-rich.

The addition of SO<sub>2</sub> to the environment increased the amount of corrosion attack on alloy 556 (Table 3). The maximum metal affected (metal loss + maximum internal penetration) was increased by a factor of about 3. X-ray diffraction of

the surface scale revealed mixed Fe-Cr and Mn-Cr oxides. The surface scale (Figure 5) consisted of a rumpled outer layer, which was apparently chromium oxide and an inner layer which was a mixed oxide. The outer layer had spalled off in some areas. Sulfur was not detected on the surface. An examination of the material in cross-section revealed the presence of internal chromium-rich sulfides beneath the internal oxide (Figure 6).

## DISCUSSION

Sulfur can penetrate an oxide scale by ionic diffusion or via physical flaws in the scale. It is clear from the literature that physical permeation is an important mode of ingress. Thus, the oxidation resistance of an alloy, which requires the formation of a compact, adherent scale, is a good predictor of resistance to attack by  $\text{SO}_2$ . It is reasonable to expect that porous or friable scales will provide poor resistance to sulfidation attack.

Although thermodynamics predict that the sulfides of the major elements will not be stable in the  $\text{SO}_2/\text{O}_2$  environment used in this study, both alloys formed internal sulfide. This indicates that sulfidation probably occurred by permeation of  $\text{SO}_2$  molecules through flaws in the scale. It is clear that this occurred much more easily for Type 304 than for alloy 556. The porosity in the scale on Type 304 is probably a major factor in its behavior. The oxidation resistance of the stainless steel was found to be poor at  $1800^\circ\text{F}$  ( $982^\circ\text{C}$ ). This alloy is normally a chromia-former but obviously underwent breakaway oxidation under the test conditions. The oxidation resistance deteriorated in the presence of  $\text{SO}_2$ , leading to the complete conversion of metal to oxide and sulfide. It is likely that sulfur accelerated the initiation of breakaway oxidation. Sulfide formation in the subscale region caused a depletion in chromium, which is then not available for healing of the scale. This accelerated the breakaway oxidation. In addition, sulfur anions penetrated the metal via grain boundaries, due to the high diffusion rate of sulfur, and combined with chromium to form chromium sulfide. The formation of sulfide resulted in a chromium depletion in the grain boundary area which thus became susceptible to subsequent oxidation. Chromium sulfide was again decomposed by incoming oxygen as a result of the greater stability of the oxide, resulting in the liberation of sulfur ions for further sulfidation reactions. The sulfidation reaction front thus ran ahead of subsequent oxidation. Chromium depletion of the matrix, which results from this sulfidation attack, can lead to the formation of nickel sulfides. This was not, however, observed in this study.

Alloy 556 exhibited good oxidation resistance in the absence of sulfur, forming a thin, compact scale. As a result, the alloy was little affected by the addition of sulfur to the environment. Although the oxide scale contained Fe and Mn, there was no evidence to suggest that this caused a deterioration in the properties of the scale relative to sulfur. It has been suggested that some elements, manganese in particular, may lead to a breakdown of an oxide scale in a sulfidizing environment. The formation of internal sulfides in the  $\text{SO}_2$ -containing environment reinforces the point that even good oxide scales will eventually be penetrated by sulfur. It is clear, however, that a good scale is highly effective in retarding the ingress of sulfur.

## CONCLUSIONS

Based on the present study on Fe-base chromia formers, oxidation resistance appears to be a reasonable criterion for selecting materials for use in oxidizing

environments containing 10% SO<sub>2</sub>. The corrosion reaction under the present test conditions was found to be dominated by oxidation. A material which forms a compact, adherent scale in a purely oxidizing environment will form a similar barrier to retard sulfur ingress in SO<sub>2</sub>/O<sub>2</sub> environments. However, the scale will eventually be penetrated by sulfur in some form, leading to the formation of internal sulfides.

