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DEVELOPMENT OF SURFACE TREATMENTS AND ALLOY MODIFICATIONS FOR CORROSION-RESISTANT OXIDE SCALES

J. H. DeVan

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Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6138

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Harry C. Williams
Authorizing Official
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ABSTRACT

Alloys based on the long-range ordered system Fe₃Al are under development at Oak Ridge National Laboratory in support of coal conversion and combustion materials requirements. Of particular interest is the performance of these alloys in coal gasifiers involving product gases with relatively low oxygen activities ($\leq 10^{-20}$ atm) and high sulfur activities ($\geq 10^{-8}$ atm). Using H₂S-H₂-H₂O gas mixtures, several experimental iron-aluminum alloys have been tested to assess the effects of aluminum concentration on oxidation-sulfidation response at 700 to 800°C in a simulated gasifier environment. Metallographic and chemical analyses of the corrosion product scales and the underlying alloy were performed to determine the role of respective metallic elements on the sulfidation-oxidation processes. These results, together with thermogravimetric analyses, are discussed in terms of the apparent corrosion mechanisms and optimization of alloy composition for exposure to coal-derived environments.

More recently, the corrosion performance of an Fe-28% Al-2% Cr alloy has been evaluated in gases produced by an operating gasifier. The reaction products and scale morphologies under actual service conditions were generally similar to the laboratory test results except for the presence of an ash deposit on the gasifier specimens.

INTRODUCTION

Because of high temperatures and the presence of sulfur, chlorine, and other oxidants in coal-derived environments, metal components in coal combustion and conversion systems are subject to severe corrosion. Accordingly, the objective of the present work is to develop protective scales on iron-based alloys in mixed-oxidant (oxygen-sulfur) environments for coal-related applications at 500 to 800°C. The experimental approach involves (1) development of protective oxide scales by modifying oxide chemistry and/or microstructure to reduce the transport of sulfur through the scales; (2) formation of a sulfur-diffusional barrier under or above the protective scale to minimize the sulfur attack; and (3) study of the effects of alloy chemistry, oxide morphology, and temperature on the breakdown of protective scales. To this end, corrosion studies during the last two years have concerned the oxidation-sulfidation properties of Fe₃Al-based alloys being

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developed at the Oak Ridge National Laboratory. Developmental alloys containing additions such as Cr, Nb, Mo, Zr, Y, and B were exposed to H₂S-H₂-H₂O gas mixtures at 700 and 800°C, respectively. These studies¹ have established that chromium must be limited to levels of about 2% in Fe₃Al-based alloys to perform acceptably in simulated gasifier environments. Additions of niobium and molybdenum appeared to be beneficial in reducing sulfidation attack in similar environments, but vanadium and manganese additions were detrimental. Additions of yttrium and zirconium also proved beneficial, apparently by blocking sulfur diffusion in the scale, since neither of these elements perceptibly affected scale adherence. Increasing the aluminum level from 28% (standard for Fe₃Al-based alloys) to 35% effectively masked any third-element effects, as all alloys tested with 35% Al performed as well or better in H₂S-H₂-H₂O than the binary Fe₃Al.

In the last year, comparative screening tests of developmental alloy modifications have been superceded by studies of the mechanisms of oxidation/sulfidation processes in the alloys with particular emphasis on the effects of chromium additions. Further insight into the kinetics of scale growth has been provided by thermal cycling tests of both as-surface-finished and preoxidized Fe₃Al alloys. In the past year, exposure of an Fe₃Al alloy containing 2% Cr to the product gas of an operating gasifier has provided a comparison of corrosion behavior under actual gasifier conditions with our laboratory test results.

LABORATORY TEST RESULTS

Preoxidation Studies

Three Fe₃Al-based alloys (PS28, -29, and -30 in Table 1) were preoxidized in dry air at 800°C for 7 h and then were exposed to a 5.35% H₂S, 79.23% H₂, 1.70% H₂O, 13.72% Ar mixture at 800°C for 100 to 200 h in a continuously recording microbalance system. Results were compared with tests of the same three alloys without the preoxidation treatment. Preoxidation lowered the weight gain of the 5% Cr alloys (PS28 and -29) by a factor of 4 over a 120-h period. However, the parabolic rate constant of the latter alloys did increase slightly after 75 h. Preoxidation of the 2% Cr alloy (PS30) reduced the weight gain to an imperceptible level with no change over a

