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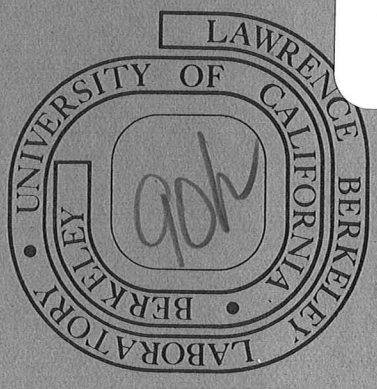

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Corrosion of Fe-10Al-Cr Alloys by Coal Char

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Abstract

Corrosion of iron-base alloys at 982°C (1800°F) by coal char is observed and the phase morphologies discussed. No sulfidation was observed at 50 hours exposure. After 100 hours, internal aluminum-rich sulfides were observed along with thick outer scales of iron oxide. The species causing the high-temperature induced corrosion are probably sulfides and sulfates, present in most coal chars. Possible mechanisms for the corrosion are also discussed.

Key words: iron-aluminum-chromium, corrosion, coal char

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INTRODUCTION

With the current energy crisis, increased attention has been focussed on coal as an abundant source of fossil fuel. A promising way to utilize coal is to convert it to synthetic natural gas (SNG) and petroleum-type products. There are problems in coal-gasification because at the reaction temperatures of 870° to 982°C (1600° to 1800°F) and pressures of up to 60 to 70 atmospheres, the reaction products become quite corrosive to containment materials.

The off-gas from a typical gasifier contains large percentages of CO, CO_2, H_2, CH_4, H_2O, and H_2S .[1] These gases, particularly H_2S , can be quite corrosive. To compound the problem, the particulate by-product of gasification is char, a light, friable material which contains (see Table 1) about 25-50% fixed carbon and the balance inorganic oxides, sulfides, and sulfates (including FeS and $CaSO_4$, respectively).[2]

Considerable work is being done on gas-metal corrosion of alloys,[3-6] but very little has been done on corrosion of alloys by coal char. This work describes some preliminary screening experiments to observe the behavior of char on Fe-10Al and Fe-10Al-Cr alloys at coal-gasifier operating temperatures.

This investigation is concerned with iron-base alloys that form external Al_2O_3 scales. In alumina forming alloys the transition from internal to external Al_2O_3 formation occurs around 7 wt.%. To be certain of forming an external Al_2O_3 scale, 10 wt.% Al was added to the alloys.

EXPERIMENTAL

The furnace used was a Lindberg horizontal tube furnace equipped with a 3.8 cm o.d. mullite tube. The ends of the tube were sealed with compression-type Viton o-ring seals. For introduction of the samples into the heat zone, one end of the furance was equipped with a 3.8 cm i.d. ball valve. For introduction of the appropriate gas, the other end was equipped with a gas inlet nozzle, metering valve, and a vacuum pump to remove all traces of air from the furnace.

The temperature of the furnace was calibrated before and after each run since there was no provision for continuous, on-line monitoring. Temperature variation was ±2°C as determined by a long-term calibration using a chromel-alumel thermocouple and Doric digital indicator.

The samples were prepared by cutting coupons about 1 cm × 1 cm × 0.5 cm. All six faces were polished to 600 grit and washed with ethanol.

The gas used was argon with approximately 6-10 ppm of oxygen as an impurity. The carbon-carbon monoxide equilibrium kept the P_{O_2} much lower than that present in the argon.

The sample coupons were placed in a high-purity alumina boat half-filled with synthane process coal char from Illinois #6 coal and inserted into the furnace which was kept at a constant 982°±2°C. All three samples were exposed in the same boat, with about 1 cm between samples. The exposure times were 24 hours, 50 hours, and 100 hours. At the end of the runs, the samples were removed, and their surfaces examined by scanning electron microscopy (SEM). They were then mounted in bakelite, cross-sectioned, and once again examined by SEM and energy dispersive x-ray analysis (EDAX).

RESULTS

All three alloys had suffered corrosion by char. Although there was no catastrophic corrosion up to 50 hours, the Fe-10Al and Fe-10Al-5Cr alloys were catastrophically corroded at the end of the 100 hour run. The -10Cr containing alloy suffered only very little external and internal corrosion. No sulfur was detected in any of the alloys after 24 or 50 hours exposure.

