

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

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### **ABSTRACT**

Aluminum-rich coatings made by chemical vapor deposition and pack cementation on ferritic (e.g. Fe-9Cr-1Mo) and austenitic (Type 304L) substrates are being evaluated at 650°-800°C. For oxidation testing, a humid air environment was used to quantify coating performance, as uncoated substrates experience rapid oxidation at these temperatures. A main goal of this work is to demonstrate the potential benefits and problems with alumina-forming coatings. The higher exposure temperatures were selected to accelerate the degradation of the coating by interdiffusion with the substrate. A general conclusion of this testing was that coatings with less Al and a ferritic Fe(Al) structure could be more durable than higher Al content aluminide coatings which have a large thermal expansion mismatch with these substrates. A lifetime model has been developed using diffusion and oxidation observations to predict coating performance as a function of temperature and initial coating composition. To test and improve the model, additional experiments are now being 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. Because of the unexpectedly low level of Al measured at coating failure (~3.5at.% at 700°C), exposures of specimens with thick (~200µm) high Al content coatings were stopped after 10kh at 800°C and 20kh at 700°C because extremely long times to failure were predicted. Post-exposure Al concentration profiles for these specimens were measured using electron microprobe.

### **INTRODUCTION**

Coating or alloying the surface of high-performance alloys with Al to improve environmental resistance by forming a protective external alumina scale has been studied for many years.<sup>1-13</sup> Alumina-forming coatings are commonly used at higher temperatures (>900°C), such as thermal barrier coatings,<sup>4</sup> where the slow growth rate of an alumina scale is desirable. Coatings rich in Cr or Si (chromizing or silicizing) are used at lower service temperatures. However, compared to Cr<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>, the superior stability of Al<sub>2</sub>O<sub>3</sub> in the presence of water vapor<sup>14</sup> could be a significant issue for steam or exhaust gas environments. With the higher temperature goals associated with use of ultra-supercritical (USC) steam in coal-fired power plants,<sup>15</sup> the higher performance potential for alumina-forming coatings may be desired.

The central goal of this project has been identifying the potential benefits and problems associated with Al-rich coatings on Fe-base ferritic (e.g. Fe-9Cr-1Mo, T91) and austenitic (e.g. Fe-18Cr-8Ni, 304L) substrates to justify their usage and improve their durability.<sup>13,16-22</sup> Laboratory studies were conducted at 650°-800°C on model aluminide coatings made in a controlled, laboratory-scale chemical vapor deposition (CVD) process.<sup>12</sup> Some of the problems identified have been thermal-cycling degradation<sup>17</sup> associated with the coefficient of thermal expansion (CTE) mismatch between aluminide phases and typical Fe-base substrates,<sup>16</sup> the loss of strength due to the interdiffusion of Al into the substrate,<sup>19,20</sup> and the mechanical durability of brittle, high-Al aluminide phases such as Fe<sub>2</sub>Al<sub>5</sub>.<sup>11,12</sup> In order to quantify the benefit of Al-rich coatings, a coating lifetime model<sup>21</sup> was developed, based on long-term oxidation<sup>22</sup> and interdiffusion studies.<sup>21</sup> One of the main findings has been that thin ferritic phase coatings with relatively low Al contents can be more durable and effective than higher Al content aluminide phase coatings. As this project nears its conclusion, current results are reviewed on the oxidation behavior of Al-rich CVD coatings and future research goals are outlined, particularly associated with testing and improving the coating performance model.