175 h period. There was little change in the general appearance of preoxidized alloys that occurred during the H₂S exposure (i.e., the surfaces retained the bronze-colored oxide formed during preoxidation). However, in the case of a 5% Cr alloy (PS28), examination by SEM revealed the growth of flat needles and blades at the sharp corners formed by the intersecting sides of the specimens (Fig. 1). Energy-dispersive spectrographic analysis showed the growths to consist predominantly of iron sulfides with some aluminum also present. These growths are apparently responsible for the increase in the parabolic rate constant after 75 h and obviously reflect a mechanical breakdown of the preoxidized surface scale at points of disregistry (i.e., sharp corners).

The preoxidation results support our previous findings that the compatibility of Fe₃Al alloys with H₂S derive from the relatively fast kinetics of protective Al₂O₃ scale growth compared to the growth of nonprotective CrS and Fe_{1-x}S scales.¹ Adding chromium to the alloys at concentrations above 2% accelerates the growth of chromium and iron sulfides, as manifested by much greater weight gains compared to alloys with lesser chromium levels and the coverage of exposed surfaces by an FeS outer scale. Based on the preoxidation test results, chromium in the alloy does not affect the stability (or growth rate) of a preformed Al₂O₃ scale in H₂S. However, if a mechanical breakdown in this scale occurs, the presence of chromium leads to preferential growth of FeS, as opposed to Al₂O₃, in the replacement scale. Thus, chromium acts to promote the growth of sulfides relative to Al₂O₃ but does not appear to affect the transport properties of the Al₂O₃ scale.

Table 1. Compositions of test alloys

Alloy designation	Al	Cr	Nb	Zr	Other
PS28 (FAL)	28	5		0.1	0.05B, bal Fe
PS29 (FALM)	28	5	0.5		0.05C, bal Fe
PS30 (FAS 28-8)	28	2			0.05B, bal Fe
PS33 (FA135)	28	2	0.5		0.05B, bal Fe
FA117	28	2	0.8	0.1	0.5Mo, 0.03Y, 0.06B, bal Fe

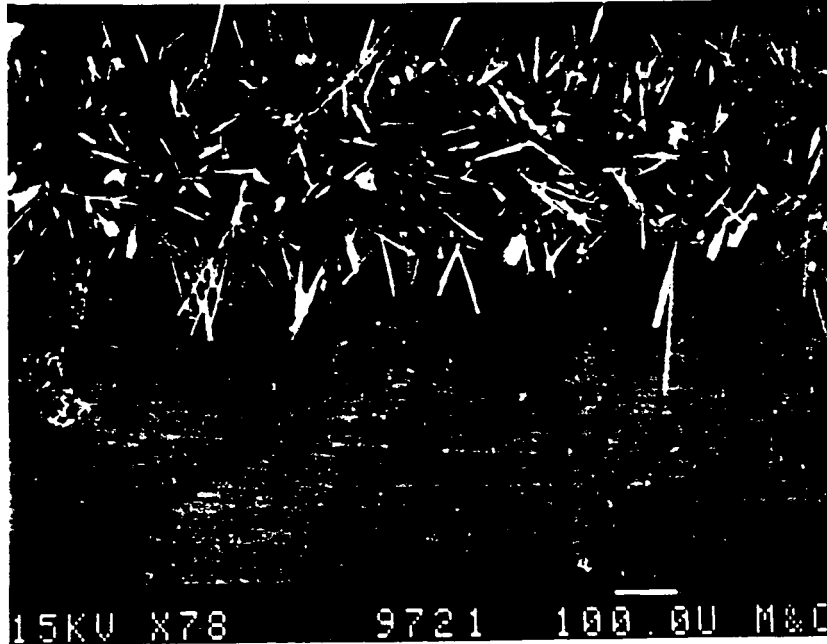


Fig. 1. Scale formed on preoxidized coupon of Fe-28% Al-5% Cr alloy (PS28) exposed to simulated gasifier atmosphere at 800°C.

