DEFINING FAILURE CRITERIA FOR EXTENDED LIFETIME METALLIC COATINGS

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INTRODUCTION

Aluminide coatings have been studied for many years because of their excellent corrosion resistance in oxidizing, sulfidizing, carburizing and water-containing environments.1-5 They are of particular interest for improving the corrosion resistance of Fe-base alloys to achieve higher operating temperatures in fossil energy systems where sulfur and water vapor can cause severe oxidation problems.1,5-12 One of the factors that inhibits their application is a lack of sufficient data about their potential benefits in terms of lifetime and applicable environments. In order to address that issue, model coatings are being fabricated at ORNL for corrosion testing and diffusion studies in order to develop a comprehensive lifetime evaluation approach for aluminide coatings. One ferritic (Fe-9Cr-1Mo) and one austenitic alloy (304L) have been selected as substrate materials for study. An important issue in developing a lifetime model is defining the coating failure criteria. As the Al in the coating is consumed by corrosion or back-diffusion in the substrate, there will be a critical Al content, below which the coating is no longer effective in protecting the underlying substrate. In order to help define these limits in various environments and as a function of temperature, model alloys have been cast with Al contents from 10-20% Al (all chemical compositions are given in atom percent) and Cr contents up to 10%. Testing of these alloys will help simulate coating performance as the coating becomes depleted in Al. Another factor that could reduce coating lifetime is the thermal expansion mismatch between Fe3Al and the substrate.5 This difference could cause cracking or deformation that could reduce coating life. Corrosion testing using thermal cycling is of particular interest because of this potential problem.

Initial work used relatively thin (50-60µm) coatings produced by chemical vapor deposition (CVD) that performed well in cyclic testing at 800°C in a simulated exhaust gas environment (air with 10vol.% water vapor), but poorly in a sulfidizing environment.5 However, application temperatures for these substrate alloys are likely to be lower such that subsequent testing was conducted at 700°C. Because of the poor performance of the thin coatings in sulfidizing environments, thicker coatings with higher Al contents were produced using a higher Al activity CVD process. Initial results are presented on the oxidation performance of these coatings. Thicker coatings also are now being annealed at 500°-800°C for up to 10,000h to determine diffusion rate constants.

EXPERIMENTAL PROCEDURE

The substrates used in this study were Fe-9Cr-1Mo and 304L (Fe-18Cr-9Ni nominally) to represent the performance of ferritic and austenitic alloys, respectively. The laboratory-scale CVD reactor and coating process have been described elsewhere.[5] The CVD process was selected for controlled laboratory studies and should produce coatings similar to a well-controlled, above-pack process that could be used commercially. In order to increase the coating thickness and Al content in the CVD process, the standard exposure was increased from 6h at 900°C to 4h at 1050°C and the Al activity was increased by including Cr-Al alloy pieces in the reactor during deposition.[13]

For comparison in the oxidation testing, model alloys with Al contents of 11-22% and Cr contents of 0-10% were cast using induction melting and a water-cooled copper mold. The alloys were annealed for 4h at 1300°C and were polished to a 0.3µm finish prior to oxidation testing. All oxidation coupons and coated specimens were cleaned in acetone and alcohol prior to oxidation.

Previous work[5] reported oxidation results at 800°C. The current work focuses on 700°C as a more realistic application temperature for the substrate alloys. Cyclic oxidation testing in air with 10±0.5vol.%H_2O was conducted in an automated test rig with a cycle consisting of 1h at temperature and 10min cooling at room temperature. Both ends of the vertical reaction tube were closed and the water vapor was controlled in the carrier gas by a water injection system described elsewhere.[10] Before and after exposure, selected specimens were examined by light microscopy, field emission gun, scanning electron microscopy (SEM) equipped with energy dispersive x-ray analysis (EDXA), x-ray diffraction (XRD), and electron probe microanalysis (EPMA) using wavelength dispersive x-ray analysis. The surface product of cross-sectioned specimens was protected by Cu-plating the specimen prior to mounting in epoxy.

RESULTS AND DISCUSSION

AS-DEPOSITED COATING CHARACTERIZATION

Figure 1 shows an example of a coating made by a high Al activity process. It is almost an order of magnitude thicker than the coatings made by the low activity CVD process.[5] Also, the outer, high-Al content layer has increased in thickness from 3-5µm to 50-60µm. For comparison, the EPMA profiles for the two types of coatings are shown in Figure 2. The high Al activity coatings also have a significantly higher Al content. Using XRD, the outer layer may be β-FeAl. However, with the small volume of material, it is difficult to differentiate this phase from Fe_3Al. One issue with the thicker coatings is the presence of cracks at the coating-substrate interface, arrows in Figure 1. These cracks were particularly severe for the coatings on 304L causing through-thickness cracking in some cases and delamination of the coating. These cracks may be a result of the thermal expansion mismatch between substrate and coating.[5] The cracking problem was alleviated by using a post-deposition anneal in the CVD reactor for 2h at 1150°C.[13]