Figure 1 shows cross sections of Fe-10Al, Fe-10Al-5Cr, and Fe-10Al-10Cr alloys after 24 hours exposure to char at 982°C. Scanning electron micrographs of the surface of the samples show formation of an uneven aluminum oxide layer with several thick protrusions. Cross-sectioning through these protrusions shows that they are primarily Al_2O_3 (Figure 1a,b). Both the Fe-10Al-5Cr and Fe-10Al-10Cr alloys showed considerable Al_2O_3 penetration into the alloy (Figures 1c,e). The formation of uneven Al_2O_3 layers on the Fe-10Al-10Cr alloy left behind chromium-enriched regions in the alloy near the scale-alloy interface (Figures 1f,g). There was much less enrichment in the -5Cr system. All of the alloys exhibited uneven penetration as shown in Figures 1c and e.

After 50 hours exposure, the situation was much the same. The appearance of the three alloys was similar to that shown in Figure 1. The surface scale appeared rough and uneven. Penetration into the bulk of the alloy was not noticeably greater in any of the three systems as compared with 24 hours exposure.

The situation changed dramatically after 100 hours exposure. Figure 2 shows electron micrographs of the surfaces of all three alloys

after 100 hours. The surface has extensive scaling which appears to have spread out, slag-like, from the corners and edges. Under high magnification (Figures 2b,d), this expanded scale consists of long, needle-like protrusions with a smooth, molten surface appearance. EDAX analysis of these needles reveals that they are almost entirely iron oxide. Such growths appeared on the Fe-10Al and Fe-10Al-5Cr alloys but not on the Fe-10Al-10Cr alloy. Instead, on the -10Cr alloy, small, oval protrusions of Al_2O_3 formed after 100 hours exposure.

Cross-sectioning of the alloys revealed that although the scale was predominantly iron oxide, increasing amounts of aluminum began to appear in the scale towards the uncorroded metal. Finally, at the interface of the uncorroded alloy and the furthest penetration of the corrosion, sulfur appears, invariably as aluminum-rich sulfide. These sulfides appear as grey or black needles in optical micrographs (Figure 3a,b) and occur only in the Fe-10Al and -5Cr alloys. No such penetration occurs in the -10Cr alloy. Figure 4 shows an EDAX analysis of such a region in the Fe-10Al-5Cr system. The x-ray mapping technique provides a good contrast between the aluminum- and sulfur-rich regions and the aluminum- and sulfur-poor regions. Figures 4b-d show that the dark grey inclusions are rich in aluminum and sulfur and poor in Fe . Further examination reveals that there is a chromium-rich region that appears as a thin but uneven layer in the external scale (Figure 4e). Underneath that but still in the external scale is an aluminum-rich region followed by a region of apparently unreacted alloy. Next comes the portion of the alloy penetrated by aluminum sulfide.

After the 100 hours tests, the coal char had taken on a red, powdery appearance, typical of Fe_2O_3. This implied that between 50 and 100 hours of exposure, all the carbon had been oxidized and lost from the system. The P_{O_2} subsequently had risen to the level present in the argon, about 6-10 ppm (about 10^{-5} atmospheres). This is sufficient to oxidize all the FeO and FeS in the char to Fe_2O_3.

DISCUSSION

The partial pressure of oxygen over the char is about 10^{-5} to 10^{-6} atmosphere. At the char-alloy interface in these experiments, the partial pressure of oxygen should be much lower than 10^{-6} atmosphere because of the reaction between carbon in the char and oxygen in the argon. Thermodynamically, it should be below 10^{-19} atmosphere. After 24 and 50 hours exposure, there was still sufficient carbon left to maintain this situation, but between 50 and 100 hours the carbon was completely oxidized, and the oxygen partial pressure permitted to rise to that level present in the argon.

After both 24 hours and 50 hours exposure, only an uneven Al_2O_3 layer was formed on any of the alloys. At the conditions presumed to exist at the char-alloy interface, Al_2O_3 is the only stable phase. The reasons for the uneven nature of this layer are not well understood, and it may be due to the differences in the availability and partial pressure of oxygen at the char-alloy interface. Between 50 and 100 hours, extensive scaling appears on both the binary and the -5Cr alloy. This corrosion seems to have formed a liquid slag. Cross sectioning of the alloys shows extensive internal penetration and the

formation of aluminum-rich sulfide inclusions. This indicates that the slag formed might initially be a liquid sulfide or an oxide-sulfide eutectic which later becomes completely oxidized.

Examination of the composition of char (presented in Table 1) and the morphology of the corrosion of the alloys reveals that sulfur for the corrosion reaction must have come from FeS and/or $CaSO_4$. It is difficult to pinpoint whether FeS or $CaSO_4$ contributed the major amount of sulfur for the corrosion reaction, but some inferences can be made from thermodynamic considerations. Examination of CaO - $CaSO_4$ (7) and FeO - FeS (5) stability phase diagrams shows that both $CaSO_4$ and FeS could decompose to donate sulfur for the reaction. Furthermore, it is also evident that increasing the partial pressure of oxygen should increase the partial pressure of sulfur by oxidation of FeS. Decreasing the partial pressure of oxygen should increase the partial pressure of sulfur by reduction of $CaSO_4$. The experimental observation that no sulfidation occurred when carbon was still present (and the P_{O_2} low) is more consistent with the hypothesis that FeS is the principal corroding species. Further experiments are being carried out with controlled P_{O_2} to demonstrate clearly the conditions under which FeS and $CaSO_4$ become major corroding species.

