DEFINING FAILURE CRITERIA FOR EXTENDED LIFETIME METALLIC COATINGS

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ABSTRACT

Aluminide coatings have been studied for many years because of their excellent corrosion resistance in oxidizing, sulfidizing and carburizing environments. One of the factors that inhibits their application is a lack of sufficient data about their potential benefits. In order to address this issue, model coatings are being fabricated using a chemical vapor deposition (CVD process on ferritic (Fe-9Cr-1Mo) and austenitic (304L) substrates.   The performance of both high and low Al activity CVD processes is being characterized. The thicker coating produced by the high Al activity process is more resistant to a sulfidizing environment due to its higher Al content. Both types of coatings provide excellent protection during 1h cycles at 700°C in air+10 vol.%H_2O, an environment that severely attacks the uncoated alloys. Diffusion and corrosion tests are being conducted to quantify the rate of Al loss from the coating. The remaining data needed to develop a coating lifetime model is the minimum Al content needed for the coating to be protective as a function of application temperature and environment. This failure criteria is being investigated using cast Fe-Al alloys with low Al contents (10-20 at.%) at test temperatures of 700°-1200°C. In the lower temperature range, Cr present in the coatings should play an important role in determining the critical Al content of the coatings because it had a significant effect on the performance of cast Fe-Al-Cr alloys in air+10 vol.%H_2O at 700°C.

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 Fe_3Al 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 10 vol.% water vapor), but poorly in a sulfidizing environment.[5] Because application temperatures for these substrate alloys are likely to be lower, testing was conducted at 700°C. The poor performance of the thin coatings in sulfidizing environments shifted interest to thicker coatings with higher Al contents 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 changed from 6h at 900°C to 4h at 1050°C and the Al activity was increased by including Cr-Al alloy pellets 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, 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. XRD results indicate that the outer layer may be -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 normal to the coating-substrate interface, white arrows in Figure 1. For the coatings on 304L, the cracks were larger and normal to coating interface causing more severe damage including delamination of the coating in some cases. 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]

CYCLIC OXIDATION RESULTS

The low activity Al coatings along with uncoated Fe-9Cr-1Mo and 304L specimens were evaluated in 1h cycles at 700°C in air+10vol.%H_2O. Accelerated attack of the uncoated substrates, Figure 3, was similar to that observed at 800°C in wet air.[5] The uncoated Fe-9Cr-1Mo specimen showed a high mass gain due
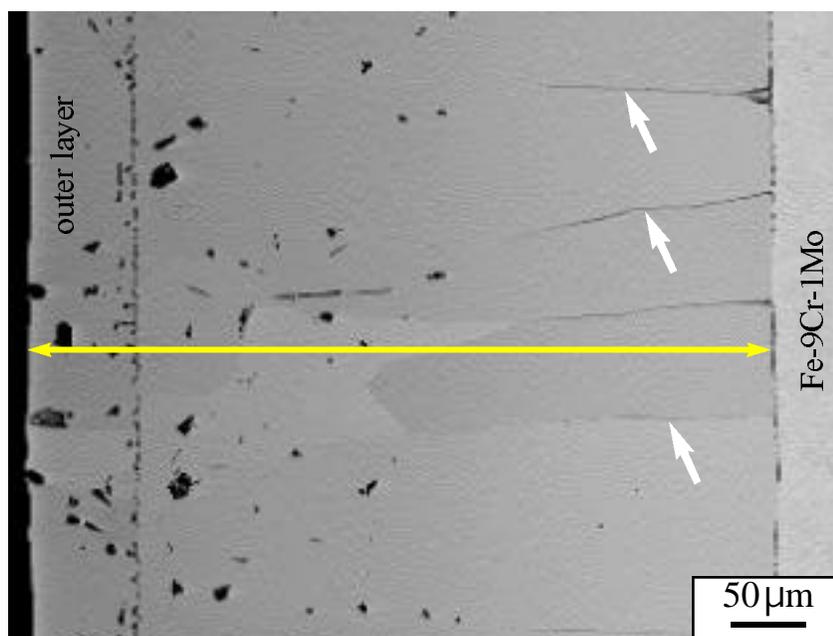

