Aluminide Coatings for Power Generation Applications

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ABSTRACT

In order to form model aluminide coatings for studying critical issues related to their high temperature oxidation and corrosion performance, a laboratory chemical vapor deposition (CVD) procedure is being used to more rigorously control the coating process in terms of composition, purity and microstructure. One ferritic (Fe-9Cr-1Mo) and one austenitic alloy (304L) were selected as substrate materials. CVD aluminizing parameters such as temperature, time, and aluminum activity were varied to fabricate an iron aluminide coating with suitable thickness and composition. One of the specific goals of the present research is to increase the thickness of the outer aluminide layer of Fe-Al coatings to improve sulfidation resistance of these alloys. It was found that raising the CVD coating temperature alone was not sufficient to increase the outer-layer thickness. Instead a higher Al activity in the CVD aluminizing process was used. However, the aluminide coatings produced in the high-Al activity process tended to crack or spall after deposition. An *in situ* post-coating diffusion treatment was included after CVD aluminization to improve coating adhesion. Finally, a Pt plating system has been set up at Tennessee Technological University (TTU) and initial Pt plating runs have been conducted for future study of Pt-modified aluminide coatings on Ni-base superalloys.

INTRODUCTION

This work is comprised of two tasks: investigations of aluminide coatings on Fe-based alloys (Task I) and aluminide coatings on Ni-base superalloys (Task II). The effort this year has focused on Task I, and the results will be presented first. Some work towards developing improved Pt-modified aluminide coatings for Task II will be summarized at the end of this report.

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 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).

In order to understand the considerations involved in forming the desired coatings and optimizing their performance, a laboratory chemical vapor deposition (CVD) procedure is being used to maximize overall control of the coating process.[7] It is expected that the coating parameters identified could readily be translated to commercial pack processing, and that some guidance could be provided for other coating processes. Moreover,

the use of a CVD process to produce model coatings in a controlled and reproducible manner maximizes the ability to study the high-temperature degradation processes that limit coating lifetimes in an unambiguous way.

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 focus is on the effects of CVD aluminizing temperature, time, and aluminum activity on coating thickness, composition and microstructure. Through this study, model coatings with suitable thickness and composition will be fabricated and then subjected to high-temperature oxidation and corrosion testing.

The ultimate goal of Task II is to investigate the influences of duty cycle length and operating temperature on the oxidation behavior of state-of-the-art bond coatings for fossil-fueled turbine engines. The study will compare protective oxide scale adherence on ultra high-purity platinum aluminide bond coatings deposited by CVD to that on coatings fabricated by traditional methods such as commercial CVD, above-the-pack aluminizing and pack cementation. Typically, (Ni,Pt)Al coatings are synthesized by first electroplating the Ni-base superalloy substrate with a thin layer of Pt ($<$ 10 μm) and then aluminizing the electroplated substrate by a low-activity CVD aluminizing procedure.[8] The thickness of the Pt layer and impurities introduced during plating have been reported to affect oxidation behavior of platinum aluminide coatings.[9-10] The current work towards developing improved Pt-modified aluminide coatings has focused on setting up a laboratory Pt electroplating system to better control the Pt deposition process.

EXPERIMENTAL PROCEDURES AND RESULTS

The substrate alloys used in Task I were one ferritic (Fe-9Cr-1Mo) and one austenitic (304L) steel. Their compositions are given in Table 1. While these particular alloys may have insufficient strength for the application of interest, they are considered to be reasonably representative of the basic compositions of the two alloy classes of interest. Prior to coating experiments, the substrate surface was polished to a 0.3 μm alumina finish and ultrasonically cleaned in acetone and methanol.

