# Performance of Al-Rich Oxidation Resistant Coatings for Fe-Base Alloys

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## ABSTRACT

This multi-layer program has examined the oxidation resistance of Al-rich coatings made by chemical vapor deposition and pack cementation on ferritic-martensitic (e.g. T91, Fe-9Cr-1Mo) and austenitic (Type 304L, Fe-18Cr-8Ni) substrates at 650°-800°C. The main goal of this work was to demonstrate the potential benefits and problems with alumina-forming coatings. To evaluate their performance, oxidation exposures were conducted in a humid air environment where the uncoated substrates experience rapid oxidation, similar to steam. Exposure temperatures were increased to accelerate failure by oxidation and interdiffusion of Al into the substrate. The final results focused on thinner coatings with less Al and a ferritic Fe(Al) structure which have a lower thermal expansion than intermetallic phases. To improve the previously developed coating lifetime model, a final series of exposures were conducted to determine the effect of substrate composition (e.g. Cr content using Fe-12Cr and Fe-9Cr-2W substrates) and exposure temperature on the critical Al content for coating failure. For the coated Fe-(9-12)Cr specimens, there was little effect of Cr on lifetime at 800°C. At 700° and 800°C, thin coated austenitic specimens (304L and 316) continue to be protective at up to double the lifetime of a similar coating on T91. This increase could be attributed to the higher Cr content or the slower interdiffusion in austenitic substrates which is illustrated with electron microprobe measurements from thicker coatings stopped after 10-20 kh.

## INTRODUCTION

The use of Al additions, either alloying or as a coating, to improve alloy oxidation resistance has been studied for many years.[1-13] Alumina-forming alloys and coatings (e.g. bond coatings for thermally barrier coatings[4,8]) are generally thought to be most effective at high temperatures (>900°C). However, at lower temperatures, the greater thermodynamic stability of $Al_2O_3$ in the presence of water vapor (compared to $Cr_2O_3$ or $SiO_2$)[14] makes alumina-forming coatings attractive for steam or exhaust gas environments. With the high temperature and pressure associated with the goals for the DOE Ultra-Supercritical (USC) steam program for coal-fired power plants,[15] the potentially higher performance of alumina-forming coatings may be needed.

The central goal of this multi-year project has been to identify the potential benefits and barriers associated with the use of Al-rich coatings on ferritic-martensitic (FM) and Fe-base austenitic alloys.[13,16-23] This information could then be used to justify the implementation and improve the durability of these coatings. Some of the initial concerns about these coatings were the coefficient of thermal expansion (CTE) difference between the aluminide phases (e.g. FeAl and $Fe_3Al$) and the substrates,[16] interdiffusion of Al into the substrate and the mechanical integrity in thermal cycling of brittle, high-Al aluminide phases such as $Fe_2Al_5$.[11,12] To help evaluate some of these issues, laboratory studies were conducted at 650°-800°C on model coatings made in a controlled, laboratory-scale chemical vapor deposition (CVD) process.[12] and, to a lesser degree, by a conventional pack cementation process.[23] In order to quantify the benefit of these coatings, a coating lifetime model[21] was developed, based on long-term oxidation and interdiffusion studies.[21,22] One of the main findings has been that relatively thin ferritic phase coatings with relatively low Al contents can be more durable and effective than higher Al content aluminide phase coatings. Some of the final results are reviewed on the long-term oxidation behavior of Al-rich CVD coatings on (9-12)Cr FM alloys and future research goals are outlined.