Figure 1. EPMA back-scattered electron image of the as-deposited high Al activity CVD aluminide coating on Fe-9Cr-1Mo. The white arrows show cracks in the coating.
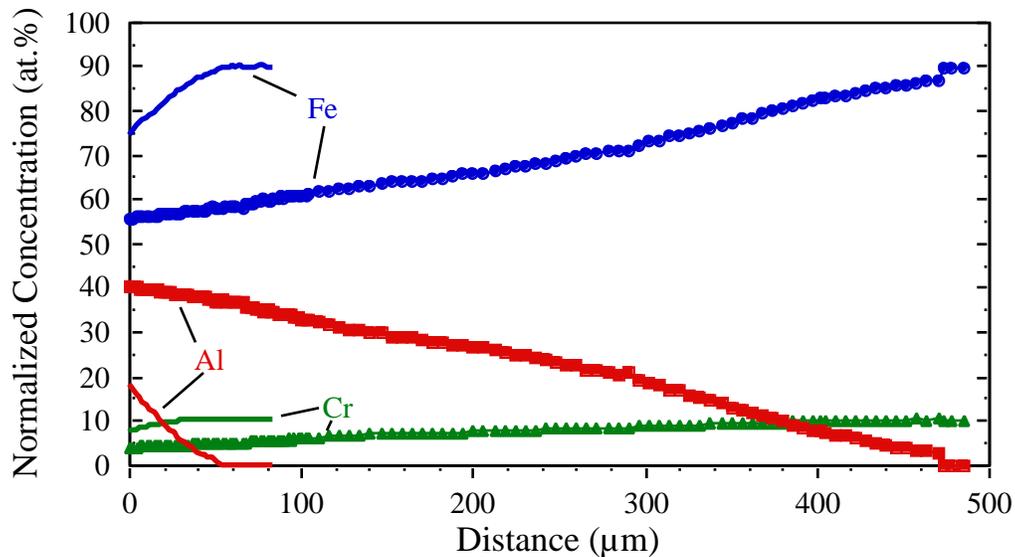
Figure 2. Fe, Al and Cr profiles in the as-deposited coatings on Fe-9Cr-1Mo using EPMA. The thinner lines show the low activity coating and the symbols the new, high Al activity coating.