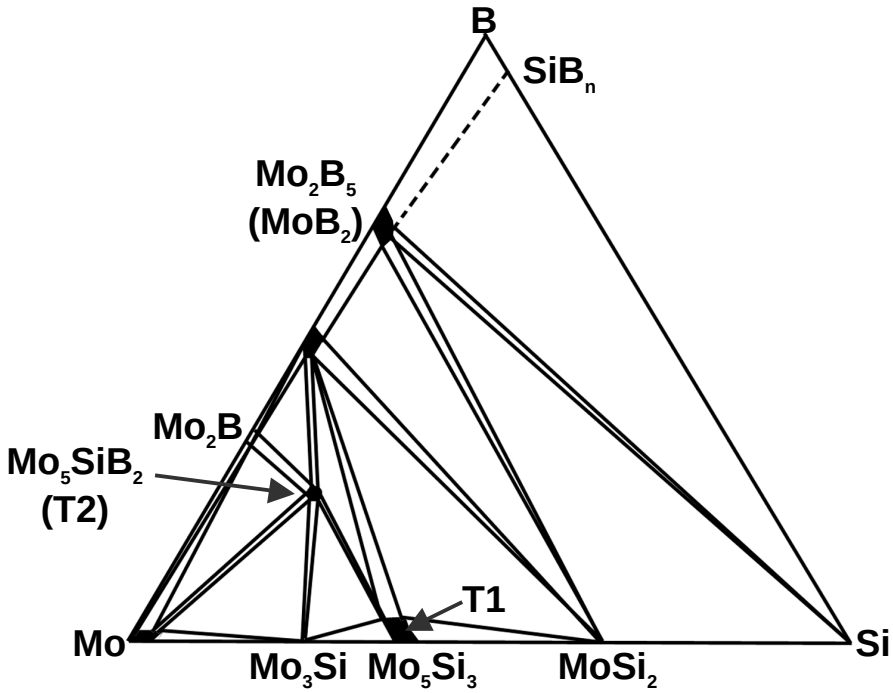

Fig. 1. A schematic Mo-Si-B phase diagram based on Nowotny et al., 1957.

Automated cyclic oxidation exposures were conducted on Mo-Si-B alloys in dry, flowing O_2 at 1200°C using a cycle consisting of 60 min at temperature and 10 min out of the furnace. Specimens were attached to alumina rods with Pt-Rh wires and mass changes were measured after 1, 5, 20, 40, 60, 80, and 100 cycles and then every 100 cycles using a Mettler model AG245 balance. The resulting gravimetric data are shown in Fig. 2. Note that the specimens containing α-Mo showed a substantial mass loss for the first thermal cycle, but that, subsequently, only modest changes in specimen weight were measured. Indeed, after the first cycle, the rates of mass change of the two Mo-Mo_5SiB_2-Mo_3Si specimens were equivalent to and less than those measured for the T1- Mo_5SiB_2-Mo_3Si coupons and not much different than that of the $MoSi_2$-containing alloy. Such observations suggest a multistage mechanism in which the α-Mo is rapidly removed by formation of volatile MoO_3 and the resulting near-surface enrichment in silicon and boron facilitate the formation of a protective borosilicate or silica layer that grows laterally to seal the remaining Mo-rich areas of the alloy from the environment. This type of process qualitatively resembles what happens in carbon-containing SiC composites under oxidizing conditions at high tmepratures[5,6] and suggests that the oxidation behavior of this multiphase system can possibly be controlled through microstructural manipulation. If so, oxidation resistance can be maximized by finely dispersing not only the most active phase (a-Mo), but also the one that can act as a source for Si (the most