## EXPERIMENTAL PROCEDURE

Substrates (~18 x 12 x ~1.5 mm) coated included commercial FM T91 (Fe-9.3 at.%Cr-0.6Mo-0.5Mn-0.3V-0.55Si-0.2Ni-0.5C-0.22N-0.005S), T92 (Fe-9.9at.%Cr-0.6%W-0.3Mo-0.5Mn-0.3V-0.32Si-0.1Ni-0.5C-0.23N-0.009S), T122 (Fe-11.4at.%Cr-0.6%W-0.2Mo-0.7Mn-0.2V-0.24Si-0.3Ni-0.5C-0.30N-<0.001S) and commercial austenitic type 304L stainless steel (Fe-19.7 at%Cr-7.9Ni-1.8Mn-0.15Mo-0.76Si-0.32N-0.09C-0.006S) and type 316 (Fe-19.9at%Cr-8.9Ni-1.7Mn-1.4Mo-1.9Si-0.24N-0.34C-0.007S). (Compositions were determined by combustion and plasma analysis.) The laboratory-scale CVD reactor and coating process for low-activity (thin coatings formed after 6 h at 900°C with ~5 µm Al-rich outer layer and ~50 µm total thickness including the interdiffusion zone) and high-activity (thick coatings formed after 4 h at 1050°C with ~20-40 µm outer layer and ~150-275 µm total thickness on T91) as well as the as-coated microstructures are described elsewhere.[12] For comparison, thick pack cementation coatings were made by a laboratory-scale process (~250 µm thick coating after 6h at 1050°C).[23] Coated specimens were cleaned in acetone and methanol prior to exposure and exposed with the as-coated surface finish. Specimen mass changes (±0.02 mg/cm$^2$ accuracy) were measured using a Mettler Toledo model AG245 balance. Cyclic oxidation exposures were conducted with a 100h cycle time at temperature with specimens in an alumina boat with faces parallel to the gas stream. An environment of air + 10vol.% water vapor was used to determine coating performance as this environment causes rapid oxidation of the uncoated substrates,[16,17,22] similar to a steam environment. Distilled water was atomized into the flowing gas stream (850 ml/min) through an alumina tube (e.g. gas velocity of 1.7 cm/s at 700°C) and was calibrated to 10±1 vol.% based on the amount of water injected. After exposure, specimens were examined by field emission gun, scanning electron microscopy (SEM) equipped with energy dispersive x-ray analysis (EDXA), and by electron probe microanalysis (EPMA) using wavelength dispersive x-ray analysis. The surface of coated specimens was examined by SEM every 2kh of exposure. Prior to metallographic sectioning, specimens were Cu-plated to protect the surface oxide.

## RESULTS AND DISCUSSION

### 650°C OXIDATION RESULTS

Figure 1 shows the mass change data for coated and uncoated FM and austenitic specimens at 650°C in air + 10% water vapor. For the uncoated FM alloys T91 and T92, the specimens underwent accelerated oxidation after an incubation period with low mass gain. The high mass gain is due to the formation of a thick Fe-rich oxide. Specimens with thick coatings made by CVD or pack cementation have completed 12kh of exposure with low mass gains, Figure 1. Because of the low mass gains, the scatter due to the ±0.02 mg/cm$^2$ error in the mass change measurement is evident. A total mass gain of ~0.2 mg/cm$^2$ is equivalent to a ~1 µm thick oxide layer. Because of the low temperature, minimal Al interdiffusion is expected.[19,21] For example, slurry coatings exposed to steam at 650°C have had lifetimes >50kh.[11] A second pack-coated T91 specimen completed 10kh at 650°C, however, characterization has not been completed. The mass gain for this specimen was similar as the others but is not shown for clarity. A T92 specimen with a thin CVD coating has completed 6 kh with a similar low mass gain as the other specimens. This specimen will be stopped at 10kh to quantify the interdiffusion rate. Figure 2 shows SEM images of