to Fe-rich oxide formation while the uncoated 304L specimen showed mass losses due to spallation of Fe-rich oxide. Both exposures were stopped after 200, 1h cycles. This behavior, though not expected in dry, oxidizing environments, 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 Alstom) was included in the test and showed similar behavior as the Fe-9Cr-1Mo specimen, Figure 3a. It also was removed from testing 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. This alloy forms a Cr-rich protective oxide and 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 with a high Al activity coating. The specimens have completed 850, 1h cycles and show 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 thermal expansion mismatch in this system may not be an important factor.
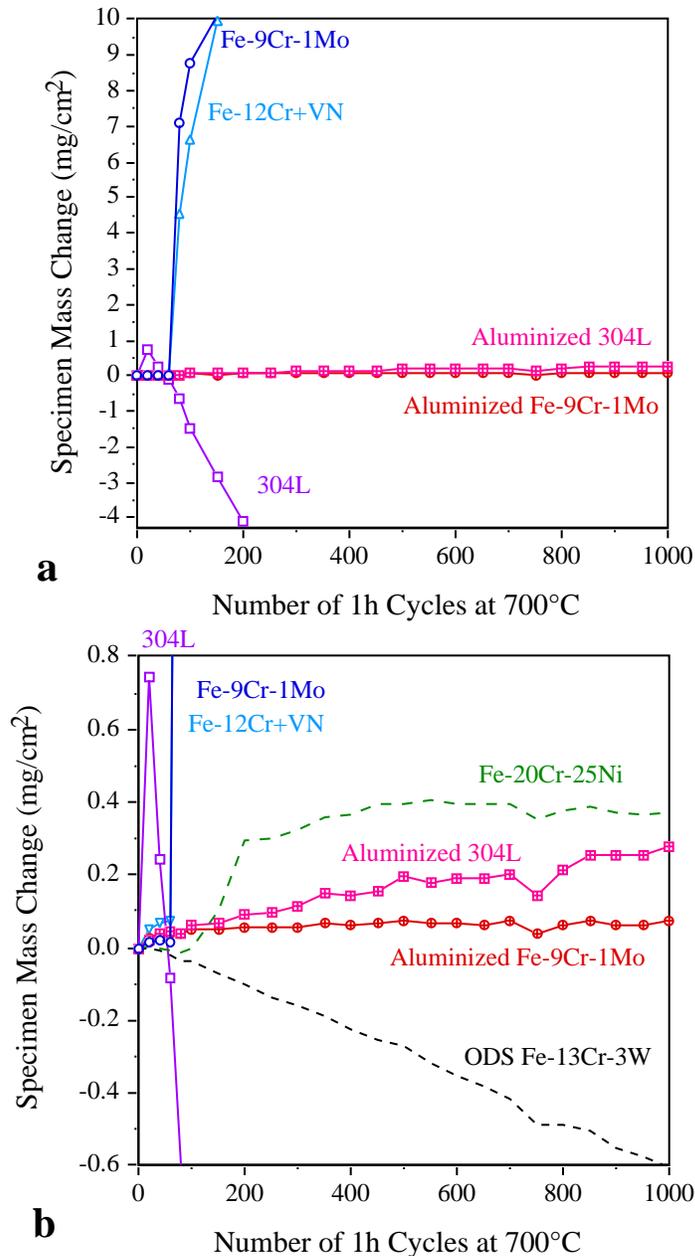
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Figure 3. Specimen mass changes during 1h cycles at 700°C in air+10%H_2O. Coated specimens were made using the low Al activity CVD process. An expanded y-axis is shown in (b).

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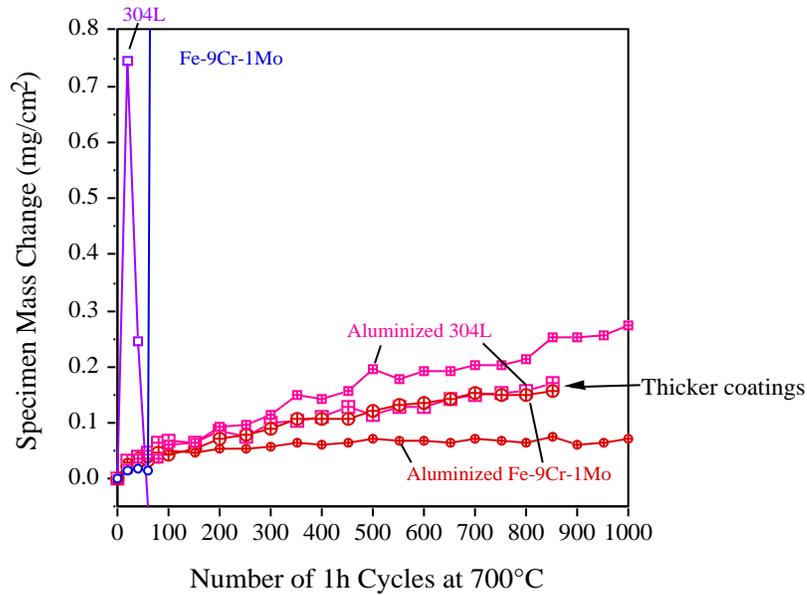
Figure 4. Specimen mass changes during 1h cycles at 700°C in air+10%H_2O. Resulted are shown for specimens coated with both the high and low Al activity processes.