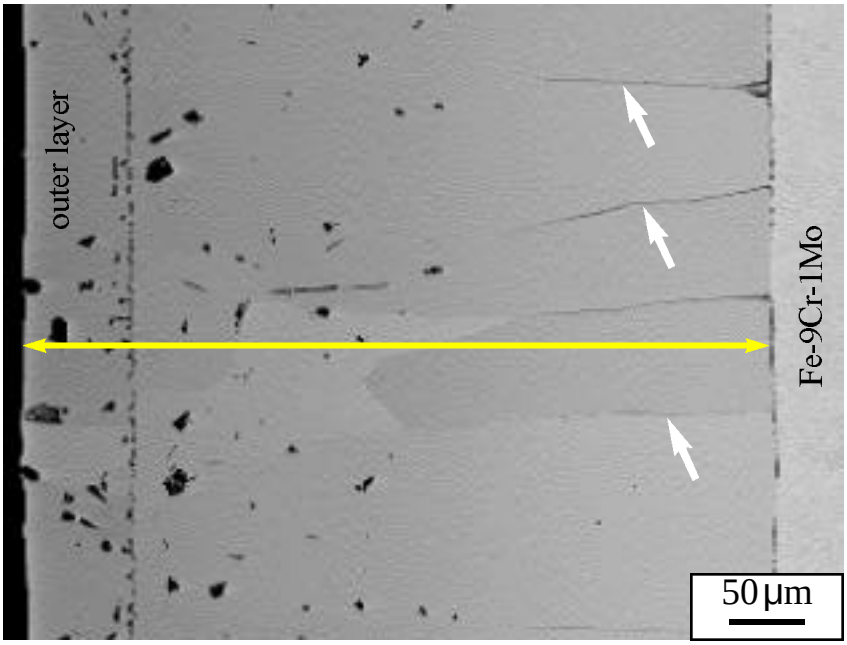

Figure 1. EPMA back-scattered electron image of the as-deposited high Al activity CVD aluminide coating on Fe-9Cr-1Mo. The white arrows show cracks in the coating.

CYCLIC OXIDATION RESULTS

The low activity Al coatings were evaluated at 700°C along with uncoated Fe-9Cr-1Mo and 304L specimens. Previous work showed severe degradation of the uncoated substrates at 800°C and a similar accelerated attack was observed at 700°C, Figure 3. The uncoated Fe-9Cr-1Mo specimen showed a high mass gain due to Fe-rich oxide formation while the uncoated 304L specimen showed mass losses due to

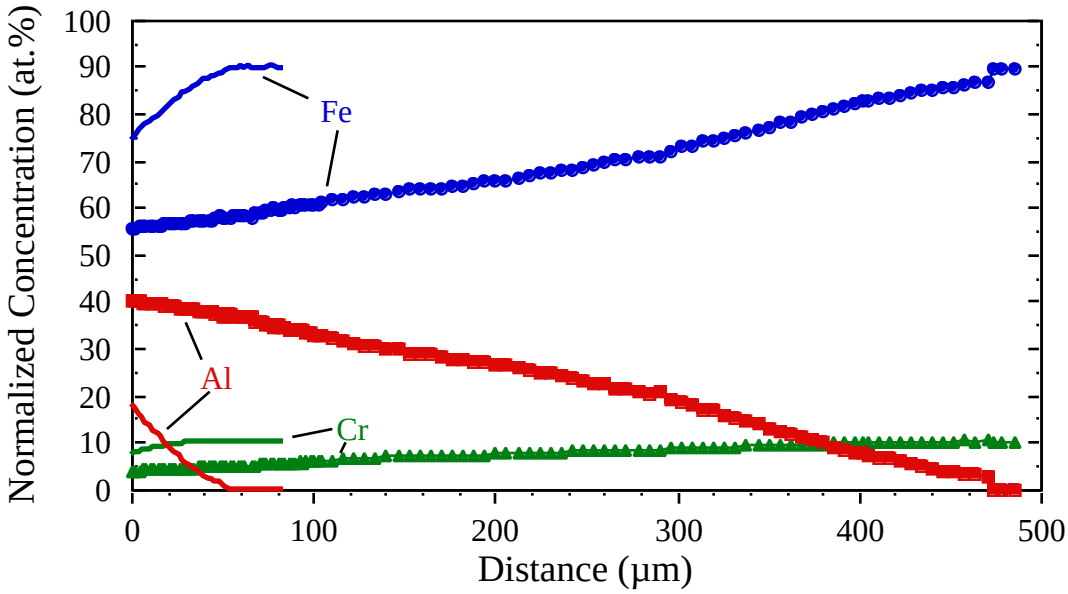

Figure 2. Fe, Al and Cr profiles in the as-deposited coatings on Fe-9Cr-1Mo using EPMA. The lines show the low activity coating and the symbols the new, high Al activity coating.