## EXPERIMENTAL PROCEDURE

Substrates (~18 x 12 x ~1.5 mm) coated included commercial T91 (Fe-9.3at.%Cr-0.6Mo-0.5Mn-0.3V-0.55Si-0.2Ni-0.5C-0.22N-0.005S), P92 (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 type 304L stainless steel (Fe-19.7at%Cr-7.9Ni-1.81Mn-0.15Mo-0.76Si-0.32N-0.09C-0.006S). The laboratory-scale CVD reactor and coating process for low-activity (thin coatings formed after 6h at 900°C with ~5µm Al-rich outer layer and ~50µm total thickness including the interdiffusion zone) and high-activity (thick coatings formed after 4h at 1050°C with ~20-40µm outer layer and ~150-275µm total thickness on T91) as well as the as-coated microstructures are described elsewhere.<sup>12</sup> Additional coatings were made by a laboratory-scale pack cementation coating process (~250µm thick coating after 6h at 1050°C).<sup>23</sup> Coated specimens were exposed with the as-coated surface finish and were cleaned in acetone and methanol prior to exposure. Mass changes ( $\pm 0.02$ mg/cm<sup>2</sup>) were measured using a Mettler Toledo model AG245 balance. Cyclic oxidation exposures were conducted with a 100h cycle time with specimens in an alumina boat with faces parallel to the gas stream. An environment of air + 10vol.% water vapor was used as a low cost (compared to steam) method for determining coating performance. These Fe-base alloys oxidize rapidly in wet air when not coated,<sup>16,17,22</sup> thereby providing an indication when the coating is no longer effective. Distilled water was atomized into the flowing gas stream (850ml/min) through an alumina tube (e.g. gas velocity of 1.7cm/s at 700°C) and was calibrated to  $10 \pm 1$  vol.% based on the amount of water injected. 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. Coated specimens were examined by SEM in plan view every 2kh of exposure in wet air. Copper plating was used prior to sectioning to protect the thin surface oxide.

## RESULTS AND DISCUSSION

### 650°C OXIDATION RESULTS

Figure 1 shows typical mass change behavior of coated and uncoated ferritic and austenitic specimens at 650°C in air + 10% water vapor. After an incubation period, uncoated T91(Fe-9wt.%Cr-1Mo) and P92 (Fe-9wt.%Cr-2W) specimens underwent accelerated oxidation with the formation of a thick Fe-rich oxide. Specimens with a thick coating made by CVD or pack cementation did not exhibit

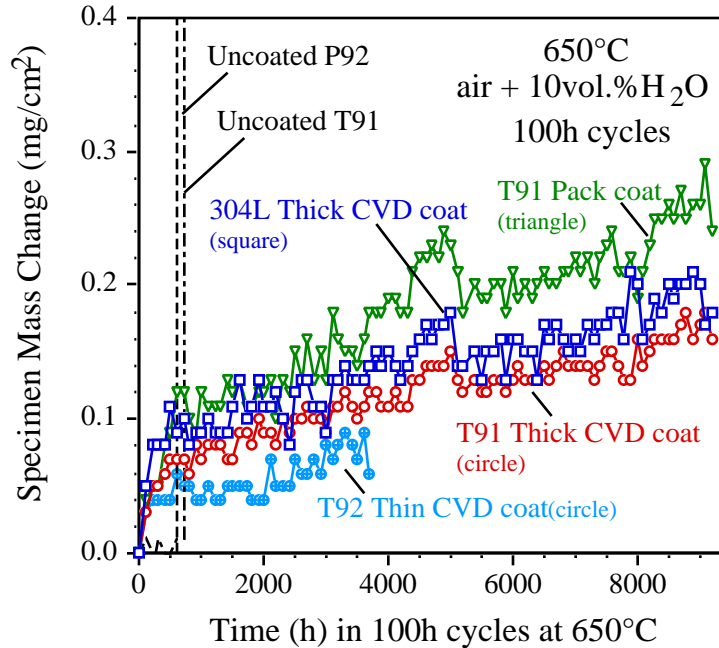


Figure 1. Specimen mass changes during 100h cycles for thick CVD coated 304L and thin, thick and pack-coated T91 (Fe-9Cr-1Mo) and uncoated T91 and P92 (Fe-9Cr-2W) alloys at 650°C in air + 10% water vapor.

accelerated attack after ~9kh of exposure. The scatter in the data mainly reflects the  $\pm 0.02 \text{ mg/cm}^2$  error in the mass change measurement. Minimal Al interdiffusion is expected at this temperature<sup>19,21</sup> and coating lifetimes can be extensive ( $>41\text{kh}$  for slurry coatings in steam<sup>11</sup>). For comparison, similar thickness coatings were made by a laboratory-scale pack cementation process<sup>23</sup> which is more relevant to commercial coating processes. A T91 specimen coated by pack cementation showed a similar low mass gain as the CVD coated specimens. A second pack-coated T91 specimen also showed a low mass gain but is not shown for clarity. A T92 specimen with a thin CVD coating has completed ~3.5kh with a similar low mass gain. One or more of the exposures will be stopped at 10kh to quantify the interdiffusion rate.