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 loss was due to the spallation of the thick oxide. The aluminized 304L specimen showed a thin, protective
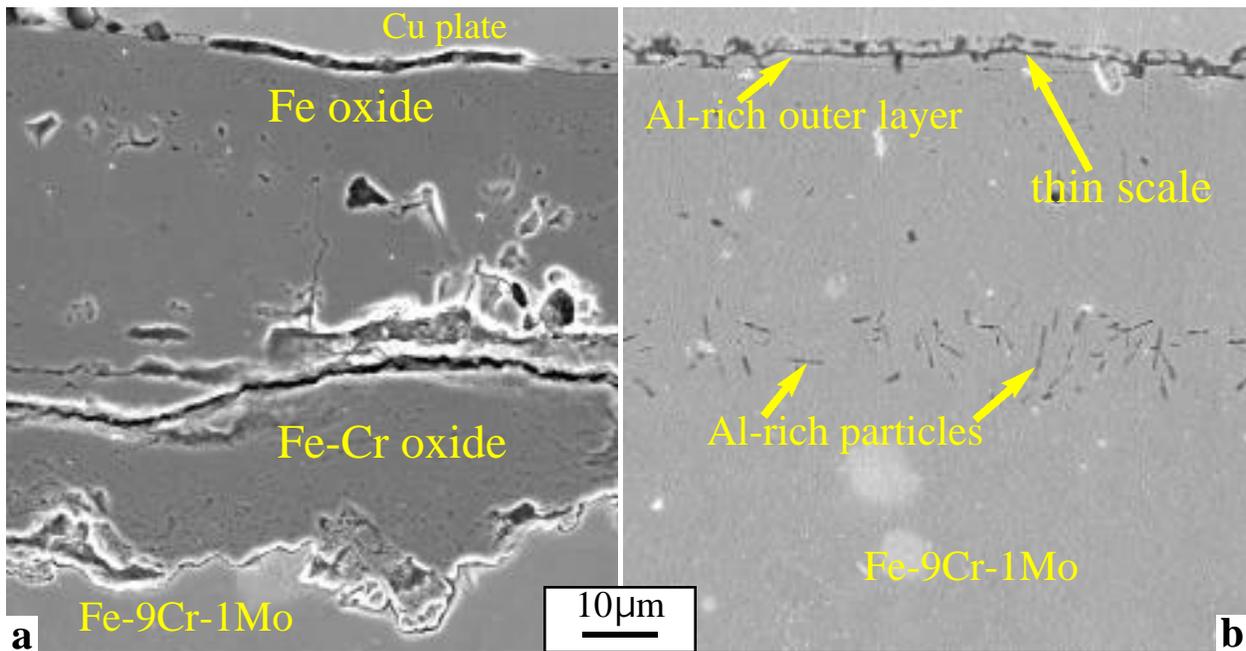

Figure 5. (a) uncoated Fe-9Cr-1Mo substrate after 200, 1h cycles and (b) low Al activity aluminized Fe-9Cr-1Mo substrate after 1000, 1h cycles at 700°C.
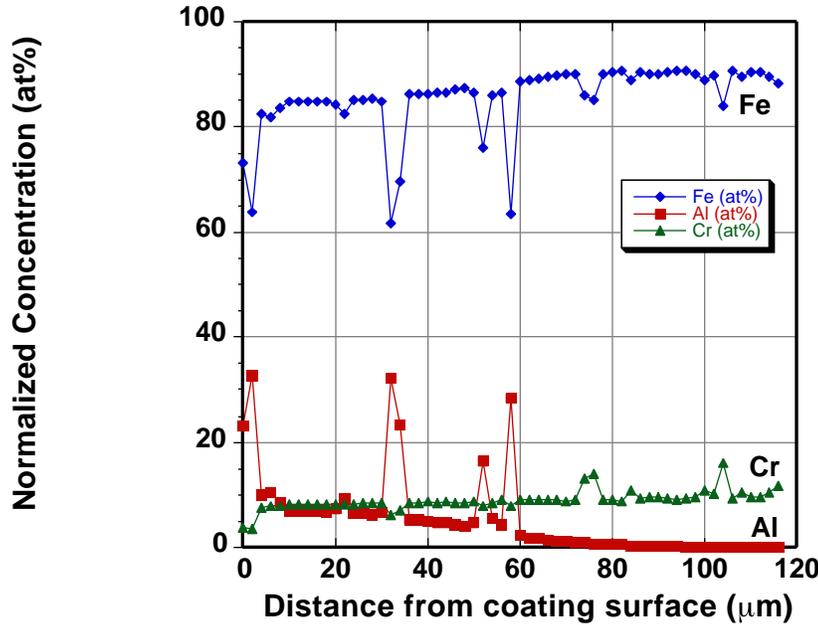
Figure 6. Fe, Al and Cr profiles in the low Al activity coating on Fe-9Cr-1Mo after 1000, 1h cycles at 700°C in air+10%H_2O using EPMA.