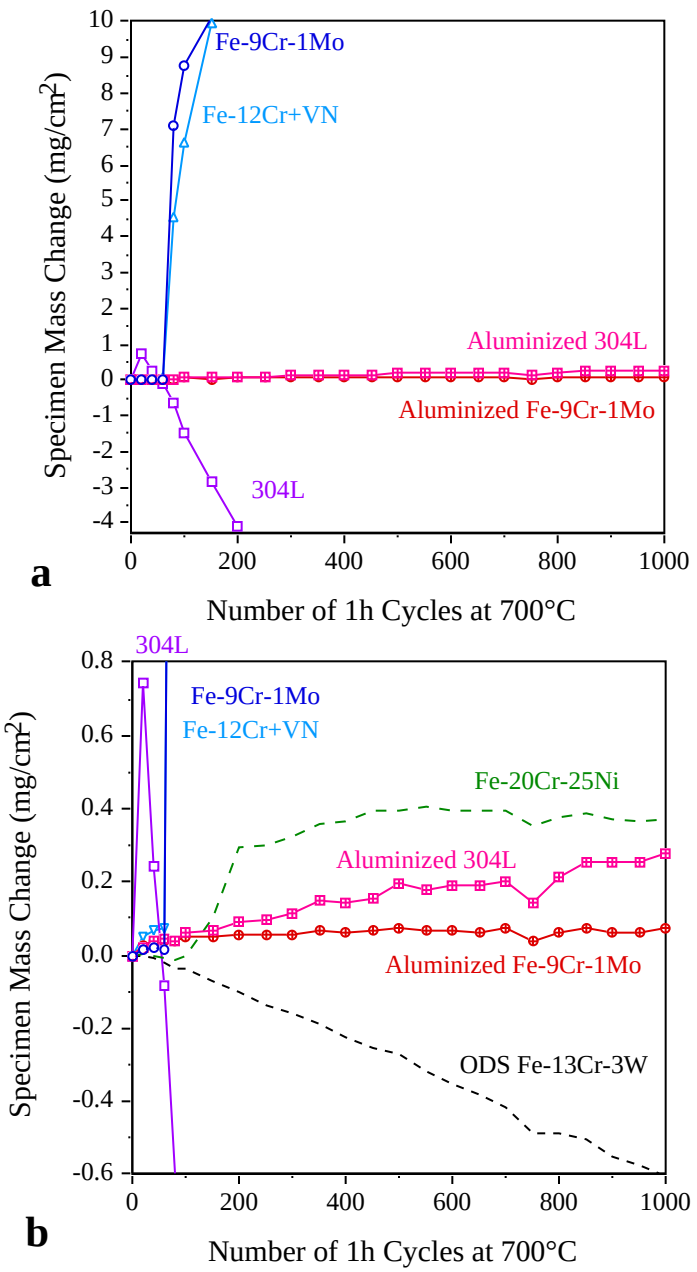

Figure 3. Specimen mass changes during 1h cycles at 700°C in air+10%H_2O. Coated specimens were made using the low Al activity CVD process.

spallation of Fe-rich oxide. Both exposures were stopped after 200, 1h cycles. This behavior would not be expected in dry, oxidizing environments but has been observed in numerous other studies containing steam or water vapor.[6-12] In contrast, the aluminized specimens of each substrate type showed only small mass gains after 1000 cycles. This improvement is attributed to the lower volatility of an external alumina scale compared to the Cr-rich scale formed on the uncoated substrates.[14] No negative effect of thermal cycling was observed in this test, however, the thin Al-rich layer in these coatings may not have generated sufficient strain to cause cracking or other associated failure during testing. Such effects could occur with a thicker coating.

For comparison, a Fe-12Cr with VN (manufactured by ABB Alstrom) was included in the test and showed similar behavior as the Fe-9Cr-1Mo specimen, Figure 3a. It also was removed after 200 cycles. A NF709 (Fe-20Cr-25Ni) specimen showed better behavior with low mass changes after 1000 cycles due to its higher Ni and Cr contents compared to 304L. (Recent work has shown that both higher Ni and Cr contents improve the performance of stainless steels in wet air.[15]) A similar low mass change was noted for an oxide dispersion strengthened (ODS) Fe-13Cr-3W specimen. The small, steady mass loss is associated with the evaporation of $CrO_2(OH)_2$.[9] This ODS alloy performs well despite its low Cr content because of its fine subgrain structure which allows for rapid, short-circuit Cr diffusion in the substrate.[16]

Similar exposures with water vapor are being conducted on specimens coated with the high Al activity process. The specimens have completed 850, 1h cycles and show very similar performance as the thinner coatings with no signs of coating degradation, Figure 4. Any thermal expansion mismatch problem should be exacerbated by the higher Al content, thicker coating and high cycle frequency but no problem has been observed yet. This suggests that the thermal expansion mismatch may not be an important factor.

POST-TEST COATING EVALUATION

Post-test characterization of the coated and uncoated specimens tested at 700°C in wet air has been completed. Figure 5 contrasts the thick, Fe-rich oxide formed on uncoated Fe-9Cr-1Mo after 200, 1h cycles with the thin alumina scale formed after 1000, 1h cycles at 700°C. The scale on the uncoated substrate consists of two layers, with the inner layer containing some Cr. The coated specimen appears very similar to the as-deposited condition with a thin Al-rich outer layer and some Al-rich particles near the coating-substrate interface, Figure 5b. However, the EPMA profile shows that the coating has a much

