Interdiffusion Behavior in Aluminide Coatings for Power Generation Applications

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ABSTRACT

One of the critical issues for the application of iron aluminide coatings is the loss of Al from the coating into the Fe-base substrate alloys which do not contain aluminum. The interdiffusion behavior between chemical vapor deposited (CVD) aluminide coatings and ferritic and austenitic substrates is being studied for times up to 10,000h in the temperature range of 500-800ºC. Coatings were synthesized using a laboratory-scale CVD reactor on representative commercial ferritic (Fe-9Cr-1Mo) and austenitic (type 304L stainless steel) alloys. The aluminide coatings on both alloys typically consisted of a relatively thin (20-25µm) Al-rich outer layer and a thicker (150-250µm) inner layer with less Al. The composition profiles before and after interdiffusion testing were measured by electron probe microanalysis (EPMA). The decrease of the Al content at the coating surface was not significant after extended diffusion times (≤ 5000h) at temperatures ≤ 700ºC. More interdiffusion occurred at 800ºC in coatings on both Fe-9Cr-1Mo and 304L alloys. Particularly, a two-phase microstructure was formed in the outer coating layer on 304L after interdiffusion of 2000h at 800°C. The interdiffusion behavior also was simulated using a computer model COSIM (Coating Oxidation and Substrate Interdiffusion Model), which was originally developed for MCrAlY overlay coatings by NASA. Reasonable agreement was observed between the simulated and experimental composition profiles although more work is needed to confirm assumptions made in the model.

INTRODUCTION

Increasing the temperature capabilities of ferritic and austenitic alloys for advanced power generation applications has been of ongoing interest for many years due to potential gains in energy efficiency and concomitant decreases in emissions. These classes of alloys generally owe their oxidation resistance to the formation of Cr-containing oxides which, especially for the ferritic steels, become less protective at higher temperatures and in steam or exhaust environments so that protective coatings will have to be considered.[1-2] Iron aluminides are well known to have excellent oxidation and sulfidation resistance due to the formation of an external, protective alumina scale.[3-6] Thus, an aluminide coating could be a good candidate for improving the oxidation/corrosion resistance of ferritic and austenitic steels provided that it can be applied with the desired composition and microstructure and be mechanically sound (that is, minimal cracking and adherent to the substrate).

Two lifetime issues of particular concern for application of iron aluminide coatings are (1) the loss of Al from the coating into the substrate alloys which do not contain any Al, and (2) possible compatibility problems between Fe-Al coatings and substrates which can have substantially different coefficients of thermal expansion (CTE).[7] In the present work, the interdiffusion behavior between chemical vapor deposited (CVD) aluminide coatings and ferritic and austenitic substrates is being studied for times up to 10,000h in the temperature range of 500-800ºC. Representative commercial ferritic (Fe-9Cr-1Mo) and austenitic (type 304L stainless steel) alloys were used as the substrate materials. Coatings were synthesized using a laboratory-scale CVD reactor in order to more rigorously control the coating process in terms of composition, purity and microstructure. The interdiffusion between the coating and substrate alloys also was simulated using a computer model COSIM (Coating Oxidation and Substrate Interdiffusion Model), which was originally developed for MCrAlY overlay coatings by Nesbitt.[8] The COSIM also was used to predict the lifetime of present aluminide coating systems based on a concentration dependent failure criterion, e.g., surface Al content drops to a critical level. While the complexity of the transport processes from experimental and theoretical studies of interdiffusion in aluminide coatings on Ni-based superalloys has been recognized,[9-11] very limited research could be found on interdiffusion behavior between aluminide coatings and Fe-based alloys.[12-13] The results from the present study could therefore provide data and insight needed as part of the process of developing a lifetime model based on coating failure criteria. It is expected that the understanding of these critical issues could readily be applied to diffusion aluminide coatings produced by other aluminizing techniques, such as commercial pack coatings.