## 700°C OXIDATION RESULTS

In order to induce failure, Al interdiffusion and oxidation were accelerated by increasing the temperature to 700°C and higher (temperatures that exceed any realistic service condition). The mass gain behavior of thin and thick CVD coatings are shown in Figure 2. As noted previously,<sup>22</sup> the thin coating on T91 exhibited a high mass gain associated with Fe-rich oxide nodule formation and coating failure after ~11 kh. The thin and thick coatings on 304L substrates showed higher mass gains than the thick coating on T91, however, no evidence of nodule formation or accelerated oxidation was observed. Based on the model predictions that failure times would exceed 100kh, the exposure of both specimens with thick coatings was stopped at 20kh for further characterization. Figure 3 shows cross-sections of the coatings on both substrates. Coating deformation and cracking at the edges of the 304L substrate (arrows in Figure 3a) also was noted by SEM examinations of the coating at earlier times and the increased oxidation associated with this degradation explains the higher mass gain for this specimen compared to T91, Figure 2. The deformation is attributed to the CTE mismatch between the austenitic substrate and the ferritic coating (Al acts as a ferrite stabilizer). The outer  $(\text{Fe,Ni})_3\text{Al}$  layer also has a different CTE but this intermetallic layer is present in coatings on both ferritic and austenitic substrates.<sup>13</sup> From Figure 3 it is clear that the thick coating on T91 did not show similar deformation as the 304L substrate after the same 20kh exposure. The small strain energy due to this thin outer layer does not appear to play a major role in the deformation.

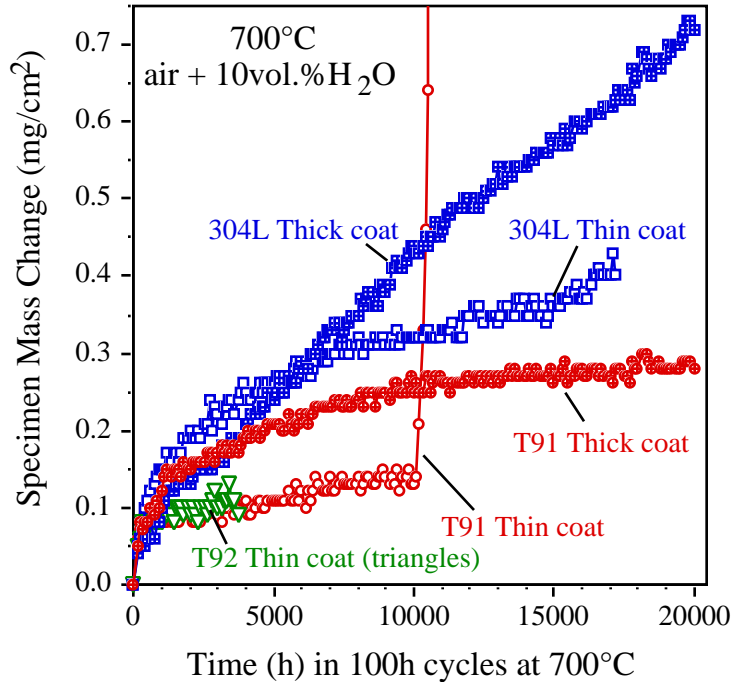


Figure 2. Specimen mass changes during 100h cycles at 700°C in air+10% $H_2O$ . Results are shown for coated specimens with different CVD coating thicknesses.

Despite the edge degradation observed after 20kh, the coating on 304L was not breached like the thin coating on T91. Aluminum profiles from these coatings are shown in Figure 4. In both cases, the maximum penetration depth had approximately doubled after 20kh at 700°C and the surface Al content had dropped significantly to ~20at.% or less in both cases.