At the conditions presumed to exist at the char alloy interface, aluminum-rich sulfides are unstable, and the alloys should form only Al_2O_3 scales. But the partial pressure of oxygen beneath the Al_2O_3 scale will be extremely small, and so aluminum-rich sulfides can form if the sulfur can diffuse through the external Al_2O_3 scale. The

experimental results indicate that sulfur does indeed diffuse through the external scale.

The experimental observation that at the end of 100 hours, two of the three alloys had slagged and the remainder of the char was porous suggests that the slag is formed as a result of the presence of the alloy and not within the char itself. In practical situations, the slagging type of corrosion may be prevented if the partial pressure of oxygen is properly regulated so the decomposition of FeS is minimized.

CONCLUSIONS

Char contains sufficient fixed inorganic sulfur to induce corrosion in iron-base alloys. At sufficiently high temperatures and oxygen partial pressures, this corrosion can appear in the form of a liquid slag on the surface of the alloy. Internal sulfides can also form as a result of this kind of attack leading to catastrophic failure of the alloy.

ACKNOWLEDGEMENTS

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ASH	Percentage
SiO_2	46.3
Al_2O_3	15.2
Fe_2O_3	14.9
CoO	6.5
MgO	1.1
TiO_2	0.6
P_2O_5	0.2
Na_2O	3.0
K_2O	1.8
SO_3	5.4
	as sulfate & sulfide

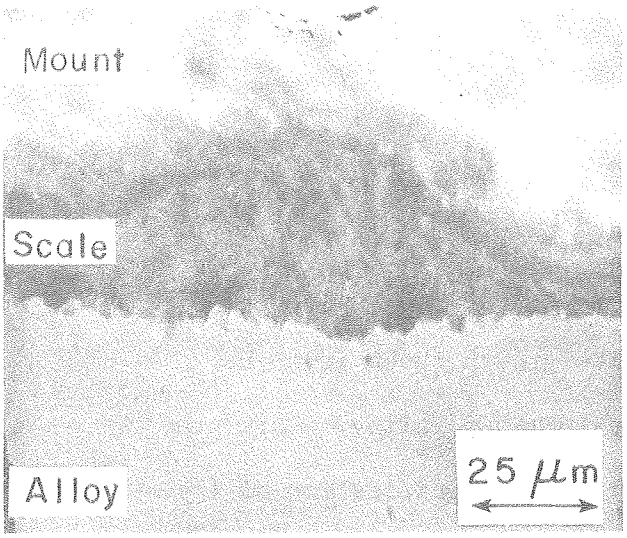
CHAR	Percentage
fixed carbon	25-50%
ash	45-70%
sulfur	<1.5%
high boiling tars	<4%

Table 1. Composition of Illinois #6 ash and coal char.

Figure 1. Cross sections of samples exposed to char and argon (+6-10 ppm O_2) for 24 hours at 982°C. The attached x-ray maps show elemental distributions as indicated.

(a) Fe-10Al alloy. Note the heavy, thick protrusion.

(b) Al X-ray map of protrusion indicates that protrusion is Al_2O_3. (c) Fe-10Al-5Cr alloy. Note the heavy, dark gray inclusion. (d) Al X-ray map indicates inclusions are Al_2O_3. (e) Fe-10Al-10Cr alloy with dark gray inclusions. (f) Cr-map showing Cr enrichment adjacent to but not in scale. (g) Al-map showing scale is Al_2O_3.



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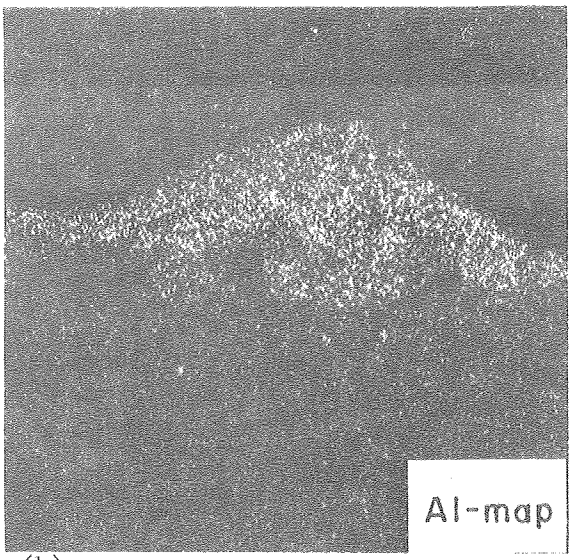