EXPERIMENTAL PROCEDURE

The substrates used in this study were commercial ferritic (Fe-9Cr-1Mo) and type 304L (Fe-18Cr-9Ni nominally) austenitic stainless steels. These particular alloys are considered to be representative of the basic compositions of the two alloy classes of interest. Prior to coating experiments, the substrate surface was polished to a 0.3µm alumina finish and ultrasonically cleaned in acetone and methanol. The iron aluminide coatings were made in a laboratory CVD reactor at Oak Ridge National Laboratory (ORNL), and details of the coating fabrication process have been reported elsewhere.[14-15]

The diffusion tests are being conducted on the coated steel specimens contained in crucibles in air for times up to 10,000h in the temperature range of 500-800ºC, as indicated in Table 1. Before and after diffusion tests, selected specimens were examined by x-ray diffraction (XRD) and field emission gun scanning electron microscopy (FEM-SEM), equipped with energy dispersive x-ray analysis (EDXA). The coatings on specimens for cross-sectional examination were protected by Cu-plating the specimen prior to mounting in epoxy. The composition profiles were measured by electron probe microanalysis (EPMA) using wavelength dispersive x-ray analysis.

Table 1. The diffusion test conditions.

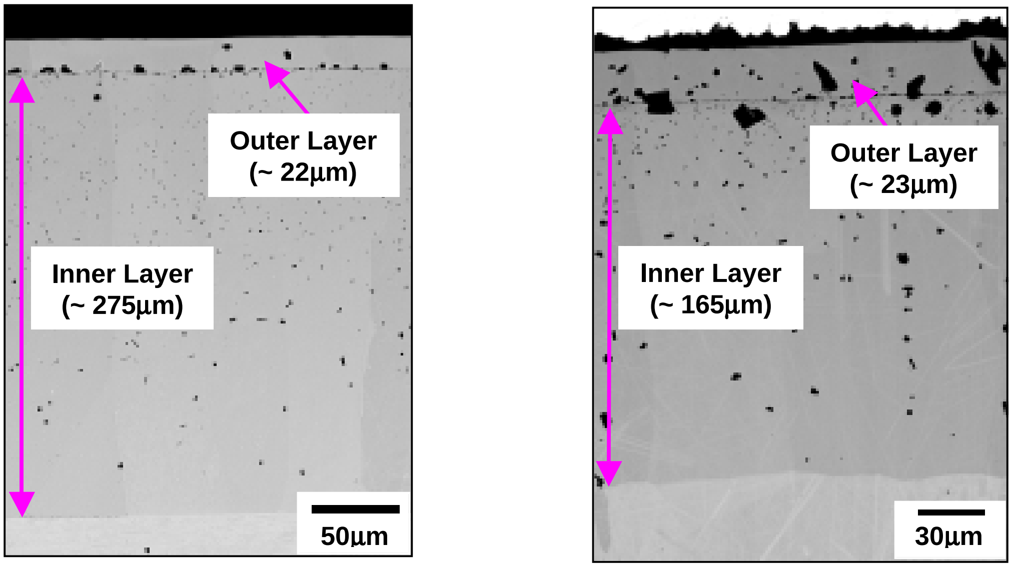
Coating System	Diffusion Temperature (°C)	Diffusion Time (h)
CVD aluminide coatings on Fe-9Cr-1Mo and 304L	500	10,000*
	600	5,000
		10,000*
	700	2,000
		5,000
		10,000*
	800	2,000