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TABLE I  
CHEMICAL COMPOSITIONS OF THE ALLOYS INVESTIGATED (WT %)

Alloy	Fe	Ni	Co	Cr	Mo	W	Ta	N	Si	Mn	Al	C	La	Zr
HAYNES® alloy 556 (UNS R-30556)	Bal	20.0	18.0	22.0	3.0	2.5	0.6	0.2	0.4	1.0	0.2	0.1	0.02	0.02
Type 304 (UNS 530400)	Bal	8.3	-	18.2	0.4	-	-	0.7	0.5	1.9	-	0.05	-	-

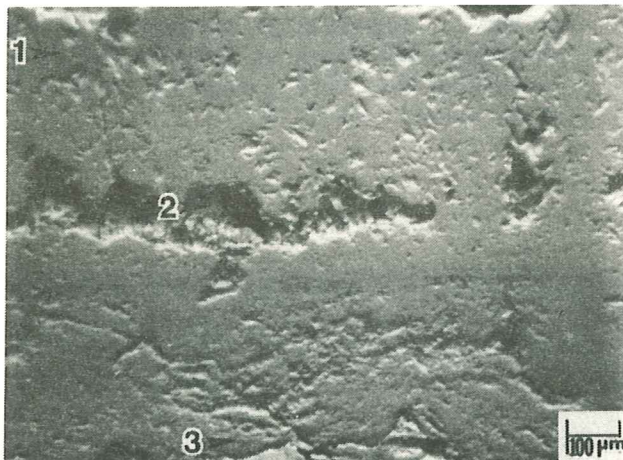
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TABLE 2  
EQUILIBRIUM PARTIAL PRESSURES OF THE  
GAS MIXTURES AT 1800°F (982°C)

Input Partial Pressures (atm)				Equilibrium Partial Pressures (atm)				
Ar	SO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub>	Ar	SO <sub>2</sub>	O <sub>2</sub>	SO <sub>3</sub>	S <sub>2</sub>
Bal	0.10	0.05	0.05	Bal	9.7×10 <sup>-2</sup>	4.9×10 <sup>-2</sup>	3.6×10 <sup>-3</sup>	10 <sup>-22</sup>
Bal	-	0.05	0.05	Bal	-	5×10 <sup>-2</sup>	-	-

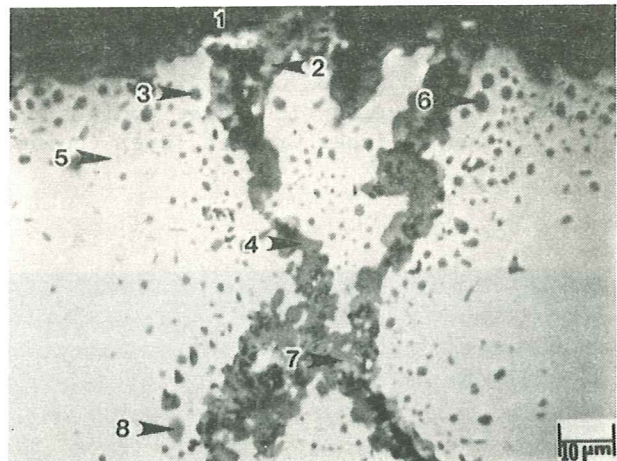
TABLE 3  
METAL LOSS AND INTERNAL ATTACK FOR TYPE 304 AND ALLOY 556  
AFTER 550 HOURS AT 1800°F (982°C) IN THE TWO TEST ENVIRONMENTS

Environment	Metal Loss (mils/side)		Maximum Internal Attack (mils)	
	Type 304	Alloy 556	Type 304	Alloy 556
Ar-5%O <sub>2</sub> -5%CO <sub>2</sub>	12.2	0.2	5.0	2.0
Ar-10%SO <sub>2</sub> -5%O <sub>2</sub> -5%CO <sub>2</sub>	Consumed ( > 24 )	2.5	Consumed	4.0