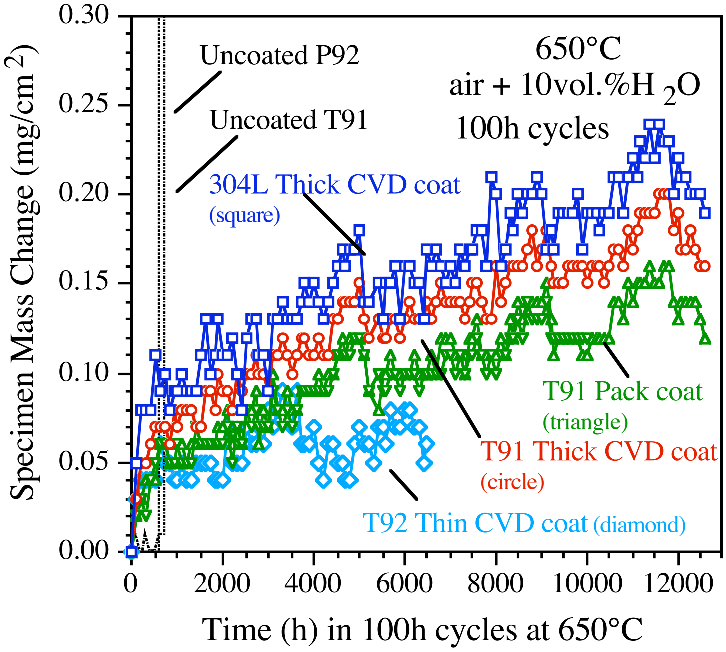

Figure 1. Specimen mass changes during 100h cycles for thick CVD coated 304L and thin, thick and pack-coated T91 (Fe-9Cr-1Mo) and uncoated T91 and P92 (Fe-9Cr-2W) alloys at 650°C in air + 10% water vapor.

the specimen corners of the thick coated 304L and T91 specimens after 12kh exposures. Cracks are evident at the edge and on the faces. While the T92 specimen with a thin coating has only reached 6kh, no cracks were evident. Cracking is attributed to the CTE mismatch between coating and substrate, particularly for the thick coatings with a thicker (20-40 µm) intermetallic outer layer.[16] Based on the low mass gain, the cracks in Figure 2 have not penetrated the coating as occurred with 1h cycles at 700°C.[17]

## 700°C OXIDATION RESULTS

Higher exposure temperatures were used to induce faster coating failure by increasing the rate of interdiffusion and oxidation. Figure 3 summarizes the data collected at 700°C in air + 10vol.% $H_2O$. As

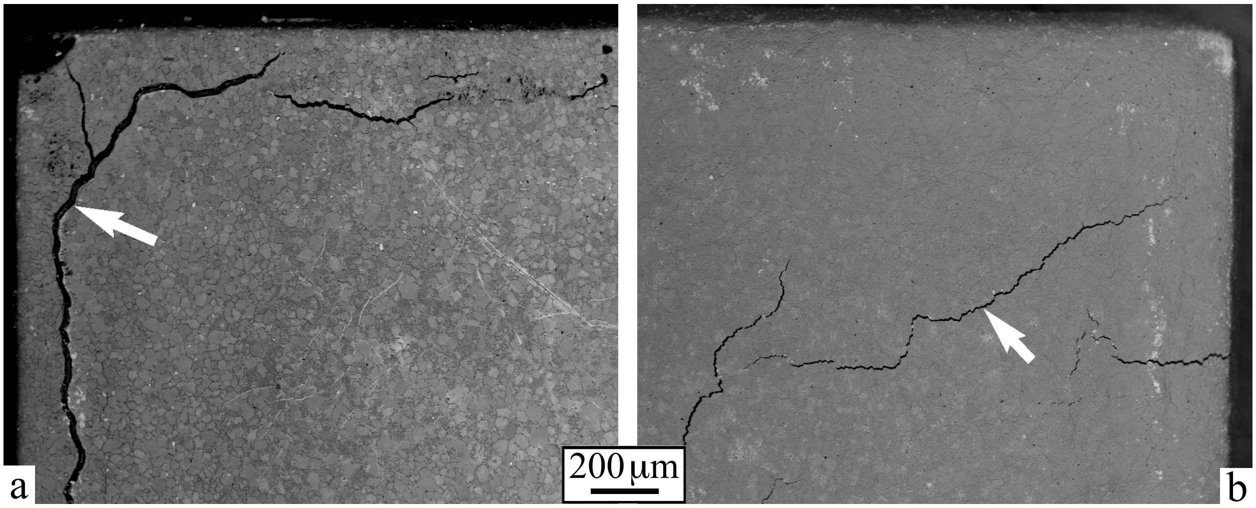

Figure 2. SEM backscattered electron images of CVD thick coatings after 12kh at 650°C in humid air. (a) 304L substrate and (b) T91 substrate. Cracks (arrows) are evident in both thick coatings.