The iron aluminide coatings were made in a clean laboratory CVD reactor at Oak Ridge National Laboratory (ORNL). The horizontal hot-wall CVD reactor used in this study is shown schematically in Fig. 1.[11] The reaction chamber consisted of an Al_2O_3 tube (5.0-cm i.d. and 61-cm length). An annular cylindrical graphite susceptor (6.2 cm inside diameter, 6.8 cm outside diameter, and 12.6 cm length) sealed in fused silica was placed around the alumina reactor tube. The susceptor was heated by a 20-kW radio frequency generator. The effective heating zone was 8 cm in axial length. The temperature variation along the axial direction of the zone was within ±5°C. The temperature at the center location of this heating zone was measured by a K-type thermocouple and controlled using a temperature controller. In order to coat all sides of the specimens for use in oxidation and corrosion experiments, a small hole (1-mm diameter) was drilled in the alloy specimens so they could be suspended in the reactor using a fine rod and a substrate holder of Al_2O_3. The substrate holder was placed in the center region of the heating zone, Fig. 1. The rate of air leaks into the reactor was typically measured to be on the order of 0.2 Pa/min at a reactor pressure of 1 Pa. Mass flow controllers were used to control the flow rate of H_2 (99.999%) and HCl (99.999%). As shown in Fig. 1, Al pellets (99.999% purity) were contained in a 450-cm^3 stainless steel vaporizer, which was maintained at a constant temperature of 300°C by using a heating jacket wrapped with heating tapes. $AlCl_3$ was generated in this vaporizer by reacting HCl with the Al pellets (i.e., Al + $3HCl = AlCl_3 + 1.5H_2$). The gas lines from the vaporizer to the reactor were heated to ~180°C, slightly above the sublimation temperature of $AlCl_3$, to prevent its condensation in the gas lines. Since an excess of $AlCl_3$ was used to ensure the uniformity of the aluminide coating, a cold trap was used to collect unreacted $AlCl_3$ waste before it entered a vacuum pump. Reactor pressure was controlled using a throttling valve interfaced with a pressure controller and a capacitance manometer.

Table 1. The composition of substrate alloys.

| Alloy	Fe-9Cr-1Mo		304L	
	wt.%	at.%	wt.%	at.%
Fe	88.46	87.75	69.70	68.59
Cr	9.26	9.87	18.29	19.33
Ni	0.16	0.15	8.75	8.19
Al	<0.01	--	<0.01	--
Mo	0.96	0.55	0.24	0.14
Ce	<0.01	--	<0.01	--
Co	0.02	0.02	0.18	0.17
Cu	0.07	0.06	0.29	0.25
Mn	0.47	0.47	1.84	1.84
Si	0.19	0.37	0.47	0.92
V	0.23	0.25	0.10	0.11
Nb	0.05	0.03	--	--
Ti	<0.01	--	<0.01	--
Hf	<0.01	--	<0.01	--
Y	<0.0003	--	<0.0003	--
Zr	<0.01	--	<0.01	--
P	0.013	0.0233	0.021	0.0373
B	0.001	0.0051	0.001	0.0051
C	516 ppm	0.2380	204 ppm	0.0933
N	480 ppm	0.1899	790 ppm	0.3100
O	26 ppm	0.0090	49 ppm	0.0168
S	8 ppm	0.0014	33 ppm	0.0057
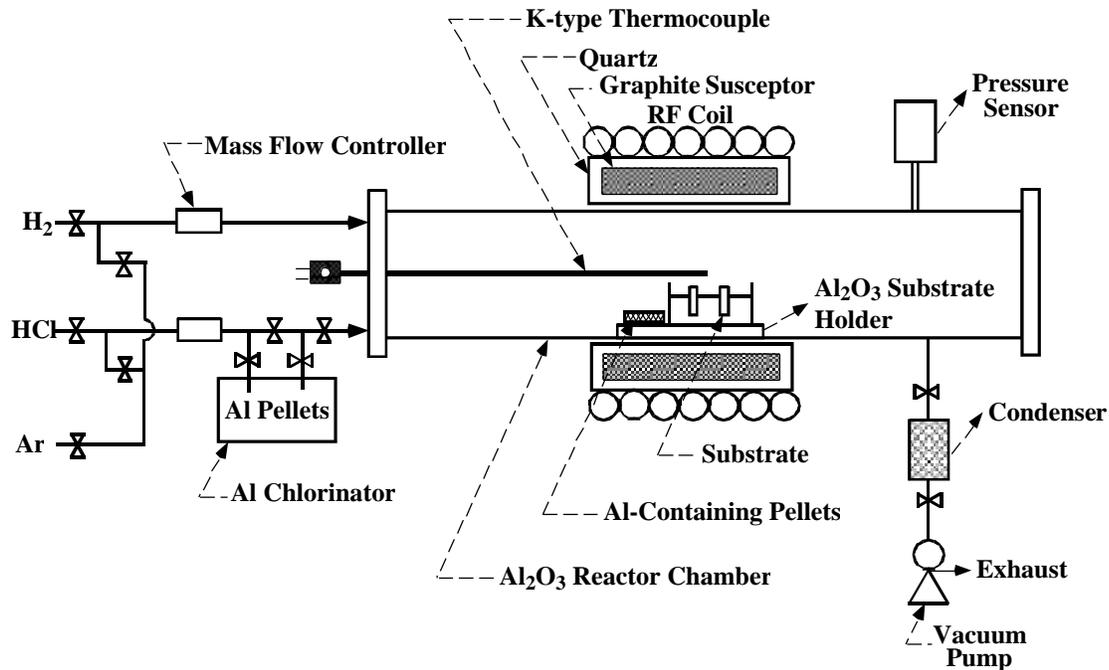
Fig. 1. Schematic diagram of the CVD reactor used for aluminizing experiments.