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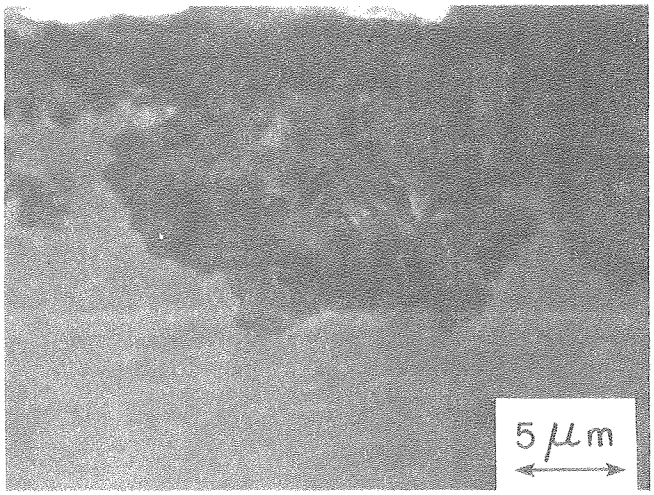

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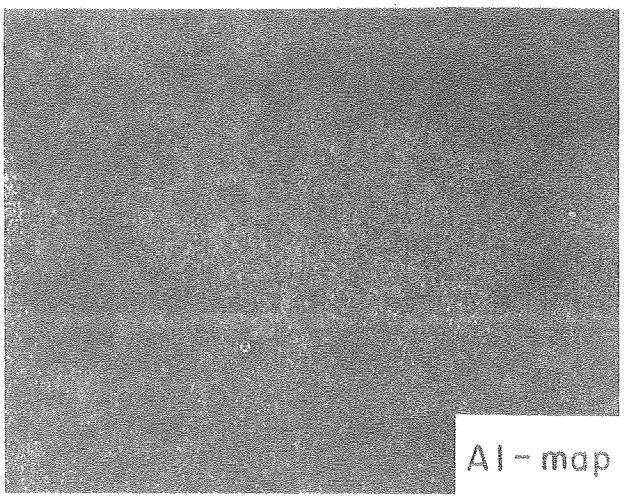

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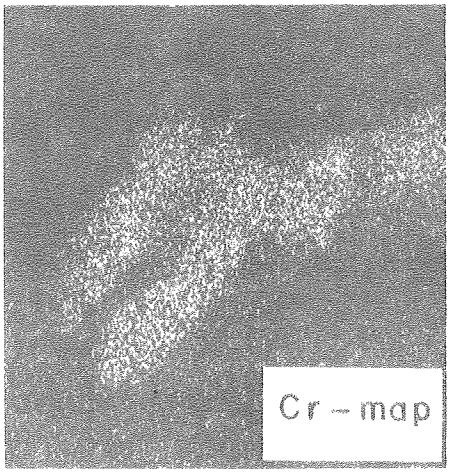

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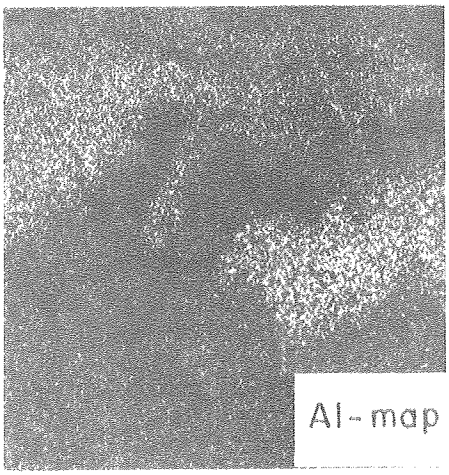

(g)