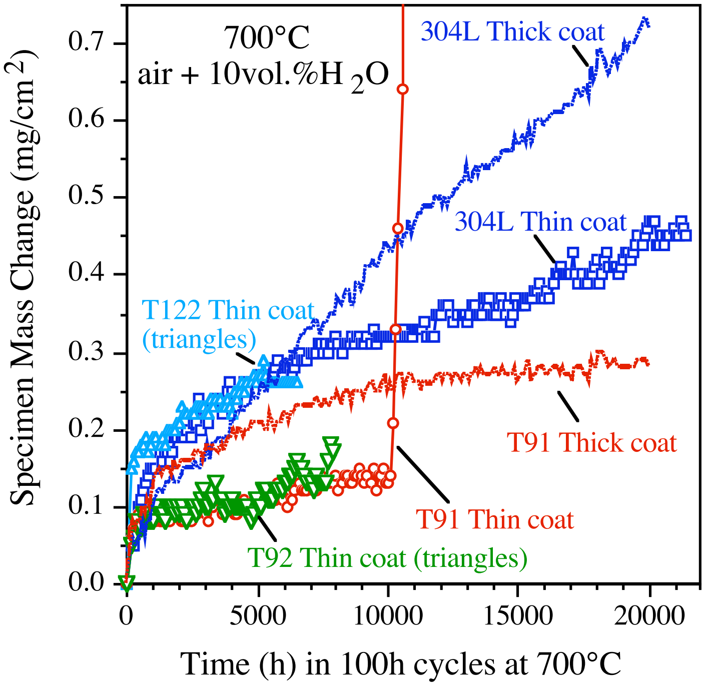

Figure 3. Specimen mass changes during 100h cycles at 700°C in air+10%$H_2O$. Results are shown for coated specimens with different CVD coating thicknesses.

reported previously, the CVD thick coated T91 and 304L specimens were stopped after 20kh because they were unlikely to fail due to their large Al reservoir. Several thin CVD coatings have been exposed. The failed thin coating on T91 has been reported previously.[22] The large mass gain increase was due to the formation of Fe-rich oxide nodules when the coating failed. A similar coating on 304L has passed 21kh without any indication of coating failure. As with the thick coating on 304L, the mass gain is higher than the corresponding coating on T91. The higher mass gain is attributed to more cracking and oxidation of the outer layer on the austenitic substrates[22] (similar to Figure 5b below). Extensive coating deformation and cracking was observed on the 304L substrate with a thick coating but the damage did not penetrate through the inner coating layer.[24] The longer life for the thin coated 304L specimen could be attributed to the higher Cr content in the substrate providing improved selective oxidation.[25] However, a more likely explanation is that the phase boundary between the Al-rich ferritic-phase coating and the austenitic substrates inhibits interdiffusion. A comparison of the interdiffusion between T91 and 304L has been presented previously.[22,24]

The specimens continuing to be exposed at 700°C include thin coatings on T92 and T122 substrates, Figure 3. The mass gain for the T122 specimen is slightly higher than that observed for T91 or T92. Failure of these specimens will provide confirmation of the low critical Al content (3.5%) observed at the failure of the coating on T91.

## 800°C RESULTS

Figure 4 shows mass gains for coatings exposed at 800°C. Figure 4a shows the complete data for the last thick coating specimen on T91 which was stopped after 20kh. Cross-sections of this specimen are shown in Figure 5. The coating had large pores after exposure, likely due to interdiffusion with the substrate as well as some Al loss due to oxidation and re-growth after scale spallation. Little specimen deformation was observed and no obvious cracking, Figure 5a. At higher magnification, Figure 5b, the Al-rich outer