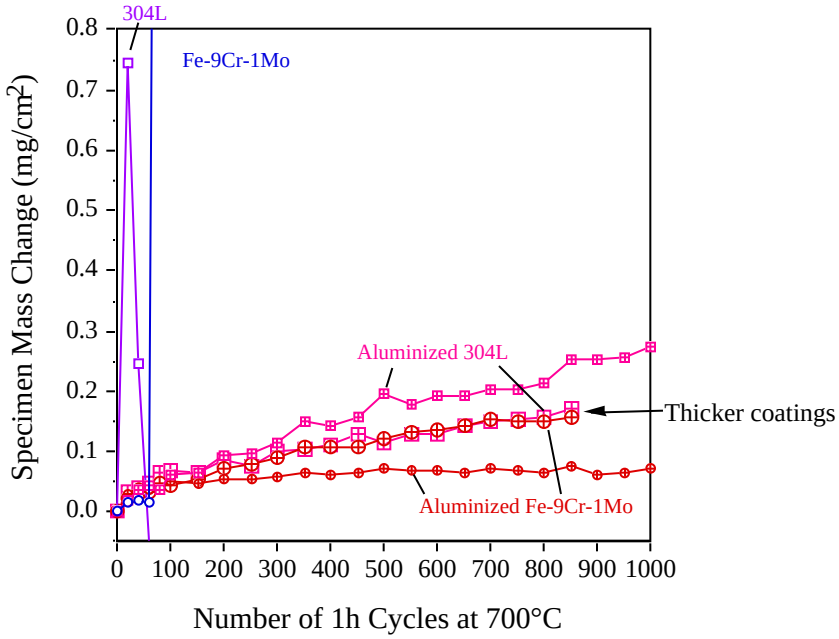

Figure 4. Specimen mass changes during 1h cycles at 700°C in air+10%H_2O. Resulted are shown for specimens coated with both the high and low Al activity processes.

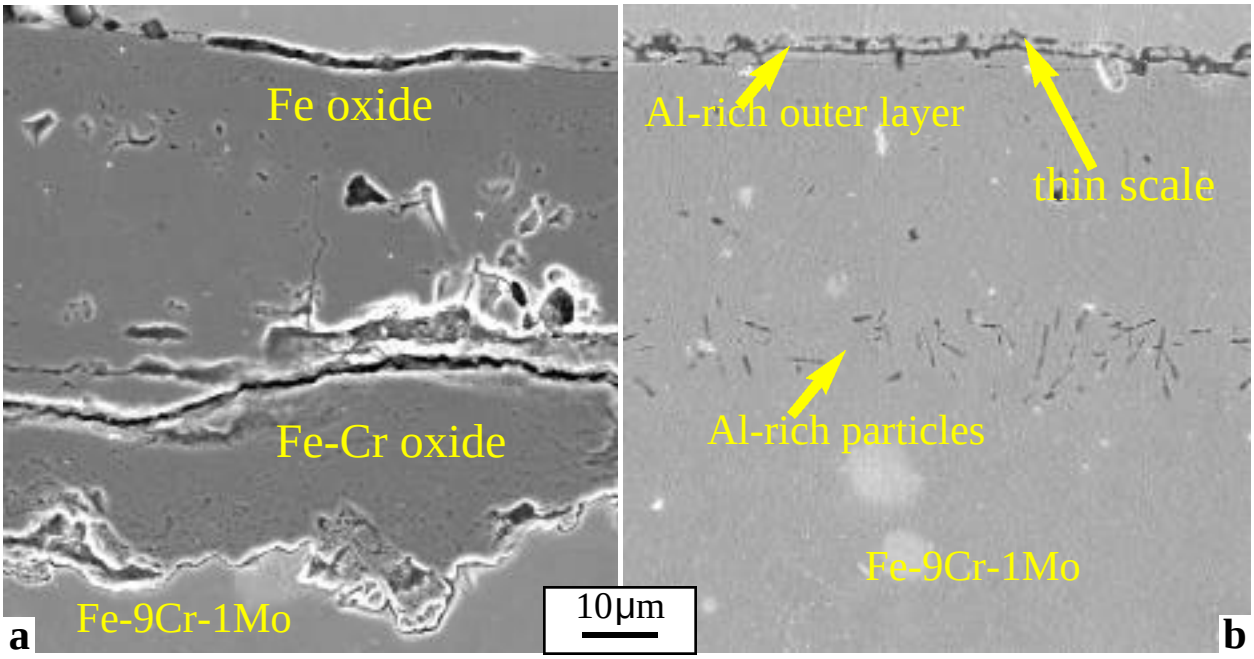

Figure 5. (a) uncoated Fe-9Cr-1Mo substrate after 200, 1h cycles and (b) low Al activity aluminized Fe-9Cr-1Mo substrate after 1000, 1h cycles at 700°C.

lower Al content after the 1000h exposure, Figure 6. There is still a high Al content in the outer layer, but the Al content rapidly decreased in the inner layer. The spikes in the Al profile are due to the Al-rich particles.