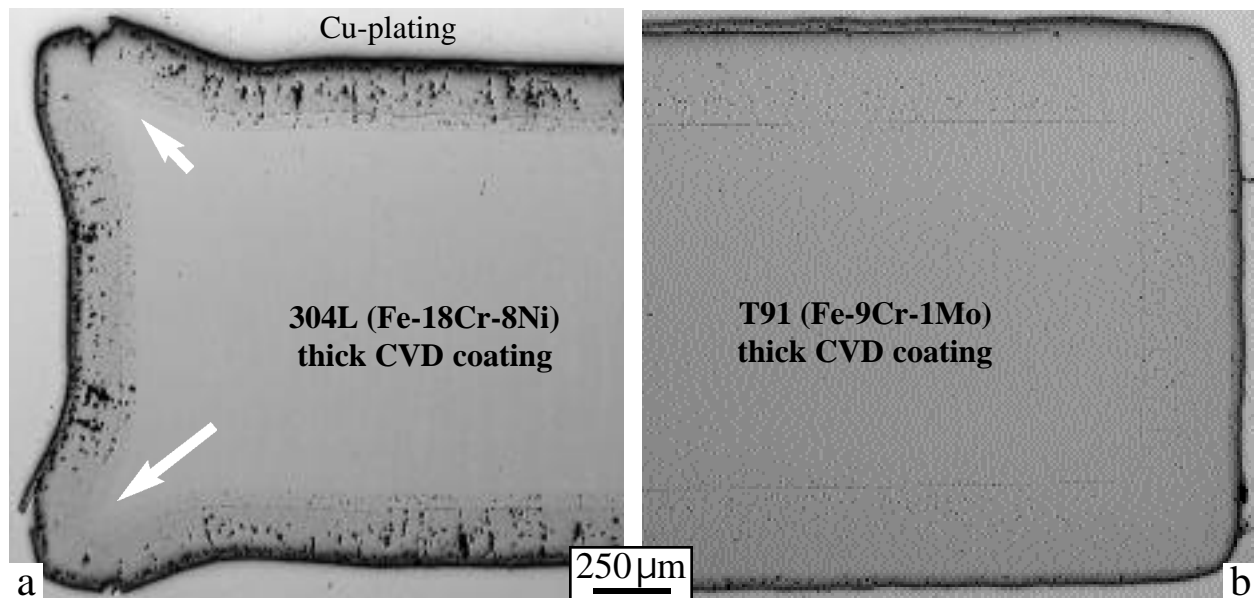


Figure 3. Light microscopy of polished sections of CVD thick coatings after 20kh at 700°C in humid air. (a) 304L substrate and (b) T91 substrate. Arrows in (a) point to the edge deformation observed with this substrate.