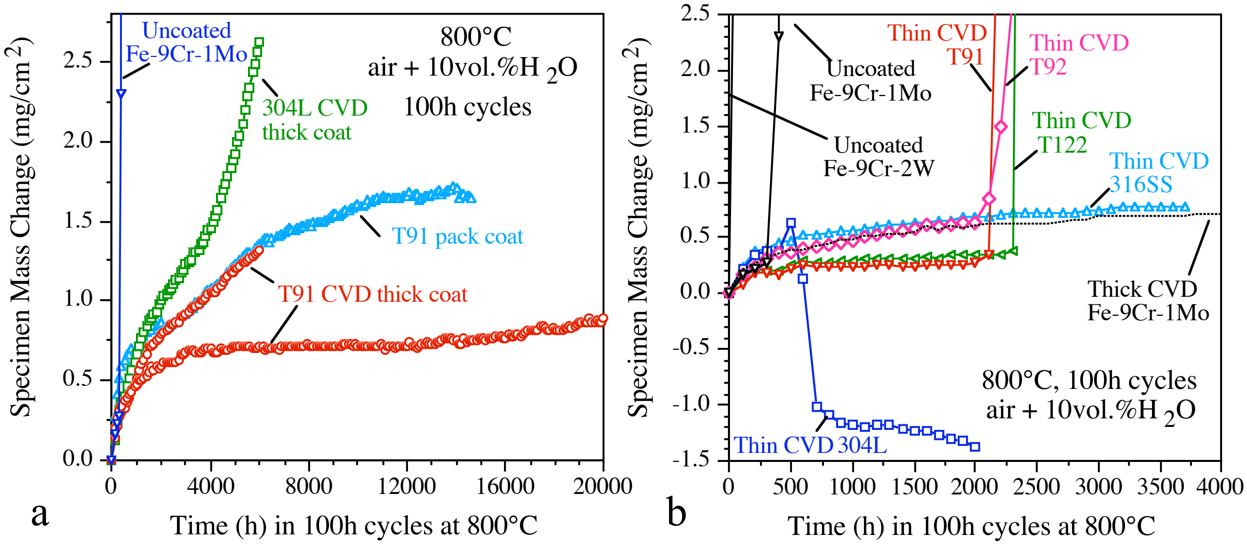

Figure 4. Specimen mass changes during 100h cycles at 800°C in air+10%$H_2O$. (a) thick CVD coatings and (b) thin CVD coatings.

coating layer was consumed in some locations resulting in $FeO_x$ formation. The higher mass gains for some coatings was likely due to variations in oxidation of this outer layer, Figure 4a. In some locations, oxide had formed at the interface between the inner and outer layer indicating little protective behavior of the outer layer. Figure 6 shows the Al profile of the coating after 20kh. Similar to a coated T91 specimen exposed for 6kh, the Al profile had reached the center of the specimen. The total starting substrate thickness was ~1.7mm.

Figure 4b shows the specimen mass change data for various thin coatings at 800°C. The early failure was for a 304L substrate that likely did not have a good quality coating. An EPMA profile after the 2kh exposure at 800°C, showed an unusually low Al content. All of the aluminized Fe-Cr substrates failed within a few cycles of each other suggesting that the effect of Cr on coating life in this composition range (8.5-10.5wt%Cr) is not significant. Figure 7a shows Al profiles from each of the three failed specimens