The phase structures of the as-deposited specimens were determined by x-ray diffraction (XRD). The surface morphologies and cross-sections of aluminide coatings were studied by field emission gun scanning electron microscopy (FEG-SEM). The coatings on specimens for cross-sectional examination were protected by Cu-plating the specimen prior to mounting in epoxy.

In total, nearly twenty CVD runs were made to examine the effects of coating temperature, time, and Al activity on the resulting aluminide coatings. The initial ORNL low-activity iron aluminide coating on steel substrates consisted of two distinct coating layers: a thin (~5 µm) Al-rich outer layer and a thick (~40-60 µm), lower Al inner interdiffusion layer.[7] Previous studies [7, 12] indicated that resistance to water vapor attack was significantly improved in the temperature range of 700-800°C up to 1000 thermal cycles when a thin outer aluminide layer was applied to steel substrates. However, this thin coating did not provide sufficient sulfidation resistance at 800°C in a sulfidizing H_2S-H_2O-H_2-Ar environment. In addition, for coatings with such a thin outer layer, it is difficult to address whether there are any potential CTE mismatch problems between substrate alloys (Fe-9Cr-1Mo: ~13.0 x 10^{-6}°C^{-1} and 304L: ~19.0 x 10^{-6}°C^{-1}) and aluminide coatings (Fe_3Al: ~20.5 x 10^{-6}°C^{-1}).[7, 13-16] Therefore, the research effort was focused on increasing the iron aluminide coating thickness, particularly the thickness of the outer layer.

The first approach to increasing coating thickness was to increase the CVD aluminizing temperature from 900°C and up to 1050°C, while other coating parameters such as time, gas flow rates and Al activity were maintained constant. The substrate alloys were aluminized for 6 hours at a reactor pressure of 13.3 kPa. Figure 2 shows the correlation between the thickness of the outer and inner layers and aluminizing temperature. It is clearly demonstrated that with increased coating temperature, the thickness of Fe-Al coating outer layer did not change significantly, while that of the inner interdiffusion zone increased about two- to three-fold.
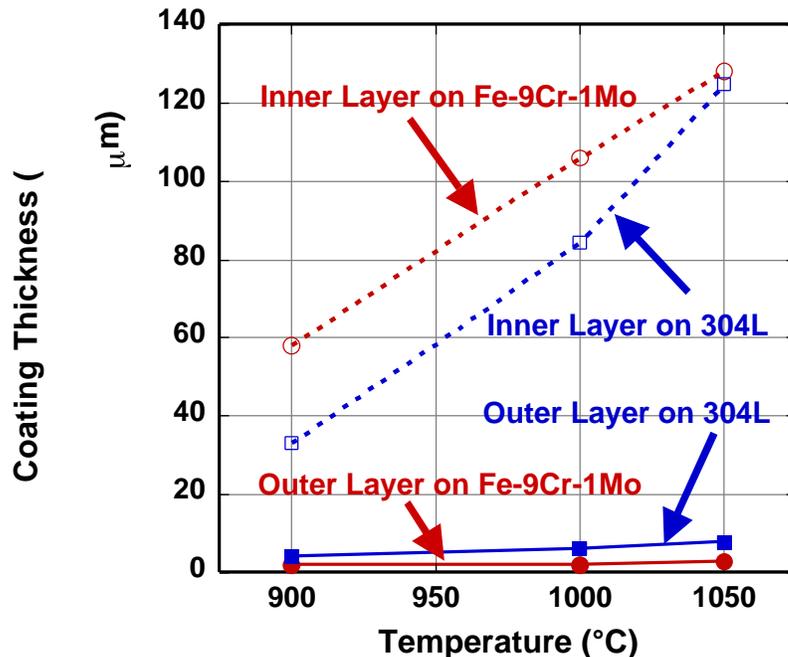

Fig. 2. The correlation of thickness of iron aluminide coating outer and inner layers with the CVD aluminizing temperature.