Effects of Thermal Cycling

We have noted previously¹ that, despite the excellent resistance of Fe₃Al-based alloys to H₂S-H₂-H₂O mixtures, there is significant scale exfoliation on cooling to room temperature following exposure of the alloys at 700 to 800°C. Despite this spalling tendency, however, repeated thermal cycling of the binary alloy between room temperature and 800°C did not significantly increase the rate of metal oxidation because the scale is quickly re-established and grows very slowly.¹ Thermal cycling tests have now been completed on an alloy containing 2% Cr (PS33 in Table 1) cycled between 800°C and room temperature, as shown in Fig. 2. The cycles were imposed after accumulated exposures of 116, 182, 248, 271, 294, 317, 340, and 410 h, respectively. The sudden decrease in weight at the time of each thermal cycle and the relatively rapid gain in weight following each cycle reflect the detachment and spalling of corrosion product scale during each cooldown. Even with this repeated removal of scale, however, the loss of metal over the 410-h period was less than 0.44 mg/cm². This loss, averaged over 400 h, translates to a wastage rate of less than 1.5 μm/year.

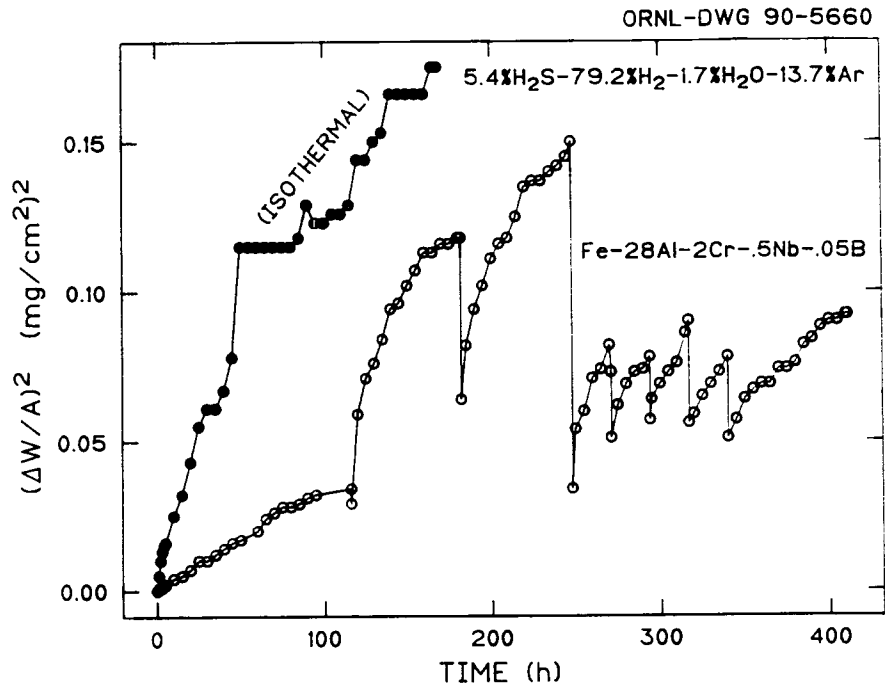


Fig. 2. Comparison of weight changes of Fe-28% Al-2% Cr alloy (PS33) under isothermal conditions and with intermittent thermal cycles to room temperature. Alloy was exposed to $H_2S-H_2-H_2O$ gas mixture at 800°C.