oxide scale, 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 was not true for sulfidation testing at 800°C, where the thin coatings performed poorly after the first
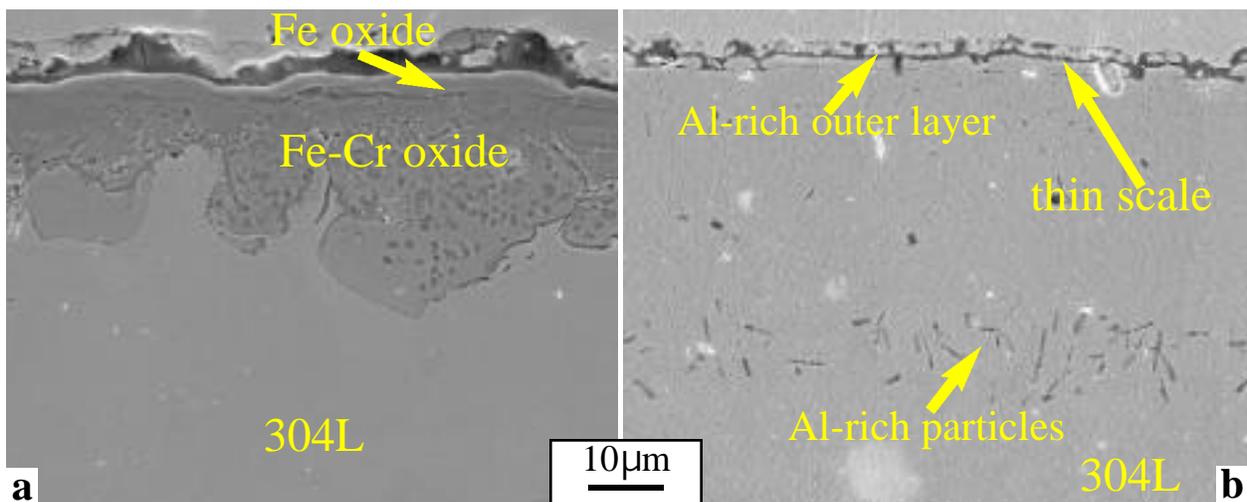