The second processing approach was focused on increasing the Al activity of the aluminizing process by adding Al-containing metal (such as Cr-Al) pellets to the CVD reactor.[8, 17] The Cr-Al pellets were included in an Al_2O_3 boat in front of the substrates, as shown in Fig. 1. The CVD aluminization process with Al-containing pellets in the reactor is described as "high-activity" aluminization hereafter. Figure 3 shows the cross-sections of as-deposited Fe-Al coatings on Fe-9Cr-1Mo and 304L in a high-activity CVD process at 1050°C for 6 hours. The thickness of aluminide outer layers increased significantly with increased Al activity, from 3 µm to 24 µm on Fe-9Cr-1Mo, and 4 µm to 25 µm on 304L, Fig. 4. However, the aluminide coating on 304L produced in this high-Al activity process cracked after deposition, as indicated by the arrow in Fig. 3(b). An *in situ* post-coating annealing treatment (by shutting down the HCl gas and holding the specimen in H_2 at the coating temperature) was then added after CVD aluminization to promote some amount of interdiffusion between coating and substrate alloys and hence increase coating adhesion. The aluminide coating on 304L (4h CVD aluminization + 2h *in-situ* annealing) is shown in Fig. 5, and no spallation was observed after post-coating annealing. It seems that the porosity in the coating outer layer increased after annealing treatment, Figs. 3(b) and 5.

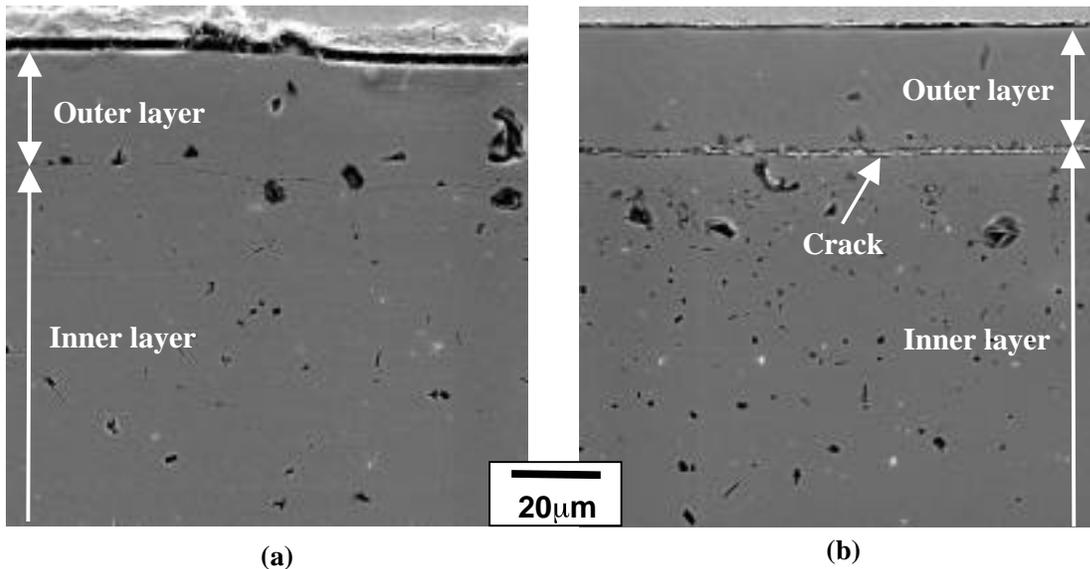(a)   (b)

Fig. 3. SEM secondary electron images of as-deposited aluminide coatings coated in a high-Al activity CVD process: (a) on Fe-9Cr-1Mo and (b) on 304L. Note cracking at the interface of coating outer layer and inner layer in (b).
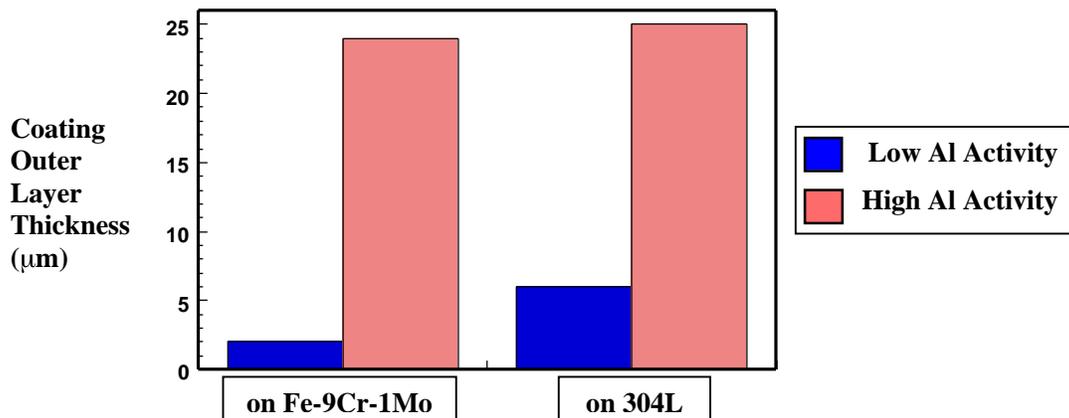