* Still in testing at the present time

RESULTS AND DISCUSSION

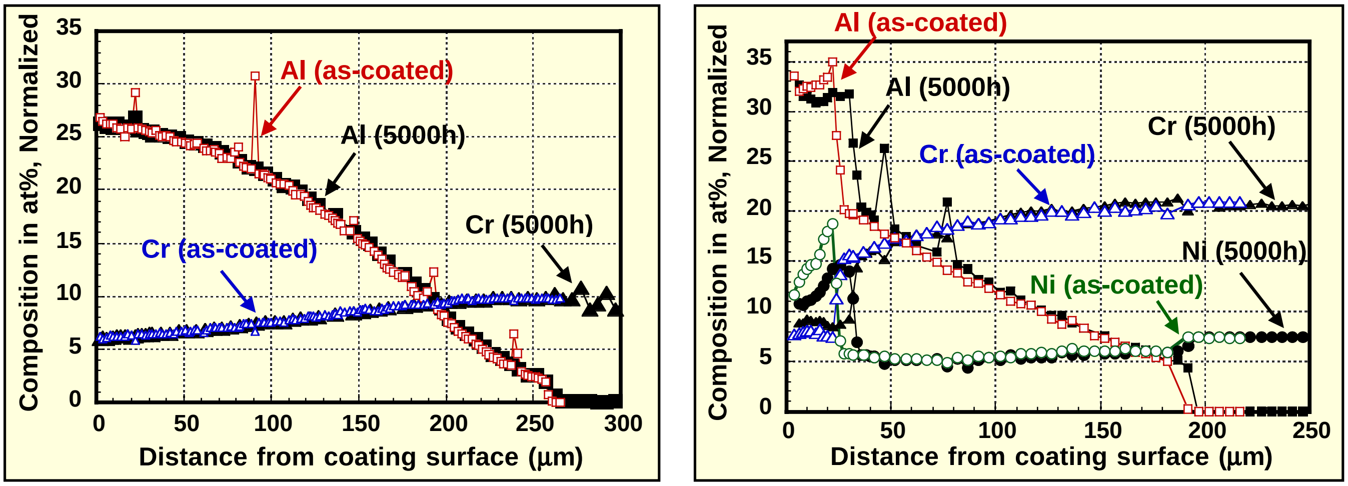
The as-deposited aluminide coatings on both alloys typically consisted of a relatively thin (20-25µm) Al-rich outer layer and a thicker (150-250µm) inner layer with less Al, as shown in Fig. 1. The EPMA composition profiles of the coated specimens before and after the diffusion tests at 600°C are shown in Fig. 2; the color plots correspond to the as-deposited compositions. Interdiffusion between CVD aluminide coatings and Fe-9Cr-1Mo and 304L substrates was negligible after 5000h at 600°C; the surface Al content remained the same as the as-deposited conditions, ~25 at% in the coating on Fe-9Cr-1Mo (Fig. 2a) and ~32 at% on 304L (Fig. 2b), respectively. It is worth mentioning that the present diffusion tests were carried out in air, and therefore the Al was consumed from both surface oxidation and interdiffusion with the substrate.

A decrease of Al at the coating surface was noticed when the diffusion temperature was increased to 700°C. As an example, the surface Al content decreased from 26 at% to 23 at% in the coating on Fe-9Cr-1Mo after 2000h at 700°C, and further dropped to 20 at% after 5000h, as shown in Fig. 3a. A decrease from 34 at% Al to 25 at% was found near the coating surface on 304L after 2000h, Fig. 3b.



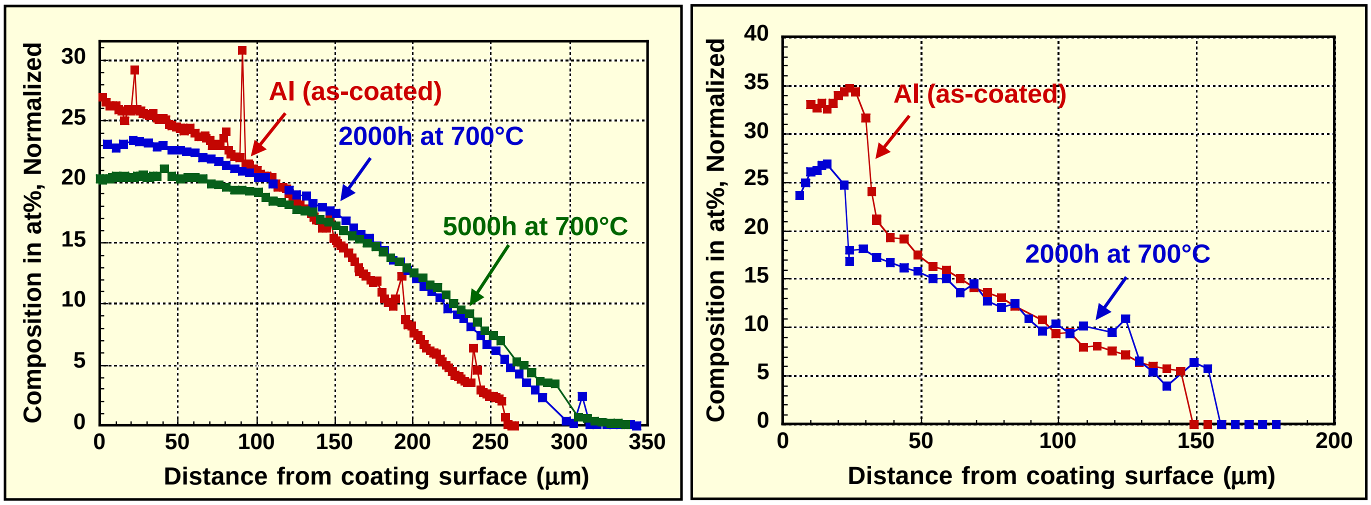
(a) (b)

Figure 1. EPMA back-scattered electron images of the as-deposited CVD aluminide coatings on (a) Fe-9Cr-1Mo and (b) 304L.