Characterization of the uncoated and coated 304L specimens showed similar results. The uncoated 304L specimen showed a thick oxide after 200 cycles at 700°C, Figure 7a, indicating that the measured mass

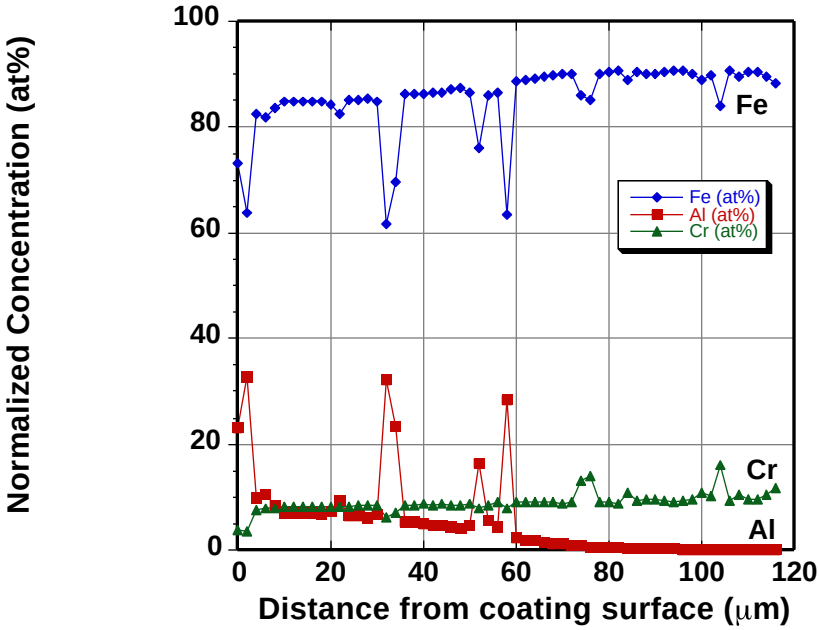

Figure 6. Fe, Al and Cr profiles in the low Al activity coating on Fe-9Cr-1Mo after 1000, 1h cycles at 700°C in air+10%H_2O using EPMA.

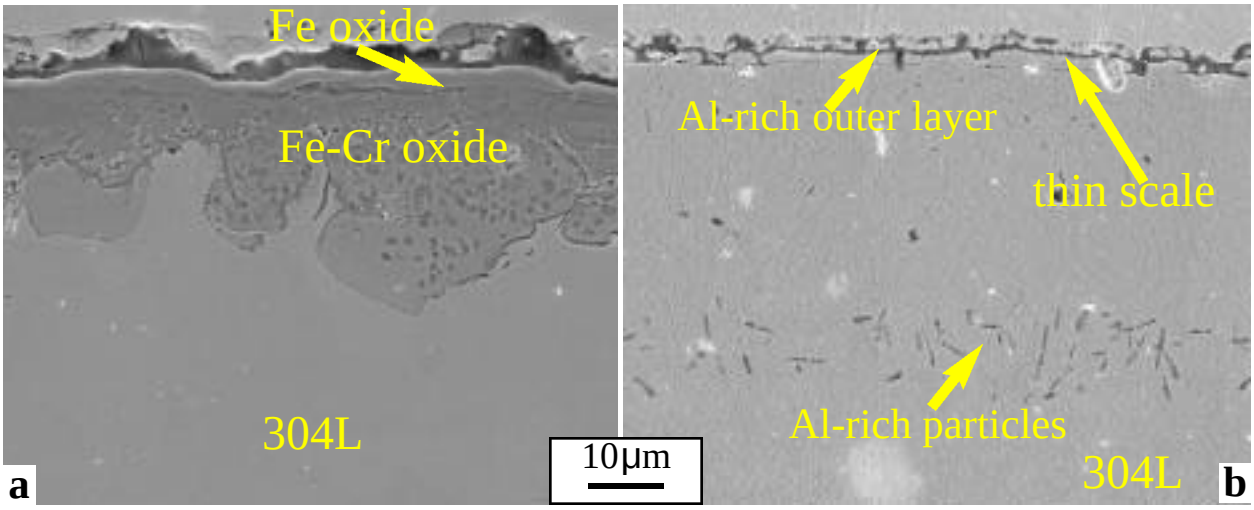

Figure 7. (a) uncoated 304L substrate after 200, 1h cycles and (b) low Al activity aluminized 304L substrate after 1000, 1h cycles.

loss was due to the spallation of the thick oxide. The aluminized 304L specimen showed a thin, protective oxide scale and an Al-rich outer layer and Al-rich particles near the coating-substrate interface. An EPMA profile of the coating, Figure 8, showed that the Al content of the coating had dropped to even lower levels than that observed on the Fe-9Cr-1Mo substrate. Below the Al-rich outer layer, the Al content was ≤5%.

FAILURE CRITERIA

The results for the thin coatings in air plus water vapor demonstrate that even low Al contents can significantly improve the oxidation behavior of ferritic and austenitic alloys at 700°C. However, the same