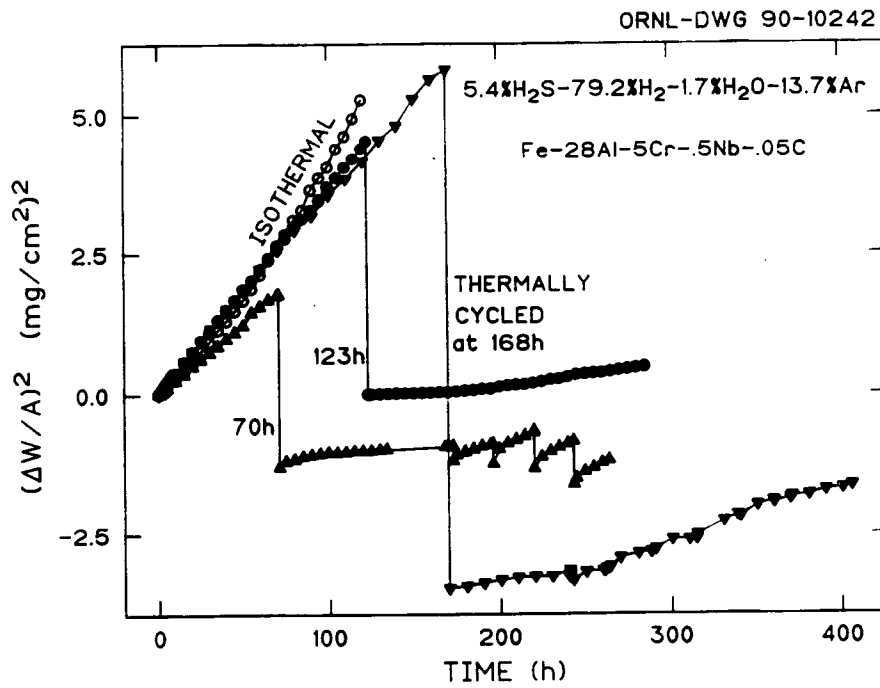


Fig. 3. Effect of thermal cycling on weight change of Fe-28% Al-5% Cr alloy (PS29).

exposed surface that accompanies the growth of the initial scale. Metallographic examinations are being conducted to determine the chemical composition and morphology of the regrown corrosion product to check the validity of these latter suppositions.

British Coal Gasifier Exposures

An Fe₃Al alloy containing 2% Cr (designated FA117 in Table 1) was supplied to the Coal Research Establishment (CRE) of British Coal Corporation for testing in their 12 ton/day gasifier at Stoke Orchard, Gloucester. The material was exposed in two successive runs (PP10 and -11) for times of 940 and 850 h, respectively. The samples (20 x 10 x 6 mm) were located in the gas cooler and were mounted on each of three uncooled corrosion probes alongside numerous other alloy compositions, all in the form of plate specimens. The probes were positioned at three different elevations along the gas cooler, the uppermost being exposed to uncooled product gas and the lower two to the same gas as it was being cooled by passage through a heat exchanger. Thermocouples were located on both sides of the specimen assembly and recorded the ranges of temperatures shown in Table 2.

Table 2. Temperatures of CRE sample probes

Test	Temperature range (°C)		
	Probe 1	Probe 2	Probe 3
PP10	870-910	680-720	560-610
PP11	800-870	600-700	460-600

Typical gas compositions and calculated equilibrium sulfur and oxygen fugacities are listed in Tables 2 and 3, respectively. The gas compositions contain a much lower concentration of H₂S than used in our laboratory tests (≤ 0.25 vs 5.4%); however, they also contain a measurable concentration of chlorides (100-300 ppm HCl), a species not yet included in our laboratory tests. Using an 800°C reference temperature, our laboratory gas mixture is more reducing ($p_{O_2} = 10^{-22}$ atm) than the CRE gasifier product gas ($p_{O_2} \sim 10^{-20}$ atm) and a factor of 10 higher in sulfur activity (10^{-6} vs 10^{-7} atm).

Table 3. Typical composition of CRE product gas

Test	Gas composition % by volume						vppm	
	CO	CO ₂	H ₂ O	H ₂	CH ₄	N ₂	H ₂ S	HCl
PP10	14	10	12	12	0.6	52	2500	300
PP11	14	9	10	11	0.6	55	1300	112

Table 4. Equilibrium sulfur/oxygen potentials

Temperature (°C)	Test	PS ₂ (atm)	PO ₂ (atm)
900	PP10	6.8×10^{-7}	4.2×10^{-17}
	PP11	1.6×10^{-7}	3.3×10^{-17}
800	PP10	2.4×10^{-7}	8.6×10^{-19}
	PP11	6.0×10^{-8}	7.6×10^{-19}
700	PP10	1.0×10^{-7}	1.3×10^{-20}
	PP11	2.8×10^{-8}	1.2×10^{-20}
600	PP10	4.2×10^{-8}	7.2×10^{-23}
	PP11	1.1×10^{-8}	6.7×10^{-23}