(a) (b)

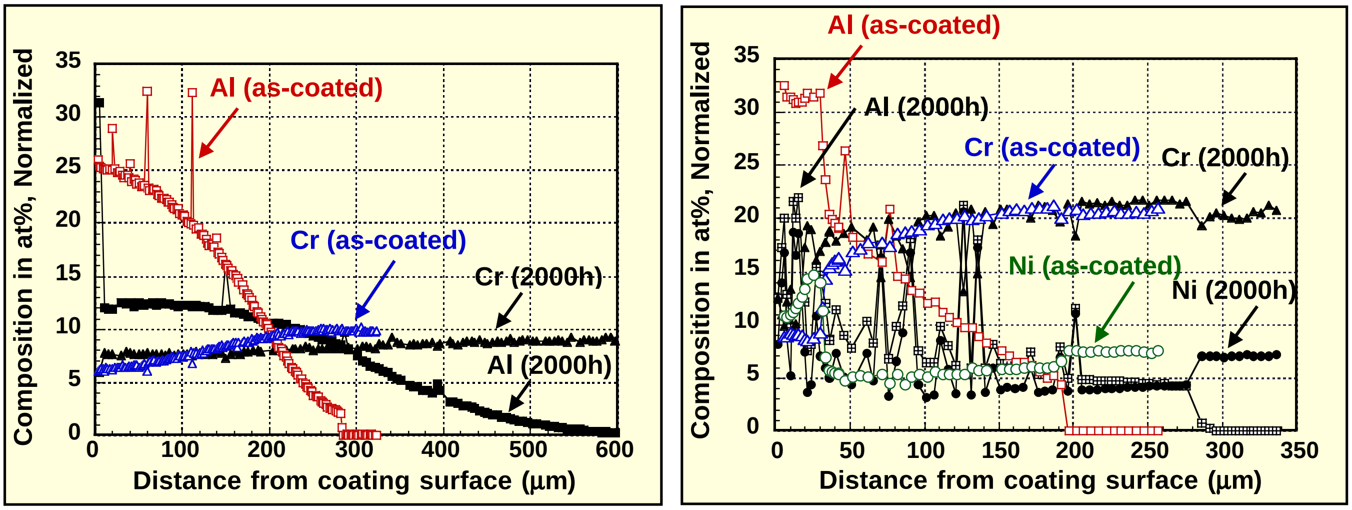
Figure 2. Composition profiles in the CVD aluminide coatings before and after diffusion at 600°C for 5000h. (a) coatings on Fe-9Cr-1Mo and (b) coatings on 304L.



(a)

(b)

Figure 3. Composition profiles of Al in the CVD aluminide coatings before and after diffusion at 700°C. (a) coatings on Fe-9Cr-1Mo and (b) coatings on 304L