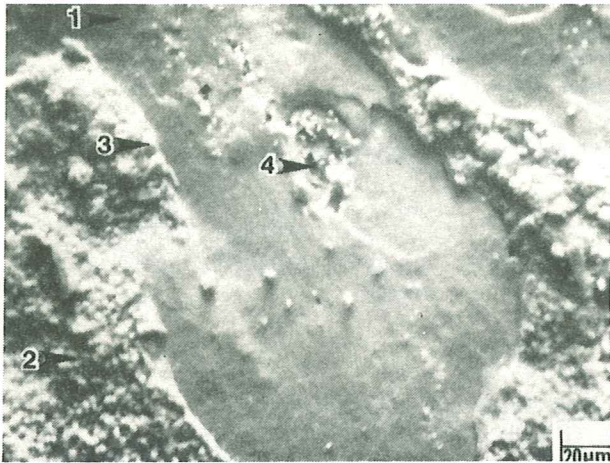
SEMI-QUANTITATIVE ANALYSIS (%)				
Point	Fe	Ni	Cr	Mn
1	88.7	1.3	-	10.0
2	88.0	4.4	3.2	4.4
3	36.0	9.1	54.9	-

FIGURE 1: SEM/EDAX of cross-section of oxide scale on Type 304 after 550 hours at 1800°F (982°C) in Ar-5%O<sub>2</sub>-5%CO<sub>2</sub>, showing porosity and variations in scale composition.



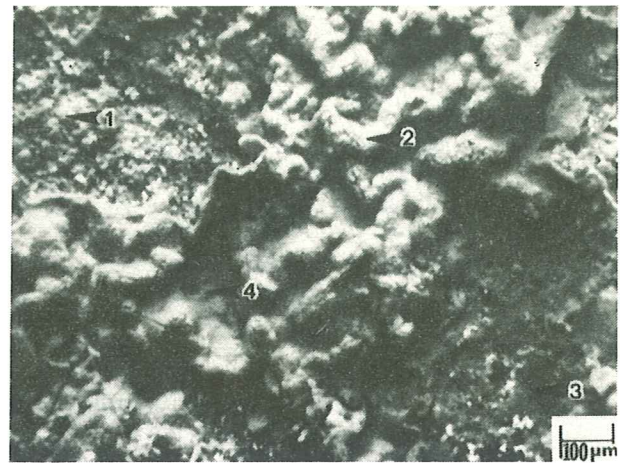
SEMI-QUANTITATIVE ANALYSIS (%)					
Point	Fe	Ni	Cr	Si	S
1	10.1	1.7	86.5	1.4	0.3
2	24.6	3.4	66.2	0.5	5.4
3	46.8	4.7	30.3	-	18.2
4	9.2	0.7	88.5	1.5	0.1
5	78.4	7.6	14.0	-	-
6	45.9	4.2	30.2	1.1	18.6
7	7.0	0.7	90.7	0.6	1.0
8	51.0	4.1	29.2	1.1	14.6

FIGURE 2: SEM/EDAX of cross-section of Type 304 after exposure at 1800°F (982°C) for 550 hours in Ar-10%SO<sub>2</sub>-5%O<sub>2</sub>-5%CO<sub>2</sub>, showing internal attack.



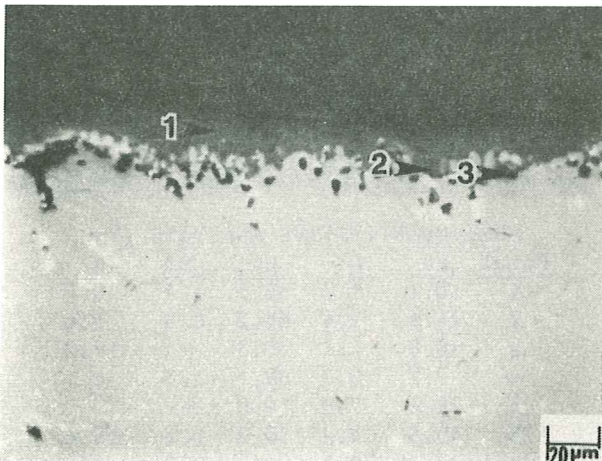
SEMI-QUANTITATIVE ANALYSIS (%)							
Point	Fe	Ni	Co	Cr	Mn	Mo	Ta
1	-	-	-	100.0	-	-	-
2	-	-	-	59.0	41.0	-	-
3	7.3	1.1	0.8	55.3	35.6	-	-
4	14.1	7.9	9.6	42.7	9.1	0.6	16.0