Visual and metallographic examinations of the specimens after exposure were initially performed by CRE. (Weight changes were not reported.) CRE reported² that the specimens had shown no visual changes except for darkening, and metallographic examinations revealed little surface attack, with one exception. This exception was the specimen from the top probe in test PP10 which had been positioned in an area where the alloy 800 support probe had suffered catastrophic attack, apparently because of NiS/Ni formation. This Fe₃Al specimen showed isolated pits with average depths of 30 to 40 μm. Following the examinations by CRE, the metallographically mounted specimens were forwarded to ORNL for additional microscopic and chemical analyses. These analyses have confirmed the excellent resistance of the alloy to attack by the gasifier product gas, even at temperatures greater than 800°C. Figure 4(a) shows the metallographic appearance of the specimen mounted on the highest temperature probe from run PP11 (see Table 2). Microprobe examination of the reaction product layer on this specimen shows a relatively thick outer

layer containing calcium and sulfur, a thinner oxide layer containing iron and aluminum, and an even thinner alumina layer at the oxide-metal interface. The morphology and chemistry of the outer layer shows it to be a very uniform and compact deposit containing ash constituents that possibly combined with calcium ($\leq 10\%$). A portion of the total sulfur ($\leq 35\%$) in the deposit can be attributed to the presence of CaS, which presumably relates to the fact the coal feed to the gasifier was mixed with limestone for part of run PP11.

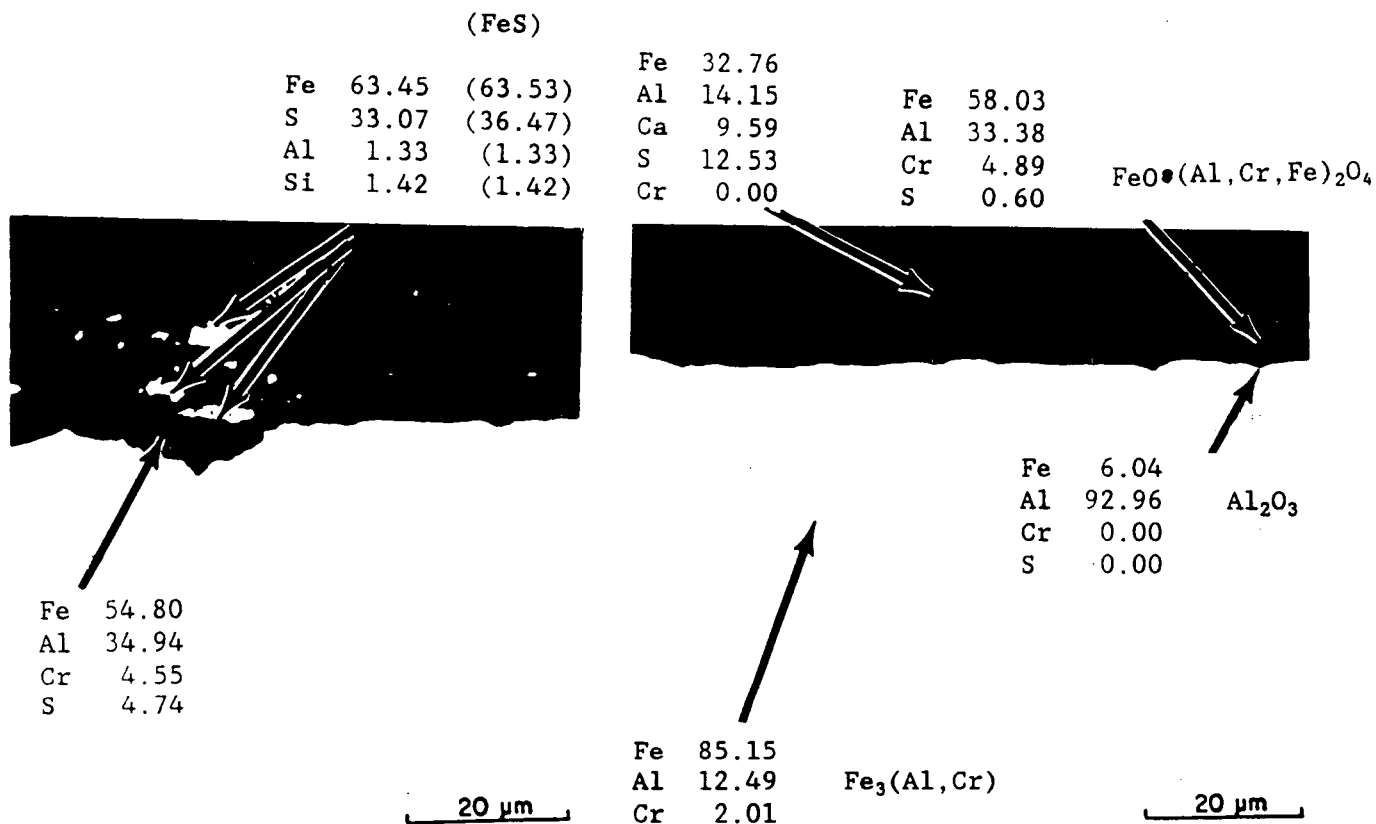


Fig. 4. Metallographic appearance of Fe₃Al + 2% Cr alloy (FA117) after exposure in run PP11 in CRE 12 tpd gasifier. (a) General appearance of surface. (b) Isolated pitted region under pyrrhotite particle. (1000X)