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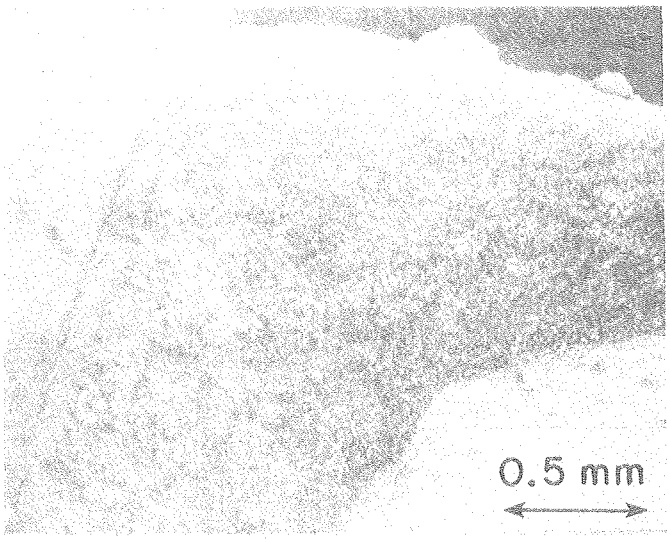
Figure 2. Surface micrographs of samples exposed to char and argon (+6-10 ppm O_2) for 100 hours at 982°C. (a) Fe-10Al alloy. Dark gray region is expanded scale. (b) High-magnification of (a). Analysis of needle-like growth shown it to be primarily iron oxide. (c) Fe-10Al-5Cr alloy. Dark gray region is expanded scale. (d) High magnification of (c). EDAX analysis also shows it to be iron oxide. (e) Fe-10Al-10Cr . No expanded scale but oval areas are thicker Al_2O_3 regions on surface.



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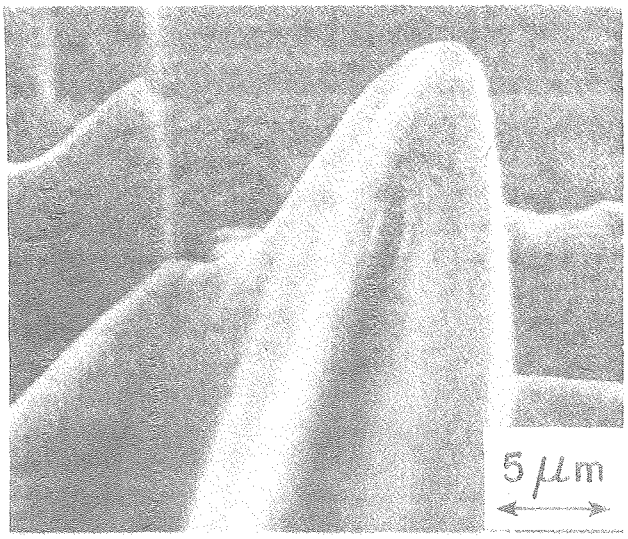

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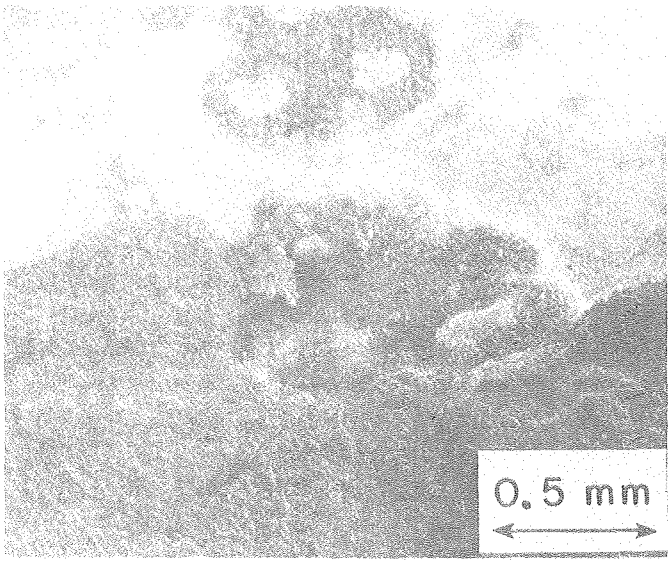

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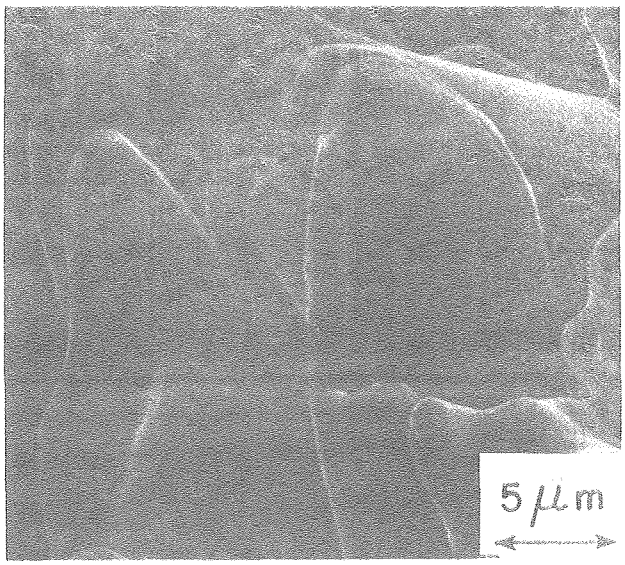