Figure 7. (a) uncoated 304L substrate after 200, 1h cycles and (b) low Al activity aluminized 304L substrate after 1000, 1h cycles.
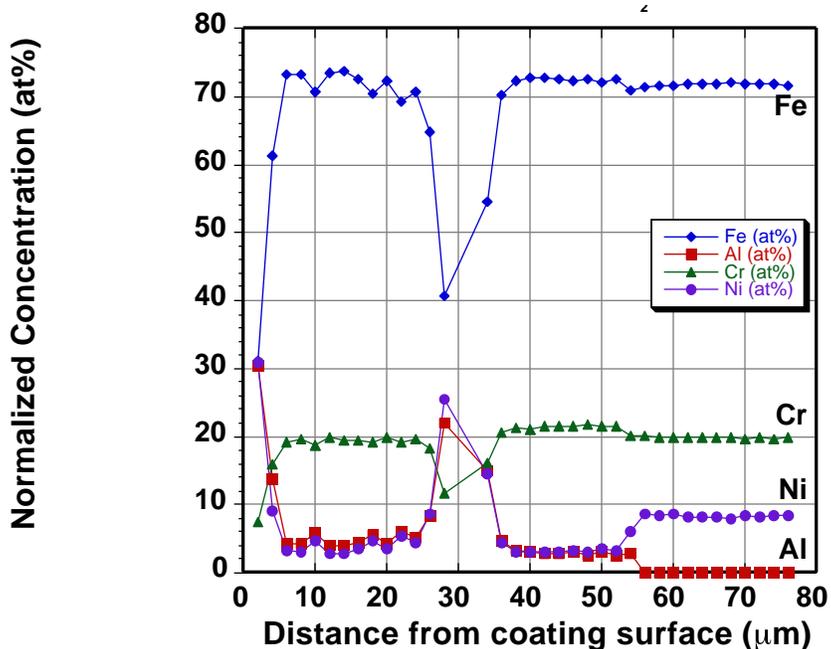
Figure 8. Fe, Al Cr and Ni profiles in the low Al activity coating on 304L after 1000, 1h cycles at 700°C in air+10%H$_2$O using EPMA.

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$_2$S-H$_2$O-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 exposure temperature. 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. Iron-based alloys with 13-22%Al and 500ppma Hf were exposed to this environment. 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 expected to improve the oxidation
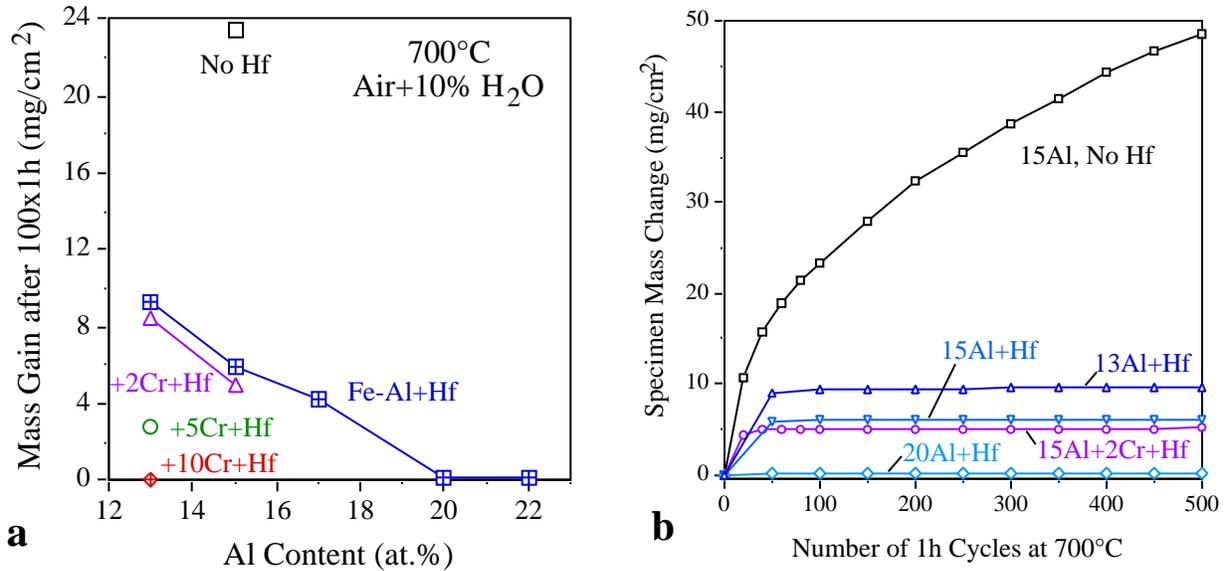
Figure 9. Mass gains for cast Fe-Al alloys after exposure in 1h cycles at 700°C in air + 10 vol.%H_2O. (a) summary of mass gains after 100 cycles and (b) mass change during 500 cycles for selected materials.

resistance by a third element effect.[18,19] 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 under these conditions.