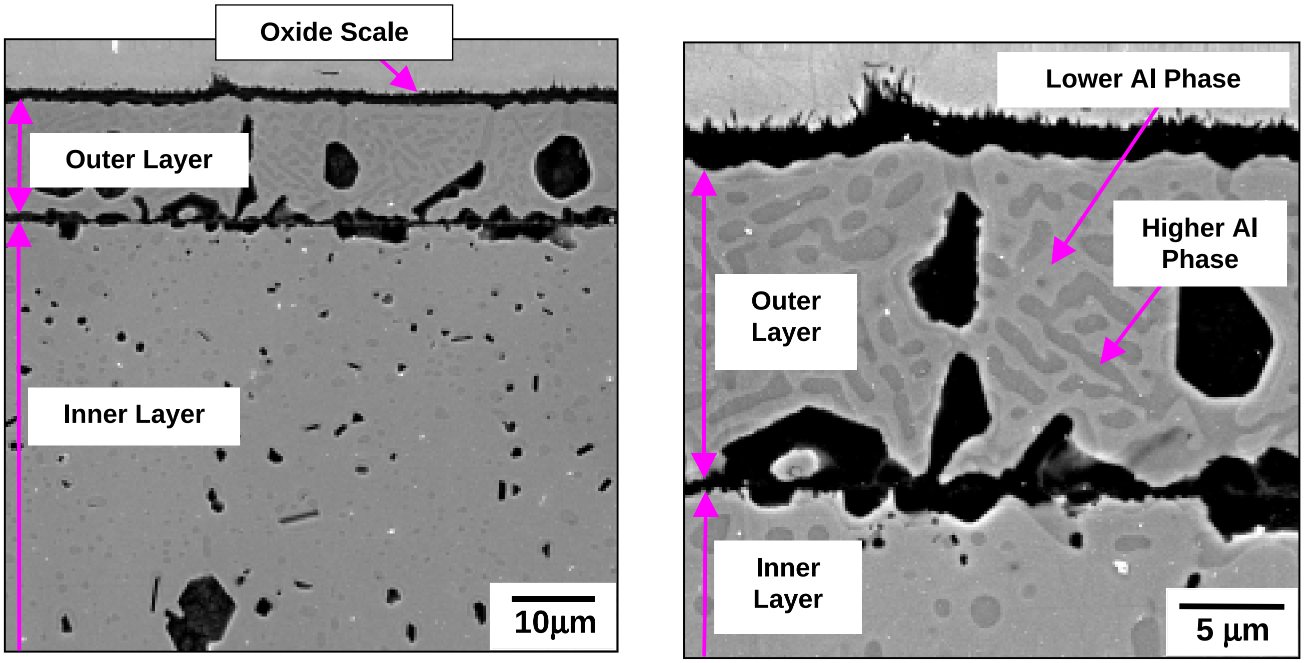


(a)

(b)

Figure 4. Composition profiles in the CVD aluminide coatings before and after diffusion tests at 800°C for 2000h. (a) coatings on Fe-9Cr-1Mo and (b) coatings on 304L.

The interdiffusion was much greater at 800ºC, as indicated in Fig. 4. A significant decrease of Al from 25 at% to 12 at% was observed in the coating on Fe-9Cr-1Mo after 2000h, Figs. 4a. The total coating thickness (outer layer + inner layer) was increased from ~275µm to ~500µm. The decrease of Al in the coating on 304L from ~32 at% to 15-20 at% led to the formation of a two-phase microstructure in the coating outer layer (Fig. 5), which also was reflected in the fluctuation in the composition profiles, Fig. 4b. The EPMA results indicated that the darker phase contained more Al and Ni (40Al-40Ni-17Fe-3Cr, in at%), whereas the lighter phase was depleted in Al but rich in Fe (9Al-4Ni-73Fe-14Cr, in at%). However, the amount of Al consumed from the coating outer layer by forming the thin oxide layer (~2µm) is relatively small, < 5 at%, as compared to the Al lost by back diffusion.



(a) (b)

Figure 5. (a) EPMA back-scattered electron image showing the two-phase microstructure in the CVD aluminide coating on 304L after diffusion test for 2000h at 800°C, and (b) higher magnification of the outer layer.

The coating composition profiles were simulated by using a finite-difference computer program COSIM,[8, 16] which was designed to model the one-dimensional, diffusional transport associated with high-temperature oxidation and interdiffusion of overlay-coated substrates. The description of interdiffusion of the individual components in multicomponent alloys is based on Onsager's formalism of Fick's law, which includes the diffusional interactions among the components, as shown below:[17]

Fick's 1st Law
$$J_j = -D_{j,j}\frac{\partial C_j}{\partial X} - D_{j,k}\frac{\partial C_k}{\partial X} \qquad \text{j, k = Al, Cr} \qquad (1)$$

and Fick's 2nd Law
$$\frac{\partial C_j}{\partial t} = \frac{\partial\left[D_{j,j}\left(\frac{\partial C_j}{\partial X}\right)\right]}{\partial X} + \frac{\partial\left[D_{j,k}\left(\frac{\partial C_k}{\partial X}\right)\right]}{\partial X} \qquad \text{j, k = Al, Cr} \qquad (2)$$