The deposit contains a relatively high concentration of aluminum ($\leq 20\%$) and essentially no oxygen, an implication that the aluminum is present as a sulfide. (The latter could occur only if the oxygen fugacity within the deposit were considerably below that of the gas.) The high aluminum and iron concentrations in the deposit appear to be indigenous to the ash, since there is no evidence of any solid-state reactions between the deposit and the

underlying metal. However, isolated shallow pits such as that shown in Fig. 4(b) were found in a few locations and were associated in all cases with iron sulfide particles incorporated in the deposit. The localized attack associated with these particles suggests that their sulfur activity was even higher than that of the surrounding deposit. Such a result could be explained if the particles had derived from pyrite (FeS_2) inclusions in the coal, given the fact that pyrite is unstable above 743°C and would decompose to yield pyrrhotite (Fe_{1-x}S) particles [observed in Fig. 4(b)] and free sulfur.

The corrosion behavior of the specimens exposed by CRE is in good agreement with that projected from the results of laboratory studies of Fe_3Al alloys containing $\leq 2\%$ Cr. There was no evidence of any species associated with chlorine, and oxide reaction products that developed below the deposited layer were typical of those seen in our laboratory studies. It should be noted, however, that the heat load required to bring the gasifier from ambient to steady-state operating conditions is supplied by operating the gasifier as a coal combustor (i.e., with excess air). Accordingly, there is an effective preoxidation treatment which, as noted in a preceding section, significantly enhances the corrosion resistance of the reference alloy on subsequent exposure to H_2S .

SUMMARY AND CONCLUSIONS

1. The oxidation and sulfidation properties of Fe_3Al alloys were studied in gas mixtures of $\text{H}_2 + \text{H}_2\text{S} + \text{H}_2\text{O}$ at 800°C . The alloys contained 28% Al and 2 and 5% Cr, respectively. The sulfidation resistance of alloys containing 5% Cr was significantly improved by preoxidation in air at 800°C prior to exposure in the mixed gas. Preoxidation produced a relatively impervious alumina scale, although sulfide reaction products did gain precedence at the edges of specimens where mechanical breakdown of the scale occurred. Thermal cycling of the 5% Cr alloy between 800°C and room temperature in the $\text{H}_2\text{-H}_2\text{S-H}_2\text{O}$ mixture resulted in a significant weight loss on the initial cooling cycle. However, the growth rate of scale thereafter was retarded compared to the rate after a comparable exposure under isothermal conditions. The beneficial effect on scale growth rate after thermal cycling appears to be associated with chromium depletion near the surface and overgrowth of alumina.

2. An Fe₃Al alloy containing 2% Cr was exposed to product gas in a British Coal Research Establishment gasifier at maximum temperatures from 800 to 900°C. After exposures of 940 and 850 h, respectively, metallographic examinations showed very little evidence of corrosion. A relatively thin two layered oxide [Al₂O₃ and FeO·(Al,Fe)₂O₃] was observed under a thicker ash deposit containing Ca, Fe, Al, and S. Small widely separated pits were associated with microscopic pyrrhotite particles occluded in this latter layer.

3. The major difference between laboratory tests and the gasifier results is the presence of a sulfur-containing ash deposit on the gasifier specimens. The relatively high calcium concentration suggests that the deposit is associated in part with limestone additions made to the gasifier. Also contained in this deposit are isolated pyrrhotite particles that appear to be vestiges of pyrite impurities in the coal. There were no detectable corrosion effects associated with chlorine impurities in the coal.