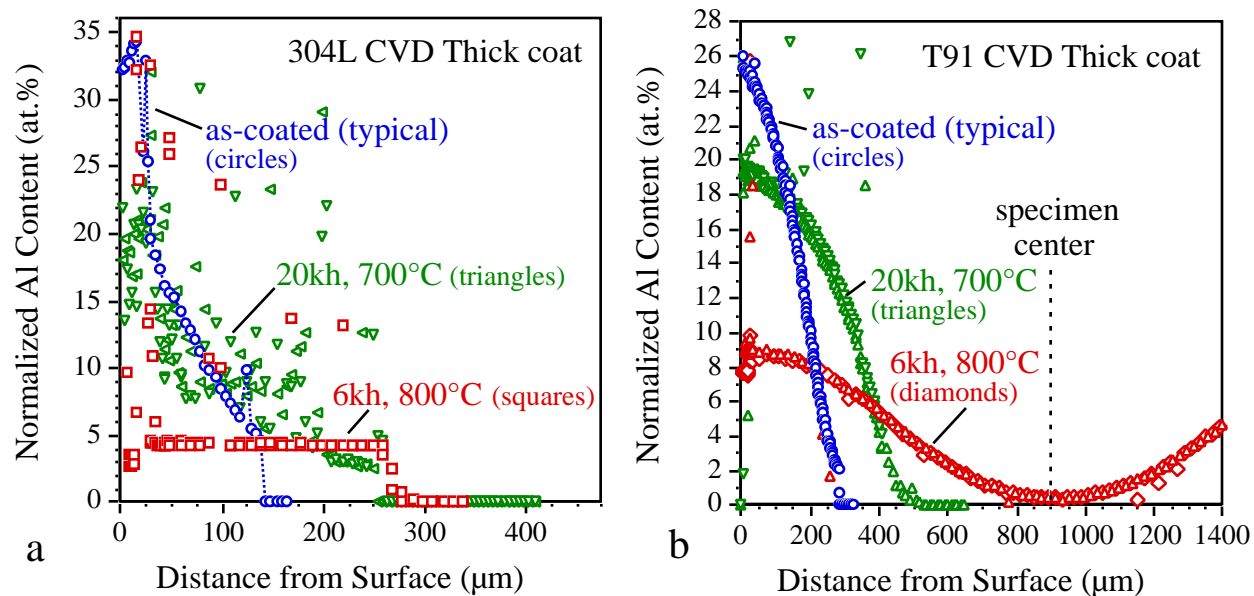


Figure 4. Normalized Al content by EPMA as a function of depth for as-deposited thick CVD coatings and after exposure for 20kh at 700°C and 6kh at 800°C for (a) 304L substrates and (b) T91 substrates. Two composition profiles are plotted for each condition.

The specimens continuing to be exposed at 700°C include thin coatings on T92 and 304L substrates, Figure 2. The T92 coating has shown a similar mass gain after 3.5kh as the same coating on T91. The thin coating on the 304L substrate has reached 17kh without evidence of accelerated attack. The longer life compared to the thin coating on T91 is attributed to the higher Cr content (19at.%) in the coating which should improve the selective oxidation of Al in the coatings compared to the 9% Cr in the T91 coating by a third element effect.<sup>24</sup> The beneficial effect of Cr was confirmed by studies of model Fe-Al-Cr alloys.<sup>25</sup>

## 800°C RESULTS

Figure 5 shows mass gains for coatings exposed at 800°C. For this condition, commercial substrates and laboratory-modified substrates also were examined with, for example, low N contents which improved the initial coating quality.<sup>18</sup> As at 700°C, the thick CVD coatings on T91 tended to show lower mass gains than those on 304L substrates. The coating microstructure on two commercial substrates (T91 and 304L) exposed for 6kh was reported previously.<sup>22</sup> Exposures of two more specimens on laboratory-made substrates were stopped after 10kh. The lower mass gain for the coating on laboratory-made 304L compared to commercial 304L could be due to the lower N content (~0 at.% vs. 0.32% in commercial alloys). However, the same type of macroscopic deformation occurred on this specimen, Figure 6a, as was observed for commercial 304L after 6kh.<sup>22</sup> For comparison, the thick CVD coating on commercial T91 after 6kh is shown in Figure 6b. (The characterization of the coating on laboratory-made T91 after a 10kh exposure has not been completed.) As mentioned earlier, there is no CTE mismatch between the ferritic interdiffusion zone of the coating and the T91 substrate. The improved coating quality on N-free 304L, associated to some degree with fewer AlN particles, may have delayed the onset of some coating defects, arrows in Figure 6a, which increased the mass gain of the coating on commercial 304L.<sup>22</sup> However, the Al profiles on the 10kh 304L specimen compared to the 6kh 304L specimen indicated a larger residual Al reservoir in the 10kh specimen, Figure 7. This difference can be attributed to a thicker initial coating on the 10kh specimen, with a mass gain of 12.7 mg/cm<sup>2</sup> compared to 8.7 mg/cm<sup>2</sup> for the 6kh specimen. The thicker coating on the 10kh specimen likely explains its lower mass gain, Figure 5a. Despite the difference in initial coating thickness on the 304L specimens, the Al content remaining in the coating after exposure was similar, ~4.7at.%, Figure 7. This Al level may reflect a quasi-equilibrium between the Al-containing ferritic coating<sup>3</sup> and the austenitic substrate. Certainly the phase difference