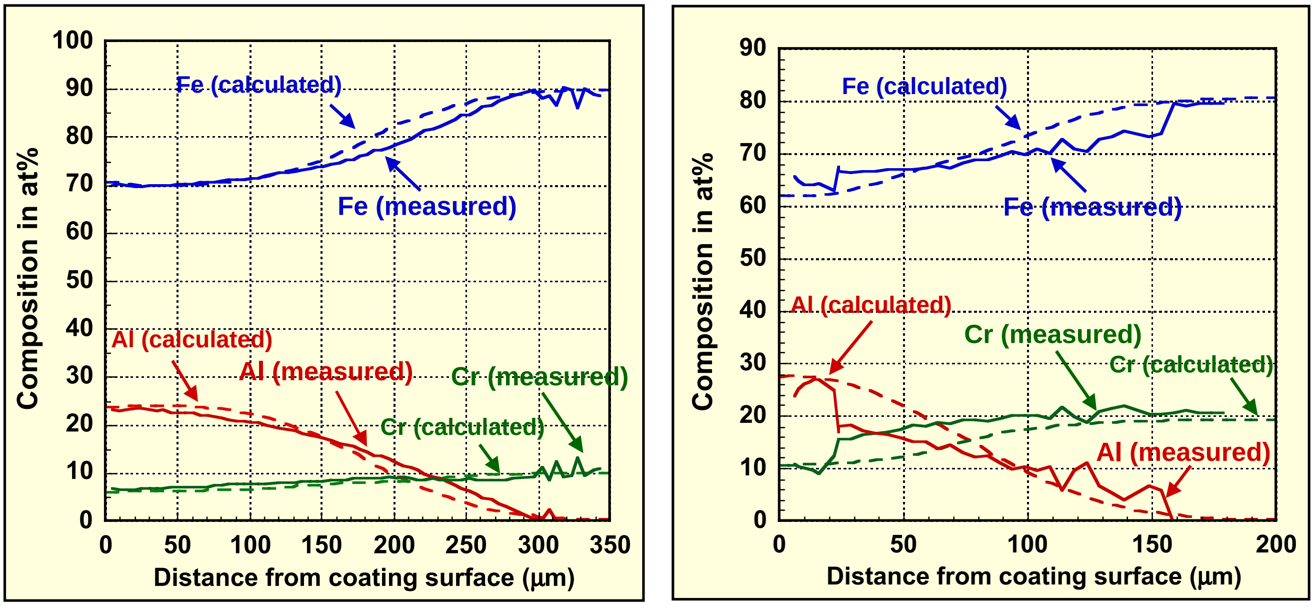
where J_j and C_j refer to the flux and concentration of component j, $D_{j,j}$ and $D_{j,k}$ refer to the four ternary interdiffusion coefficients, and X and t refer to distance and time, respectively. The description of diffusion in a ternary system requires four concentration-dependent interdiffusion coefficients, two main and two cross-coefficients. Two independent diffusion couples with a common composition in the diffusion are usually needed to determine these coefficients.[18] Various methods have been reported in the open literature to calculate ternary interdiffusion coefficients.[19-21] The major advantage of the COSIM program is the incorporation of a previously-developed oxide growth and spalling model so that it considers both the loss of Al from the coating into the substrate during interdiffusion and the loss of Al at the coating surface during oxidation.[22] Concentration profiles for up to three elements in the coating and substrate can be predicted after various oxidation exposures.

In contrast to NiCrAlY overlay coatings which exhibit a constant composition throughout the coating thickness, there is a composition gradient in the as-deposited diffusion aluminide coatings, Fig. 2. An equivalent coating composition and thickness were therefore assigned as input in the model; the product of the equivalent Al concentration and thickness was equal to the area underneath the as-deposited composition profiles. The interdiffusion coefficients were assumed to be independent of composition due to lack of correlation between composition and diffusivities in the present ternary Fe-Al-Cr system. The diffusion coefficients were adapted from Akuezue and Stringer [23] for coatings on Fe-9Cr-1Mo ($C_{Fe} = 100 - C_{Al} - C_{Cr}$), as shown in Table 2. For coatings on 304L, in order to simplify the multi-component diffusion situation, a ternary system was approximated, i.e., (Fe+Ni) was considered as one component ($C_{Fe+Ni} = 100 - C_{Al} - C_{Cr}$). The diffusivities for coatings on 304L were estimated to be 1/4~1/2 of those for coatings on Fe-9Cr-1Mo due to slower diffusion rates in face-centered cubic 304L.[24] The diffusivities at 700°C were estimated to be one order of magnitude lower than those at 800°C.[12] Figure 6 compares the simulated and measured composition profiles of the aluminide coatings on both alloys. It suggests that the calculated profiles fit well for the coatings on Fe-9Cr-1Mo, even though further investigation is required to validate the assumptions mentioned above for modeling. A larger difference was noticed between the calculated and the measured profiles for coatings on 304L; simplifying the quaternary system to the ternary system, as well as the uncertainties in diffusivity data might have caused this discrepancy.