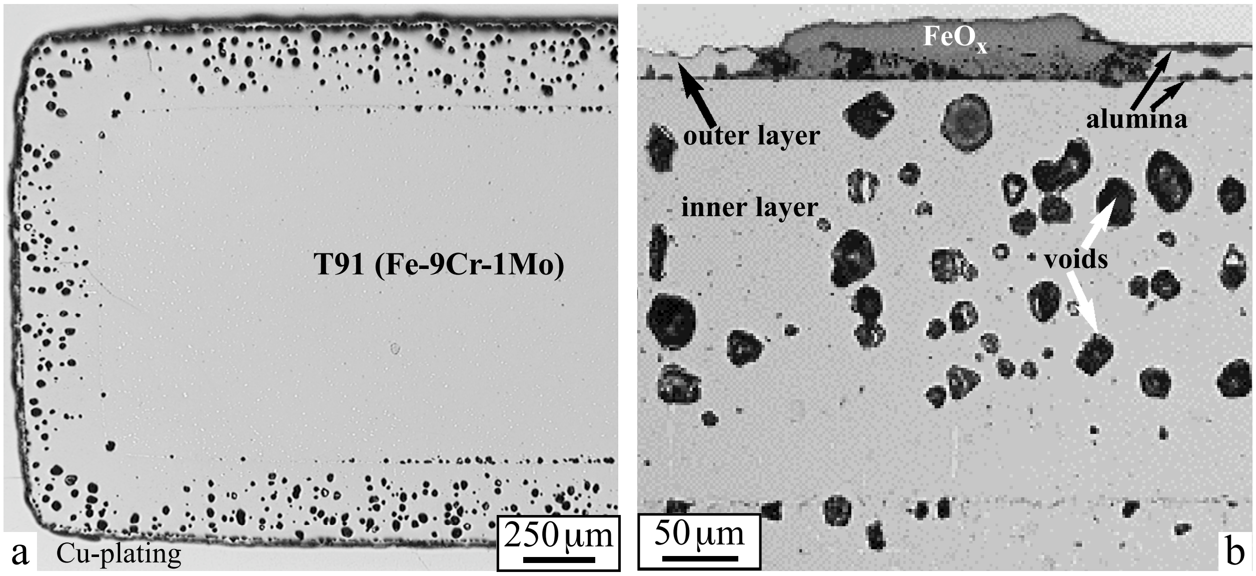

Figure 5. Light microscopy of polished sections of CVD thick coating on T91 after exposure at 800°C in humid air for 20kh. Higher magnification in (b)

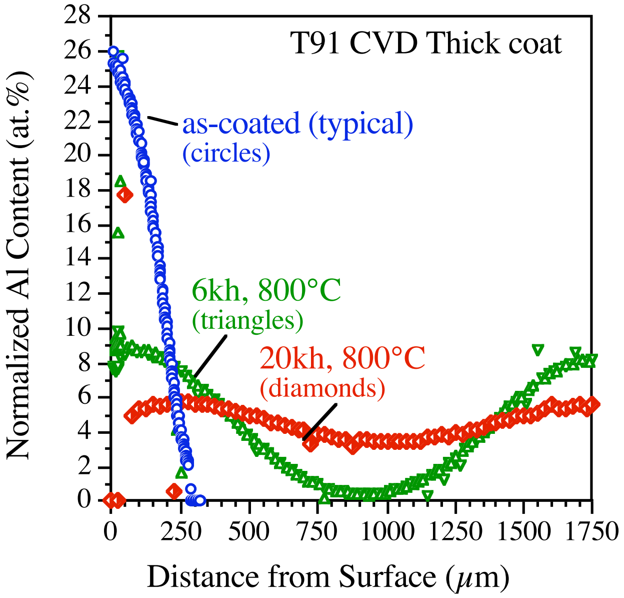

Figure 6. Normalized Al content by EPMA as a function of depth for as-deposited thick CVD coatings and after exposure for 6 and 20kh at 800°C in wet air. No failures were observed for these specimens

at 800°C. The profiles are from areas where the coating was still protective, e.g. Figures 7b and 7c, and not from areas where $FeO_x$ nodules had formed. The stray higher Al points are due to AlN particles (e.g. Figure 7c) which form due to N in the substrate. Surprisingly, the Al contents remaining in the coatings (0.5-1.1 at%) were even lower than that observed after failure at 700°C (also shown in Figure 7a). Based on prior work on Fe-Cr-Al alloys oxidized in wet air,[26,27] it was expected that the critical Al content (needed to form protective alumina) would be higher at 800°C compared to 700°C. This results suggests that the critical Al content needed for protective behavior may be inversely related to temperature. The critical Al content has a strong affect on coating lifetime predictions and higher Al contents have been