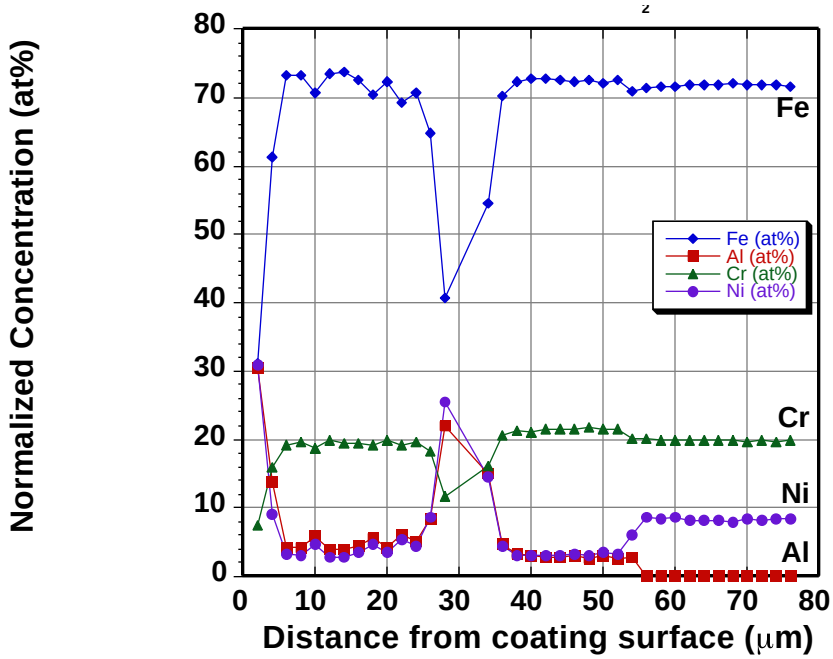

Figure 8. Fe, Al Cr and Ni profiles in the low Al activity coating on 304L after 1000, 1h cycles at 700°C in air+10%H_2O using EPMA.

was not true for sulfidation testing at 800°C, where the thin coatings performed poorly after the first cycle.[5] This raises the general question of how to define the minimum Al content required for coatings as a function of application temperature and environment. Results for sulfidation testing of coatings and cast Fe-Al both appear to indicate that ≈20%Al is needed for protective behavior.[5,17] This was an important factor in examining the higher Al activity coatings, which showed excellent performance with the Fe-9Cr-1Mo substrate during 5, 20h cycles at 800°C in H_2-H_2S-H_2O-Ar ($P_{S_2}=10^{-6}$atm; $P_{O_2}=10^{-22}$atm). The minimum Al content required for sulfidation protection is needed to model the coating lifetime. During exposure, the coating will lose Al from reaction product formation and back-diffusion into the substrate. When the Al content of the coating drops below this minimum value, the coating will no longer be protective. However, the sulfidation test was performed in a severe environment and a lower Al content may be sufficient with a lower sulfur content or lower temperature exposure. The performance of the thin coatings at 700° and 800°C demonstrate that lower Al contents are sufficient in wet air, but because no coating failures have been observed, it is not possible to define the critical Al content for this environment from these results.

In an attempt to define the failure criteria in wet air at 700°C, cast alloys were exposed in 1h cycles. Alloys with 13-22%Al and 500ppma Hf were exposed to this environment. (The Hf was added in order to improve scale adhesion[18] so that these alloys could be tested at temperatures up to 1200°C for other applications.) Compositions with less than 20%Al showed high mass gains upon initial exposure, Figure 9a. At longer times, the increase in mass was negligible, Figure 9b. In cross-section, the scales formed on the lower Al content alloys consisted of an outer iron oxide layer and an inner, Fe-Al oxide. The amount of Fe-rich oxide decreased with increasing Al content in the alloy, Figure 10. If the thick, Fe-rich oxide were to form on a coated specimen, the coating would be largely consumed. Thus, from these results it appeared that 20% Al was necessary for both sulfidizing and oxidizing environments. However, the profiles in Figure 2 show that the coating also contains a significant Cr content and this addition is