The effect of Al also was investigated at higher temperatures (1100°-1200°C) for other coating applications such as for ethylene cracking. For this testing, it was necessary to have a reactive element such as Hf in the casting to improve the alumina scale adhesion.[20] Spallation of the alumina scale would quickly deplete the Al content at these temperatures due to the faster scale growth rates. The testing also was performed with 1h cycles to accelerate the failures but the environment was dry, flowing O_2. Figure 11 shows the data obtained to date at 1100°-1200°C with the lifetimes normalized to a 1.5mm specimen
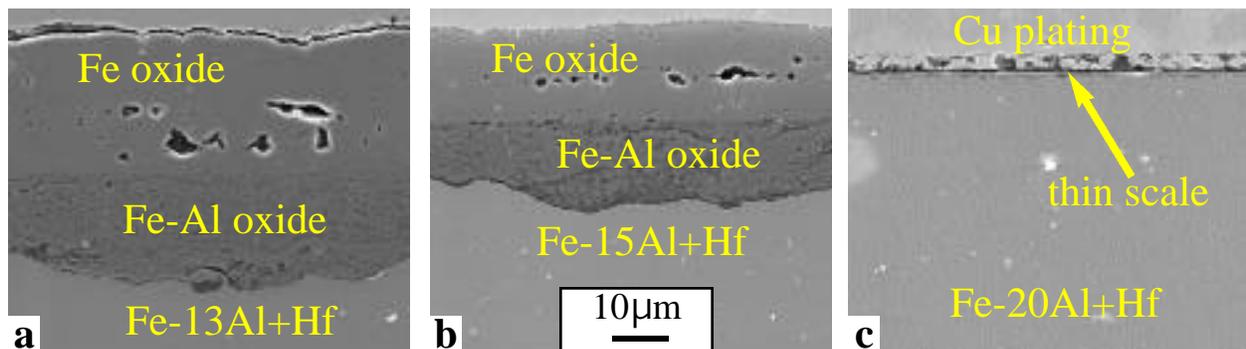

Figure 10. Polished cross-sections after 800, 1h cycles at 700°C in wet air, (a) Fe-13Al+Hf (b) Fe-15Al+Hf and (c) Fe-20Al+Hf.
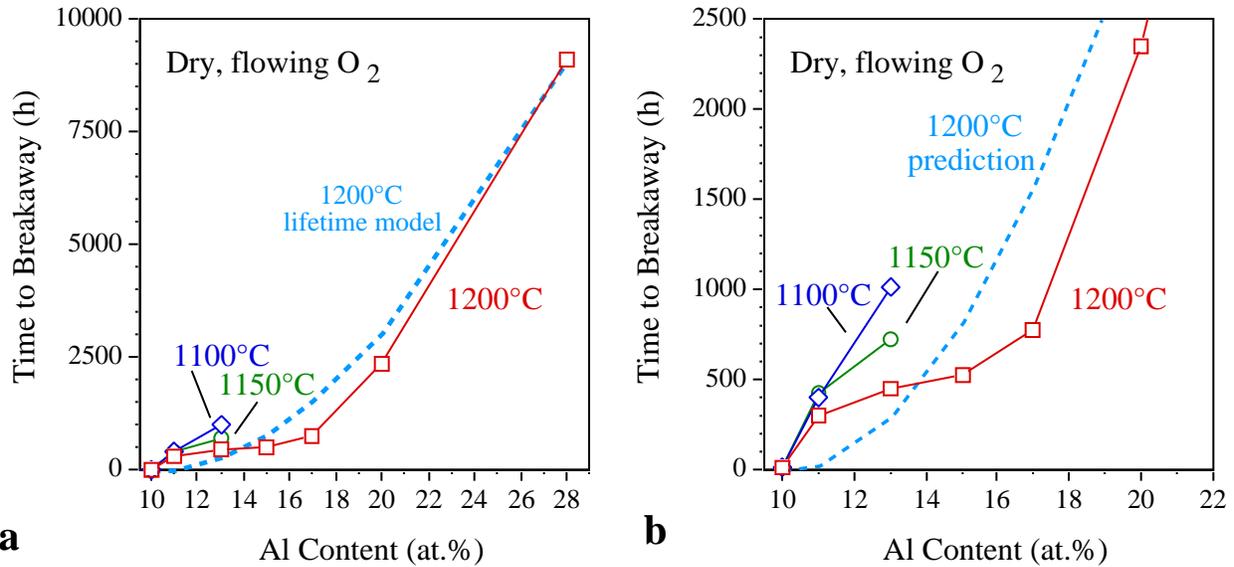
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Figure 11. Normalized time to the onset of breakaway oxidation for the cast Fe-Al+Hf alloys as a function of Al content from 1100°-1200°C in 1h cycles in dry O_2. The expanded scale in (b) shows the limited agreement between the predicted lifetimes and the measured lifetimes at 1200°C. Lifetimes are normalized to a 1.5mm thickness.