FIGURE 3: SEM/EDAX of spalled area of surface oxide on alloy 556 after 550 hours at 1800°F (982°C) in Ar-5%O<sub>2</sub>-5%CO<sub>2</sub>. An outer Mn-rich layer (points 2 and 3) and an inner Cr-rich layer (point 1) are shown.



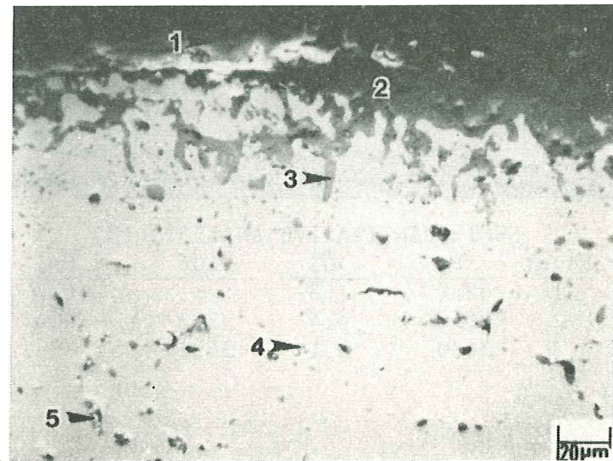
SEMI-QUANTITATIVE ANALYSIS (%)						
Point	Fe	Ni	Co	Cr	Mo	W
1	33.9	16.5	16.5	29.7	1.7	1.7
2	2.5	0.7	0.4	96.1	0.1	0.2
3	0.2	0.2	0.3	98.6	0.1	0.6
4	5.2	0.9	1.6	90.9	0.9	0.4

FIGURE 5: SEM/EDAX of surface of alloy 556 after 550 hours at 1800°F (982°C) in Ar-10%SO<sub>2</sub>-5%O<sub>2</sub>-5%CO<sub>2</sub>, showing Cr-rich scale (points 2, 3, & 4).



SEMI-QUANTITATIVE ANALYSIS (%)							
Point	Fe	Ni	Co	Cr	W	Mo	Ta
1	1.2	0.5	-	97.6	0.7	-	-
2	7.0	3.5	-	89.3	0.2	-	-
3	21.7	11.3	12.5	35.7	-	0.5	18.4

FIGURE 4: SEM/EDAX of cross-section of alloy 556 after 550 hours at 1800°F (982°C) in Ar-5%O<sub>2</sub>-5%CO<sub>2</sub>, showing thin oxide layer.



SEMI-QUANTITATIVE ANALYSIS (%)							
Point	Fe	Ni	Co	Cr	W	Mo	S
1	11.1	0.7	1.1	86.7	0.3	0.1	-
2	34.9	5.0	6.7	52.1	0.5	0.8	-
3	1.4	0.6	0.6	57.9	-	-	39.6
4	28.8	14.1	13.5	34.4	0.2	0.4	8.7
5	22.5	12.7	12.4	31.6	7.9	12.9	-

FIGURE 6 - SEM/EDAX of cross-section of alloy 556 after 550 hours at 1800°F (982°C) in Ar-10%-SO<sub>2</sub>-5%O<sub>2</sub>-5%CO<sub>2</sub> showing oxide layer and internal sulfides.