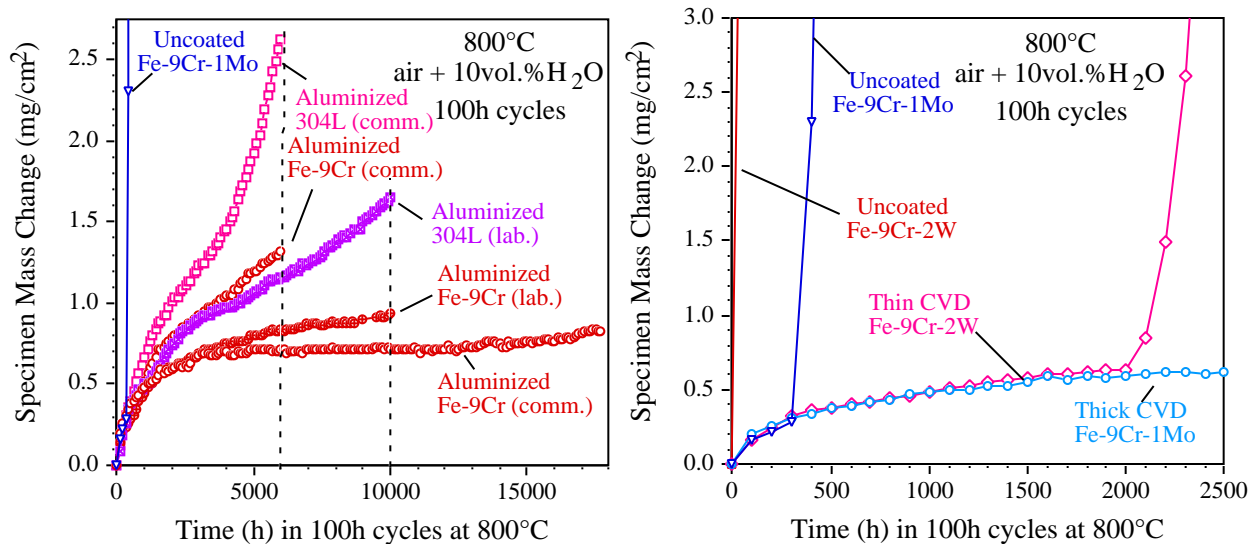


Figure 5. Specimen mass changes during 100h cycles at 800°C in air+10% $H_2O$ .

between the coating and substrate appeared to inhibit interdiffusion, especially compared to the deep Al interdiffusion observed for T91 after 6kh at 800°C, Figure 4b. After 10kh at 800°C, the outer layer is particularly Al depleted, although a few Al-rich phases, possibly NiAl, appear to exist, Figure 7.

Finally, thin CVD coatings also were evaluated at 800°C on a T92 substrate, Figure 5b. The coating recently failed after ~2100h with a large increase in mass. Up to 2kh, the mass gain of the thin coating was very similar to that observed for a thick CVD coating on T91, which continues to be protective after 17.5kh, Figure 5a. The thin coating will be characterized to determine the Al content in the coating at failure for comparison to the result at 700°C. Based on prior work on model Fe-Al-Cr alloys, the critical Al content for failure in humid air appeared to increase with temperature.<sup>26</sup> However, the critical Al value needed for protection in water vapor at 800°C is still considerably lower than the ~18% Al needed for sulfidation resistance at this temperature.<sup>16,21,27</sup> The faster failure for the thin coating at 800°C may be a better condition than 700°C to compare the effect of substrate Cr content on lifetime.