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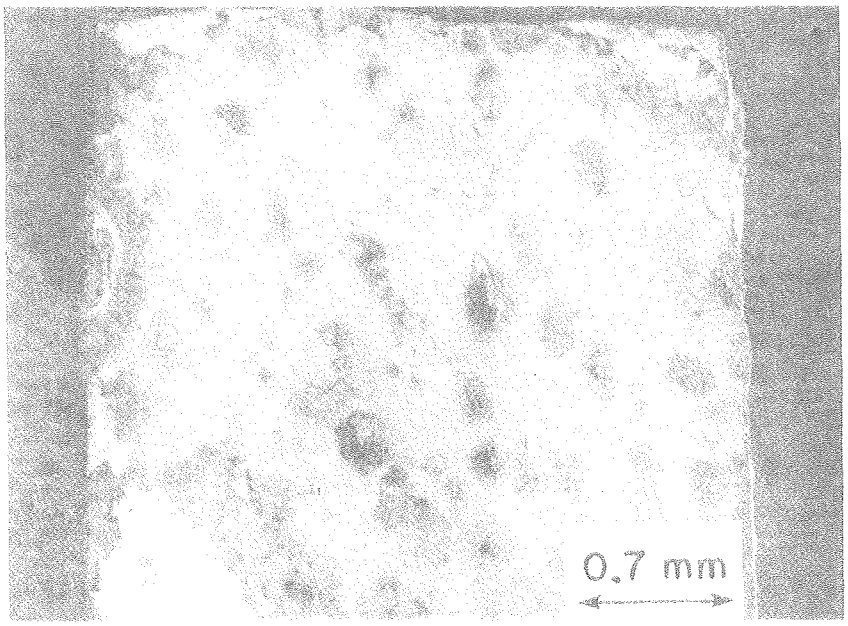

(e)

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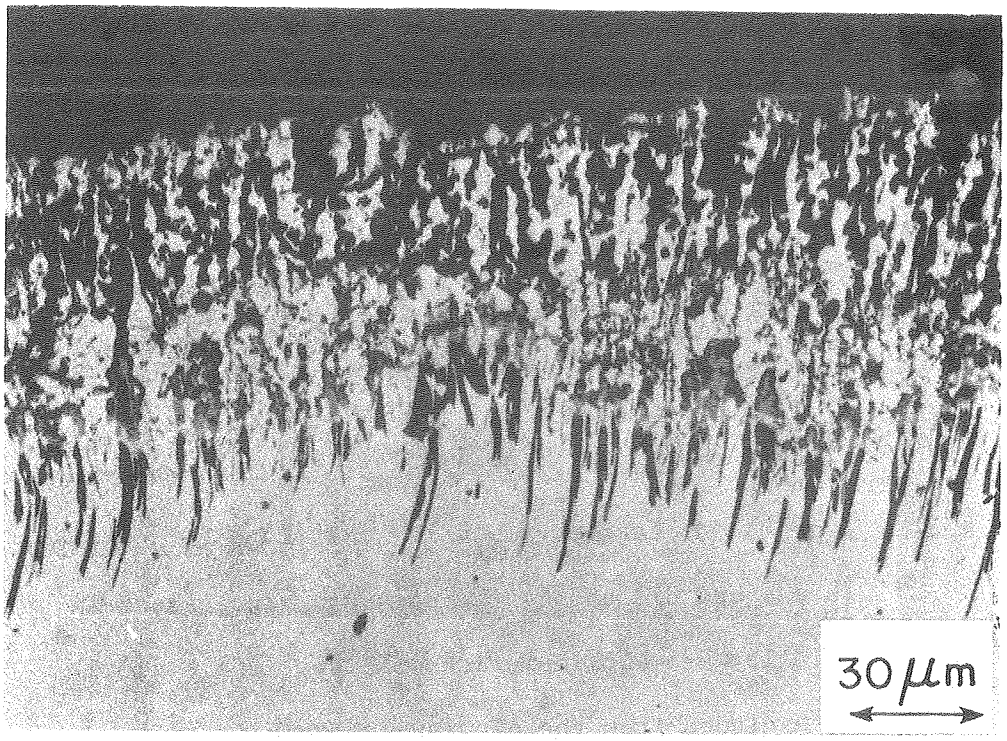
Figure 3. Optical micrographs of cross-sections of alloys after 100 hours exposure. (a) Fe-10Al . (b) Fe-10Al-5Cr . In both, the dark needles represent internal formation of aluminum-rich sulfides within the alloy itself. This region is covered by a scale which is predominantly iron oxide.