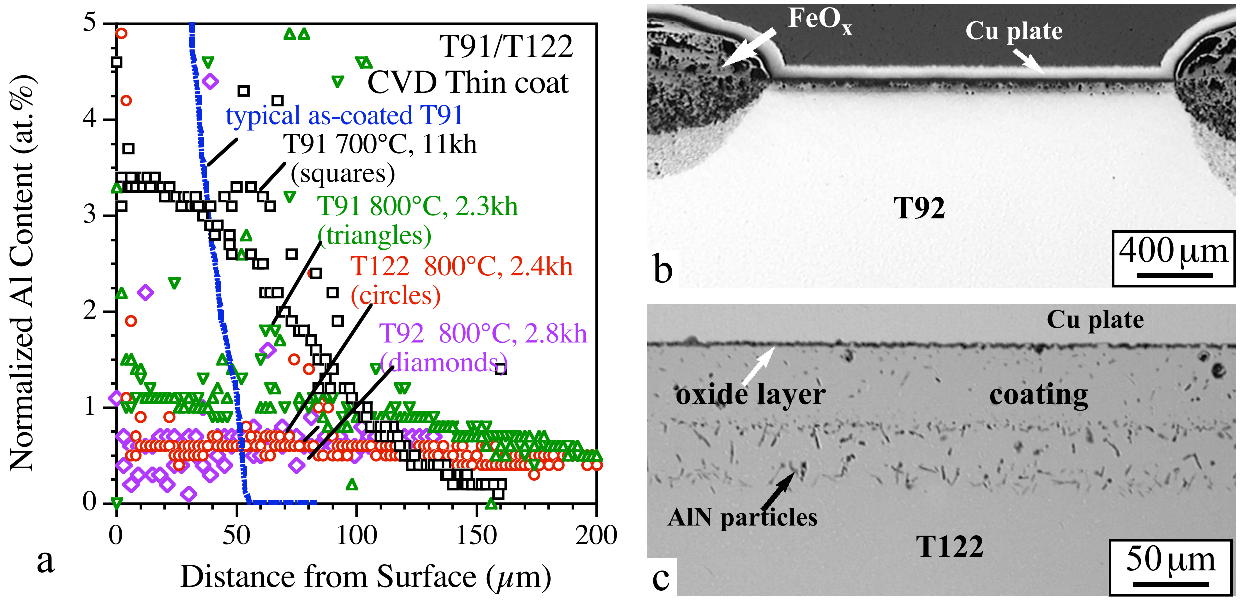

Figure 7. (a) Normalized Al content by EPMA as a function of depth for as-deposited thin CVD coatings and after exposures in wet air at 800°C. Two composition profiles are plotted for each condition after failure observed. Light microscopy of polished cross-sections after failure at 800°C (b) T92 and (c) T122 in area away from $FeO_x$ nodules.

reported for aluminide coating exposures in steam, particularly at 650°C.[12] (The difference in coating failure criteria between steam and wet air will be explored in the future.) However, because of the slow Al interdiffusion at 650°C, a coating failure of the thin CVD coating may require several years of exposure.

Finally, the remaining coating being exposed at 800°C is on a type 316 stainless steel substrate which is similar in composition to 304L except higher Mo, Si and C contents. Similar to the observation at 700°C, the thin coating on 316 has exceeded the thin coating lifetimes on FM alloys and is approaching 4kh of exposure. Again, the higher Cr content in the substrate may be beneficial but a more important factor is the phase boundary (ferritic-austenitic at the coating-substrate interface) inhibiting Al transport. This result is very promising for Al-rich coatings on austenitic boiler tubes and suggests that very long coating lifetimes can be achieved with relatively thin coatings. However, the mechanical properties of such coatings need to be evaluated. The potential for fatigue cracking is possible because of the CTE mismatch between coating and substrate.

## SUMMARY

The long-term oxidation performance of coated ferritic-martensitic and Fe-base austenitic substrates was evaluated in humid air at 650°-800°C. Higher temperatures were used to accelerate the Al interdiffusion to create coating failures. One of the last thicker (~250µm) CVD coated substrates was removed from exposure after 20kh at 800°C to determine the amount of Al interdiffusion. This coating showed no indication of cracking in the inner layer or deformation but contained large voids. Most recent coating exposures were thin (<50µm) CVD coatings in order to reduce the time to failure. Failure times of coatings on T91, T92 and T122 at 800° were within 10% of each other and ≤1at.%Al remained in the coatings at failure. Thus, substrate Cr contents in the 9-11at.% range appeared to have only a minimal effect on coating lifetime. The observed inverse relationship between temperature and critical Al content at failure needs to be further investigated as it will strongly affect lifetime model predictions at lower temperatures. Coated austenitic substrates tend to show higher mass gains than similarly coated FM alloys at 700° and 800°C. However, the time to failure of coated austenitic substrates (304L and 316) are at least a factor of 2X longer. This difference is attributed to the ferritic coating-austenitic alloy phase boundary inhibiting Al interdiffusion. A select few coated specimens will continue to be exposed if possible. However, the majority of the work on this program has been concluded.

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