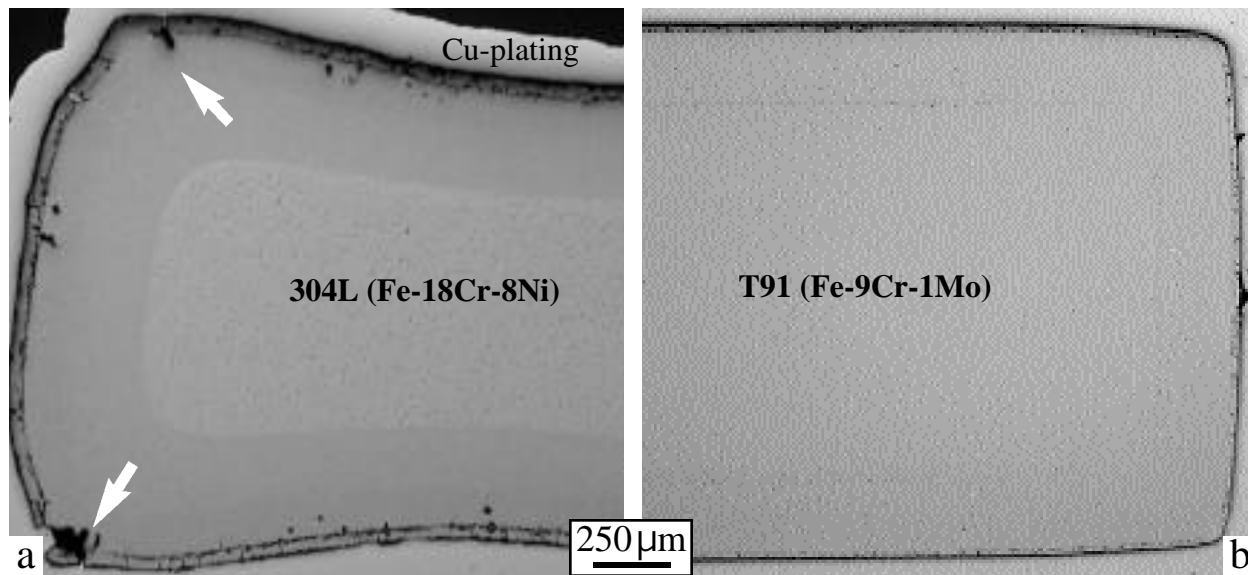


Figure 6. Light microscopy of polished sections of CVD thick coatings after exposure at 800°C in humid air. (a) laboratory 304L substrate after 10kh and (b) commercial T91 substrate after 6kh.

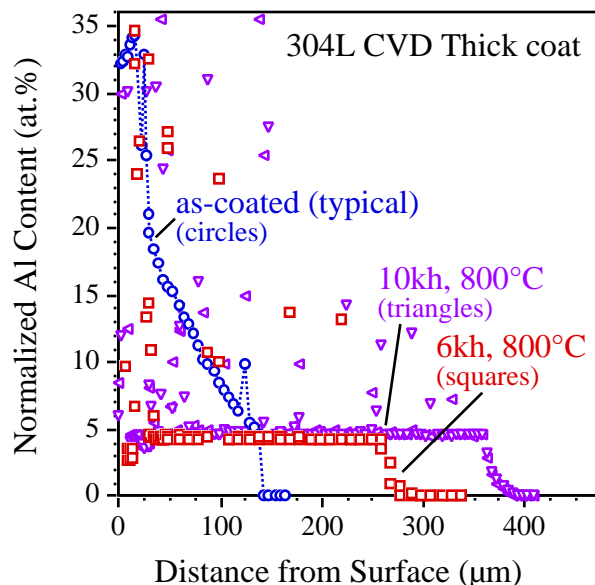


Figure 7. Normalized Al content by EPMA as a function of depth for CVD thick coatings on 304L substrates, as-coated and after exposure at 800°C. The apparent larger Al reservoir for the 10kh specimen is because the initial coating was thicker, with a mass gain of 12.7 mg/cm<sup>2</sup> compared to 8.7 mg/cm<sup>2</sup> for the 6kh specimen.

## SUMMARY

The long-term oxidation performance of coated ferritic (T91) and Fe-base austenitic (304L) substrates was evaluated in humid air at 650°-800°C. The higher temperatures were used to accelerate the Al interdiffusion to create coating failures. None of the thicker CVD coatings showed accelerated attack of the substrate and extended exposures were terminated to determine the amount of Al interdiffusion. At both 700° and 800°C, coated 304L specimens showed higher mass gains and more significant macroscopic deformation but less interdiffusion than the coated ferritic T91 substrates. The increased deformation during thermal cycling is attributed to the strain energy associated with the CTE difference between the ferritic coating and austenitic substrate. The coating-substrate phase boundary likely inhibited interdiffusion as well. Thin CVD coatings on ferritic substrates have failed at 700° and 800°C and results from these coatings will improve the coating lifetime model being developed. The thin CVD coating on 304L substrate being tested at 700°C has not failed after >17kh. In this case, the longer life for the coating on 304L is attributed to a beneficial effect of the higher Cr content in this coating compared to T91.

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