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(FeS)

Fe	63.45	(63.53)
S	33.07	(36.47)
Al	1.33	(1.33)
Si	1.42	(1.42)

Fe	12.76
Al	14.15
Ca	9.59
S	12.53
Cr	0.00

Fe	58.03
Al	33.38
Cr	4.89
S	0.60

FeO • (Al, Cr, Fe)₂O₄



Fe	54.80
Al	34.94
Cr	4.55
S	4.74

20 μm



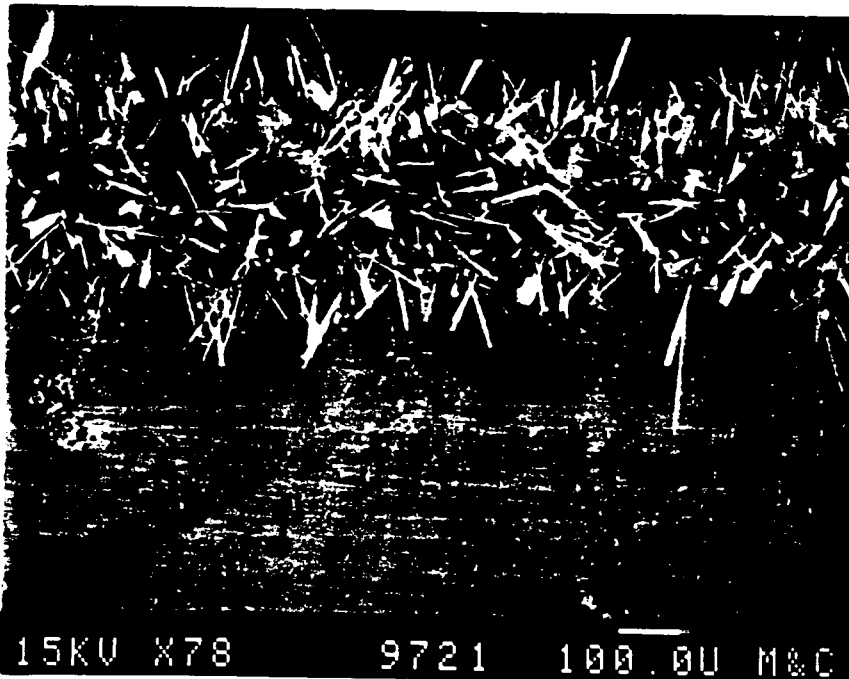
Fe	6.04
Al	92.96
Cr	0.00
S	0.00

Al₂O₃

20 μm

Fe	85.15
Al	12.49
Cr	2.01

Fe₃(Al, Cr)

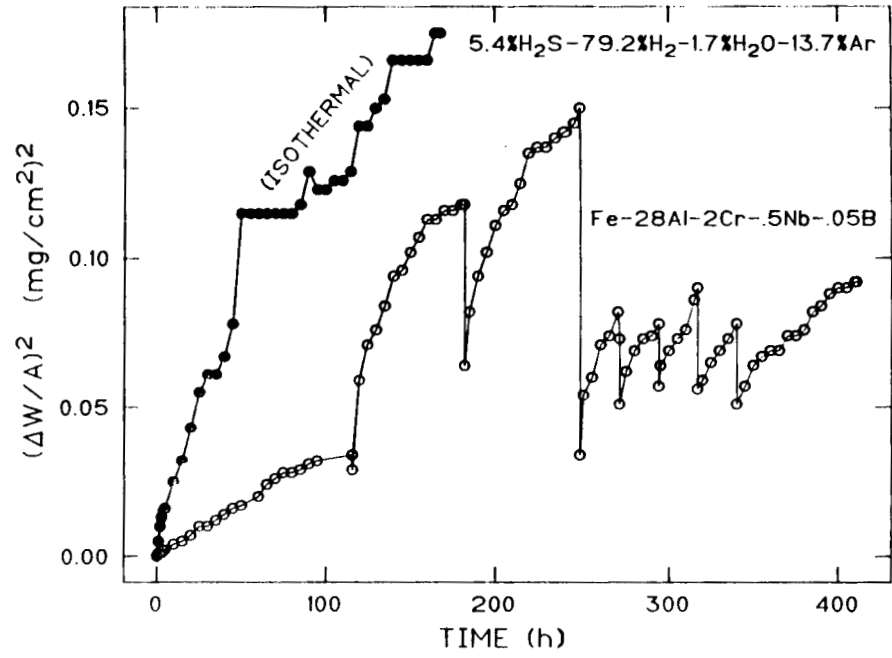


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