Table 2. Input of diffusion data in COSIM.

	Diffusion coefficients at 800°C (10^{-11} cm^2/s)			
(1 = Al, 2 = Cr)	D_{11}	D_{12}	D_{21}	D_{22}
Coating on Fe-9Cr-1Mo	2.92	-1.13	-0.52	0.60
Coating on 304L	0.83	-0.32	-0.15	0.17

COSIM also was used to predict coating lifetime based on a concentration dependent failure criterion.[8] As the Al in the coating is consumed by surface oxidation and/or back-diffusion into the substrate, there will be a critical Al content, below which the coating is no longer effective in protecting the underlying substrate. Previous studies on cast Fe-based alloys with 13-22 at% Al and 500 ppma Hf during exposure in wet air at 700°C indicated that 20 at% Al was necessary for forming protective Al_2O_3 scales.[25] However, as shown in Fig. 2 the present aluminide coatings also contained a significant Cr content (8-9 at%) and this addition was expected to improve the oxidation resistance of the coatings.[26-27] Oxidation tests in wet air at 700°C on cast alloys with 13-15 at% Al, 2-10 at% Cr and 500 ppma Hf suggested that the Cr addition had a significant beneficial effect; an alloy with only 13 at% Al performed as well as the Fe-20 at% Al+Hf specimen.[25] 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 at% Al. According to these oxidation results, three Al contents, 20 at%, 16 at%, and 12 at% were selected as the critical surface concentration at failure to predict coating lifetime; the results are given in Table 3. The current work focused on 700°C, which is a realistic application temperature for the substrate alloys. Systems I and III in Table 3 are closer to the coatings tested in the present study. These calculations suggest that with the current Al content and coating thickness, the coating lifetime corresponding to the critical surface concentration of 12 at% Al was approximately 26-27 kh, which is lower than the goal of 40 kh lifetime for power generation applications. Further increasing the Al content and/or coating thickness of as-deposited aluminide coatings could maintain the Al level required to form protective scales at the coating surface for longer period of time. Systems II and IV are included as examples to illustrate the importance of the Al content on coating lifetime. For the same equivalent coating thickness, an increase of 5 at% in the Al starting concentration could lead to an ~50% increase of the coating life. However, CTE mismatch between coating and the substrate is more likely to become a concern for thicker coatings with higher Al contents, which could cause cracking or deformation and therefore reduce coating life.[28] It should be noted that the predicted lifetimes need further confirmation due to the assumptions in the model, particularly for coatings on 304L.



(a) (b)

Figure 6. Comparison of simulated and experimental composition profiles of aluminide coatings using COSIM (only the results after 2000h at 700°C are shown here as an example). (a) the coating on Fe-9Cr-1Mo and (b) the coating on 304L.

Table 3. The initial results of lifetime prediction of coatings on Fe-9Cr-1Mo and 304L at 700°C by COSIM based on a concentration dependent failure criterion.

	Lifetime (kh)			
Critical Surface Al Concentration (at%)[‡]	Coating on Fe-9Cr-1Mo (180 μm[†])		Coating on 304L (100 μm[†])	
	System I	System II	System III	System IV
	25 at%[†]	30 at%[†]	30 at%[†]	35 at%[†]
20	7.2	13.7	8.4	12.7
16	14.3	23.9	14.1	20.7
12	28.0	44.4	25.5	37.0

[†] The equivalent coating thickness and Al content in the as-deposited coatings

[‡] Assume that the coating failure will occur when the Al concentration at the coating surface drops to these critical values.

SUMMARY

The interdiffusion behavior between CVD aluminide coatings and ferritic and austenitic substrates is being studied for times up to 10,000h in the temperature range of 500-800°C. The decrease of the Al content at the coating surface was not significant after extended diffusion times (≤ 5000h) at temperatures ≤ 700°C. Interdiffusion at 800°C led to a greater decrease of Al and the formation of a two-phase microstructure in the outer coating layer on 304L. The aluminide coating composition profiles after diffusion testing were simulated using the COSIM computer model. Initial results indicate reasonable agreement between the simulated and experimental composition profiles for coatings on Fe-9Cr-1Mo, while further investigation is needed to confirm the results. The discrepancy between calculated and measured composition profiles of the coating on 304L might be due to simplification of the quaternary system to the ternary system.

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