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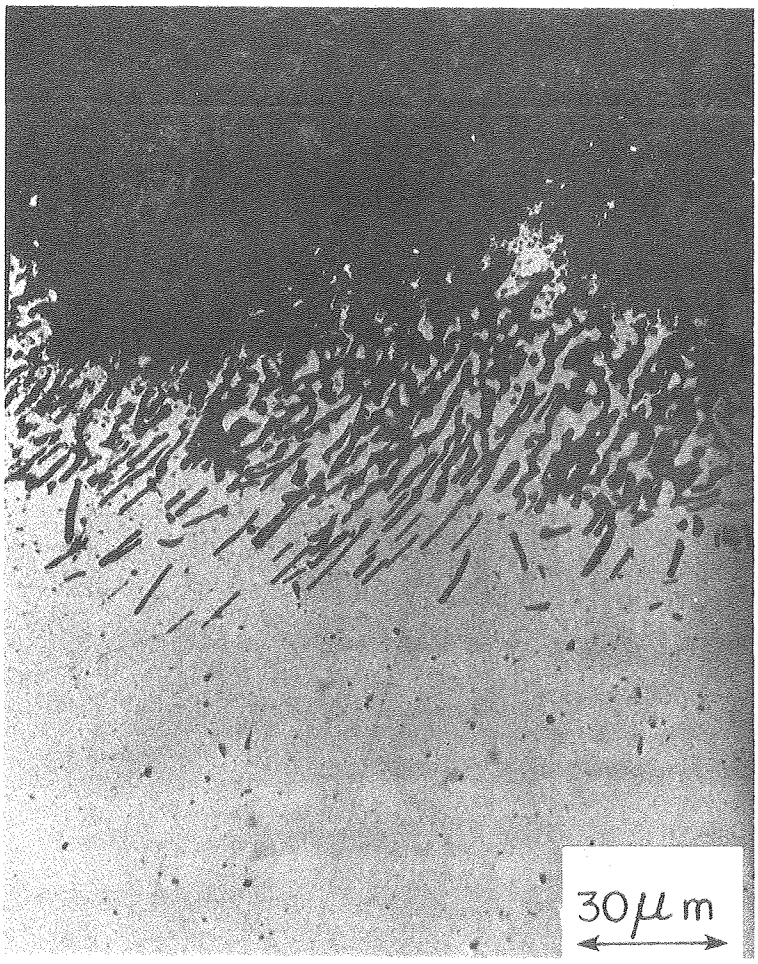

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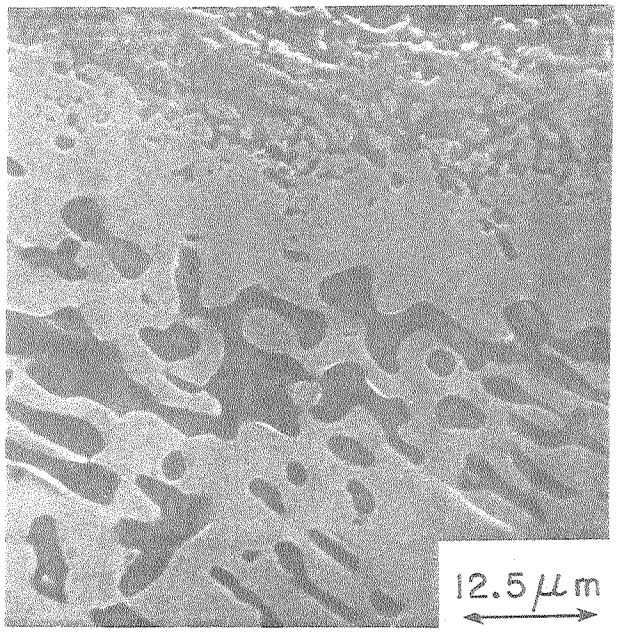
Figure 4. Cross section and x-ray mappings of Fe-10Al-5Cr alloy after 100 hours exposure. (a) Electron image. (b-e) elemental maps as indicated. Note the four distinct regions in the cross section: 1) lightest gray region is alloy itself, 2) medium gray at top of (a) is a chromium oxide (see e), 3) darker gray below that is aluminum oxide (see c and d), and 4) the dark gray inclusions in bulk of alloy are aluminum-rich sulfides (see c and d). Iron is excluded from the aluminum-containing regions (see b).