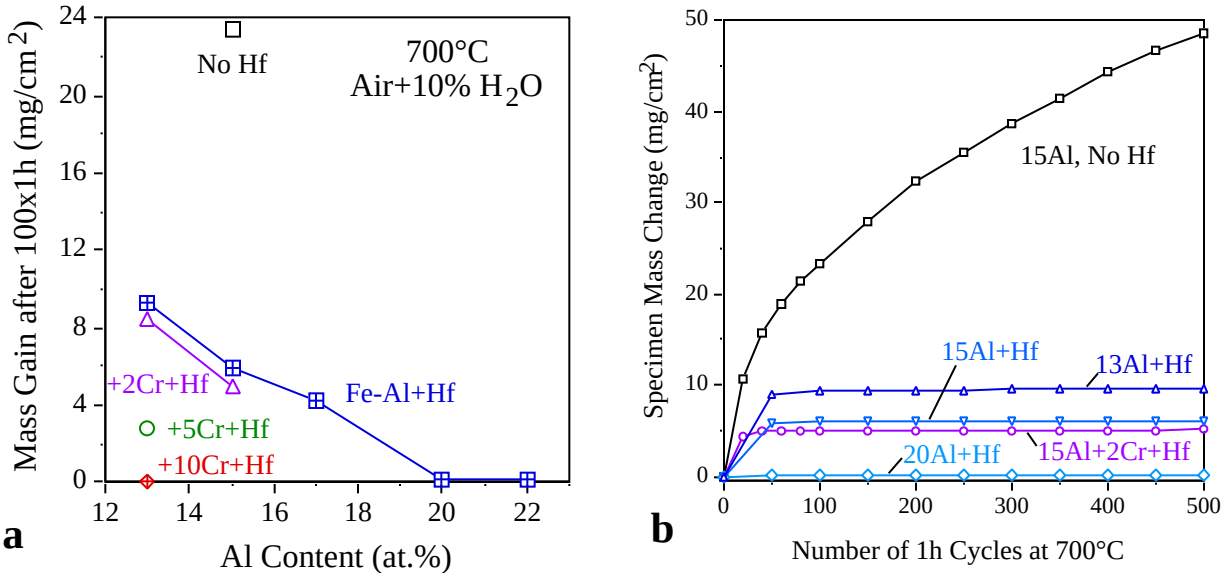

Figure 9. Mass gains for cast Fe-Al alloys after exposure in 1h cycles at 700°C in air + 10 vol.%H_2O. (a) summary of mass gains after 100 cycles and (b) mass change during 500 cycles for selected materials.

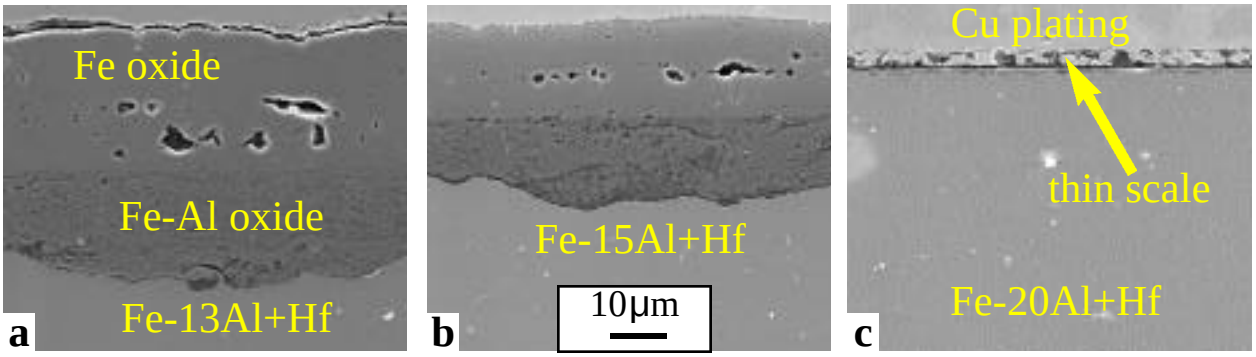

Figure 10. Polished cross-section after 800, 1 h cycles at 700°C in wet air, (a) Fe-13Al+Hf (b) Fe-15Al+Hf and (c) Fe-20Al+Hf.

expected to improve the oxidation resistance by a third element effect.[19] Cast alloys with 13-15%Al, 2-10%Cr and 500ppma Hf also were exposed in wet air at 700°C and the Cr addition had a significant beneficial effect, particularly when 10%Cr was added; an alloy with only 13%Al performed as well as the Fe-20%Al+Hf specimen. Thus, when substantial Cr is present in the coating, as is the case for the coatings on Fe-9Cr-1Mo and 304L, the critical Al content appears to be less than 13%Al. More work with lower Al content alloys is needed to specify the critical Al content in this environment. Based on these results for cast alloys it is not surprising that even the thin coatings perform well.

The addition of Hf was thought to play little role at this low temperature. However, when a Hf-free, Fe-15Al cast specimen was tested in wet air at 700°C, it performed significantly worse than Hf-doped Fe-15Al, Figure 9. Rather than showing an initial high mass gain followed by little mass change, the Hf-free material showed continuous, significant mass gain up to 500 cycles, suggesting that Hf may have a beneficial, but not yet explained, role at this temperature. This results also suggested that incorporating Hf into the coating might have a beneficial effect even for low temperature applications.

SUMMARY

In order to develop a comprehensive lifetime model for aluminide coatings on Fe-base alloys, model coatings are being made by a laboratory CVD process for diffusion and corrosion studies. Specimens made by a higher Al activity CVD process are being tested as coatings made by a low Al activity did not have sufficient Al to provide sulfidation resistance. After exposure for 1000, 1h cycles in air plus 10% water vapor at 700°C, the low Al activity coatings on Fe-9Cr-1Mo and 304L showed a protective alumina scale but low Al levels remained in the coating. For developing a coating lifetime model, the corrosion and diffusion testing will provide rates of Al consumption as a function of temperature. The remaining missing information is the critical Al content below which the coating is no longer protective. Results to date indicate that this value needs to be determined by considering the temperature, environment and both the Al and Cr contents in the coating. No thermal expansion problems have been observed during cyclic testing however, during deposition of the thick coatings, an in situ anneal was needed to ameliorate crack formation.

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