thickness. Previous results[21] for Hf-doped Fe_3Al (28%Al) also are included. As expected, decreasing the Al content reduced the time to breakaway. At each temperature, a Fe-10Al+Hf specimen began to form iron oxide after only a few cycles, thus setting the lower Al bound. Using the data for 10 and 28%Al, a lifetime model[22] was used to predict the performance of the other alloys at 1200°C, Figure 11. At present, there is not good agreement between the model and the experimental results. Additional experiments are ongoing to better model the effect of Al on lifetime at these temperatures.

In these higher temperature tests, the addition of Cr to the Fe-13Al+Hf castings did not show as clear a beneficial effect as at 700°C, Figure 12. At 1200°C, the addition of Cr increased the lifetime but the benefit did not increase with the Cr content. The addition of 10%Cr was not as beneficial as lower Cr contents at this temperature. At 1150°C, there was only a slight increase in the time to breakaway with the addition of Cr and at 1100°C there was a decrease in lifetime with the addition of Cr. As mentioned previously, Cr could change the Al activity and thereby reduce the critical Al content and increase the time to breakaway. However, if Cr decreases the spallation resistance of the casting, then it could have the opposite effect by increasing the Al consumption rate. Additions of Cr have been shown to have detrimental effects on the scale adhesion of NiAl+Hf in similar test conditions.[23]

While Hf is a critical addition at high temperatures, it was thought to play little role at lower temperatures like 700°C. 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 result also suggested that incorporating Hf into the coating might have a beneficial effect at all temperatures of
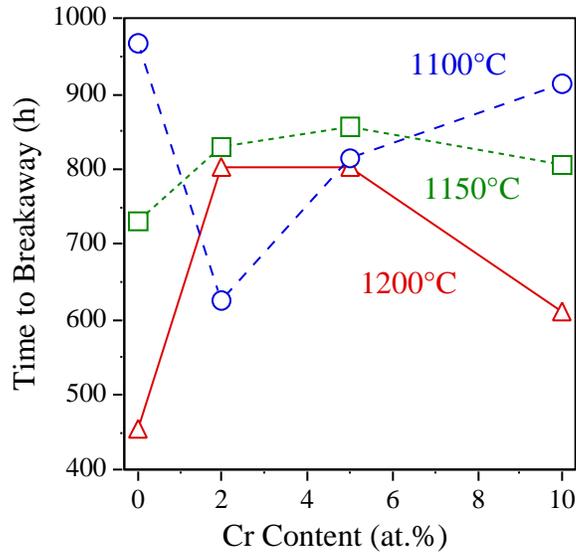
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Figure 12. Normalized time to the onset of breakaway oxidation for the cast Fe-13Al+Hf alloys as a function of Cr content from 1100°-1200°C in 1h cycles in dry O_2. Lifetimes are normalized to a 1.5mm specimen thickness.

interest for aluminide coatings.

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 and low Al levels were measured 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, post-deposition anneal was needed to ameliorate crack formation.

ACKNOWLEDGMENTS

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