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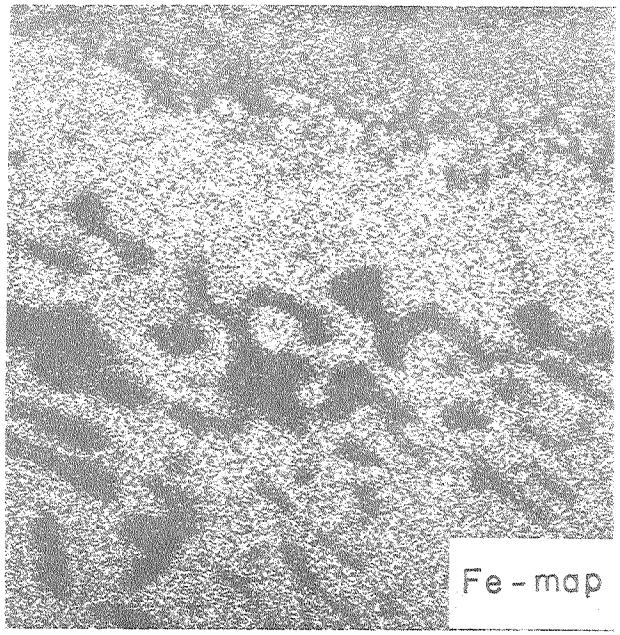

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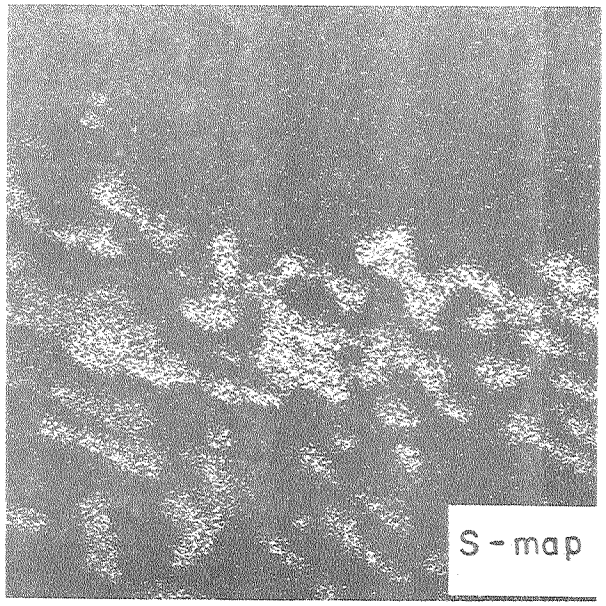

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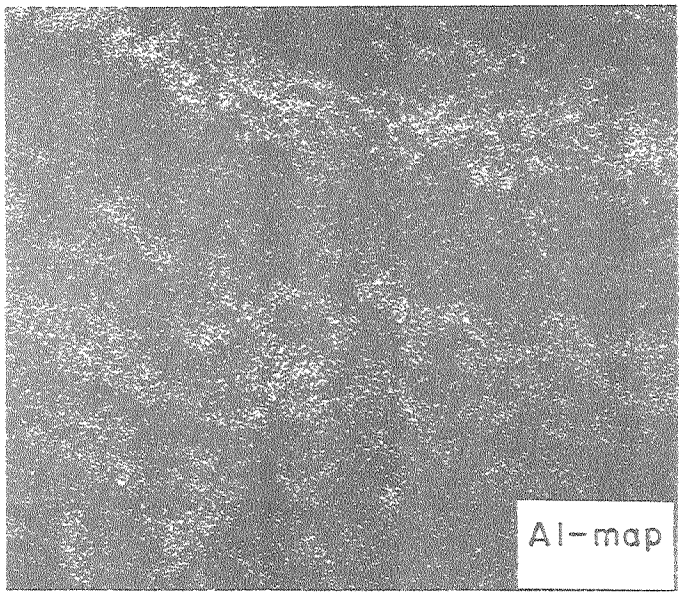

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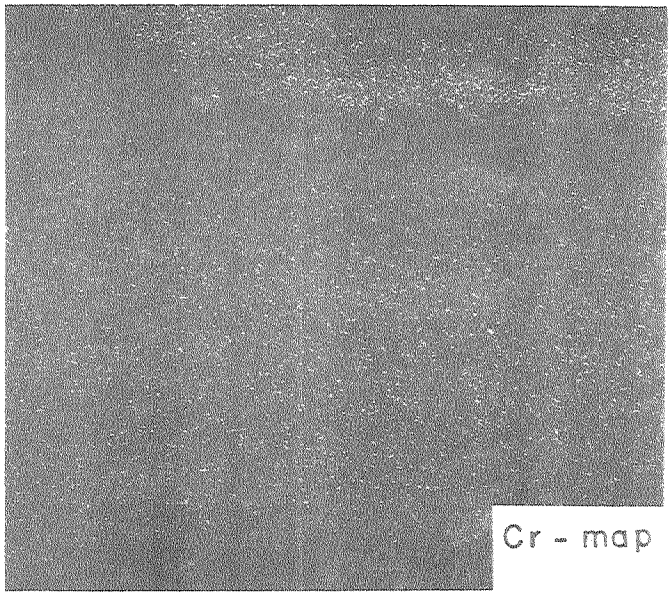

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