Fig. 4. The correlation of the thickness of Fe-Al coating outer layer and Al activity in CVD aluminization.
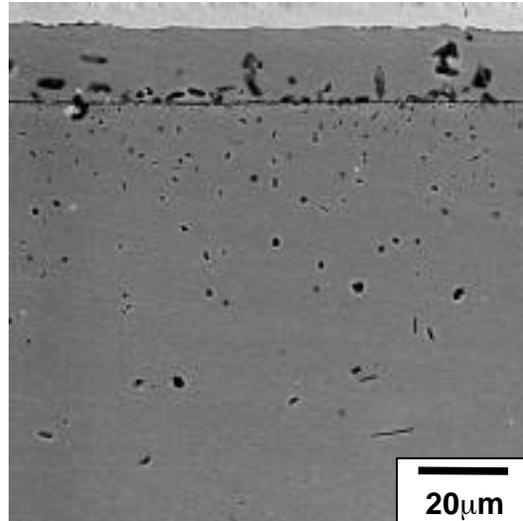
Fig. 5. SEM secondary electron images of the aluminide coating on 304L after post coating annealing.

Other types of Al-containing pellets that do not contain Cr (e.g., Fe-Al metal pellets) also were used in the CVD reactor (for environmental considerations), and the resulting coating is shown in Fig. 6. The iron aluminide coating contained polyhedral shape grains at the surface [Fig. 6(a)], which is a typical surface morphology of aluminide coatings. Using Fe-Al pellets, an outer layer coating of ~12 µm thick was formed on Fe-9Cr-1Mo after 4h aluminization + 2h annealing treatment at 1050°C, Fig. 6(b), which was thinner than the coating fabricated with Cr-Al pellets. Further experimentation will be conducted to confirm this observation.

X-ray diffraction indicated that CVD aluminization led to the formation of FeAl and /or Fe_3Al coatings [18] on Fe-9Cr-1Mo and 304L, as shown in Figs. 7 and 8. Transformation of FeAl to Fe_3Al was observed after the 2h post-coating annealing at 1050°C, Figs. 7(d) and 8(d). However, due to overlapping of XRD peaks (position of 2) for FeAl and Fe_3Al, compositional profiles were needed to help identify coating phase structures.
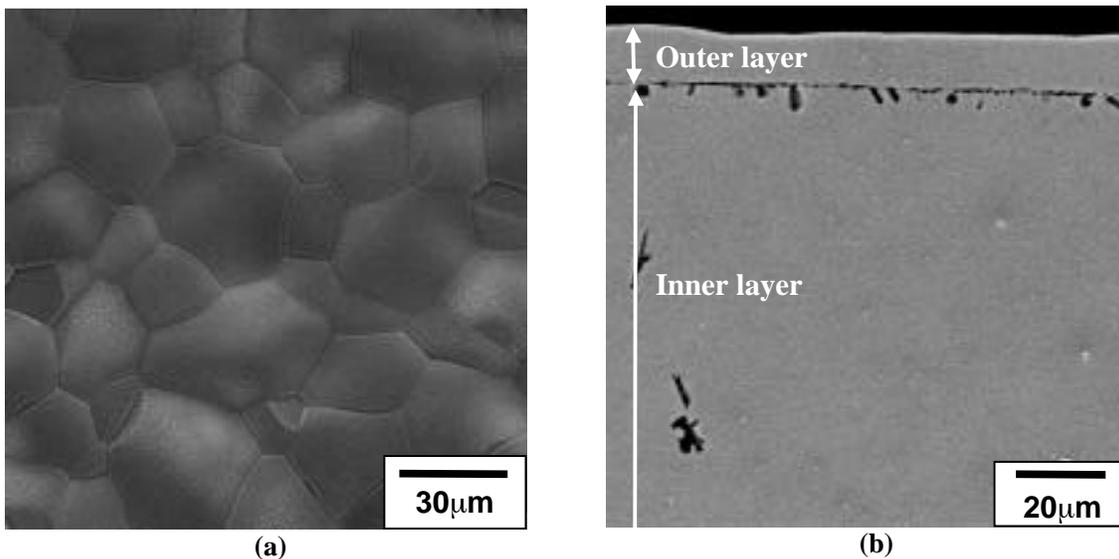

(a)

(b)

Fig. 6. SEM secondary electron images of iron aluminide coating on Fe-9Cr-1Mo using Fe-Al pellets in the CVD reactor: (a) surface morphology and (b) cross section.
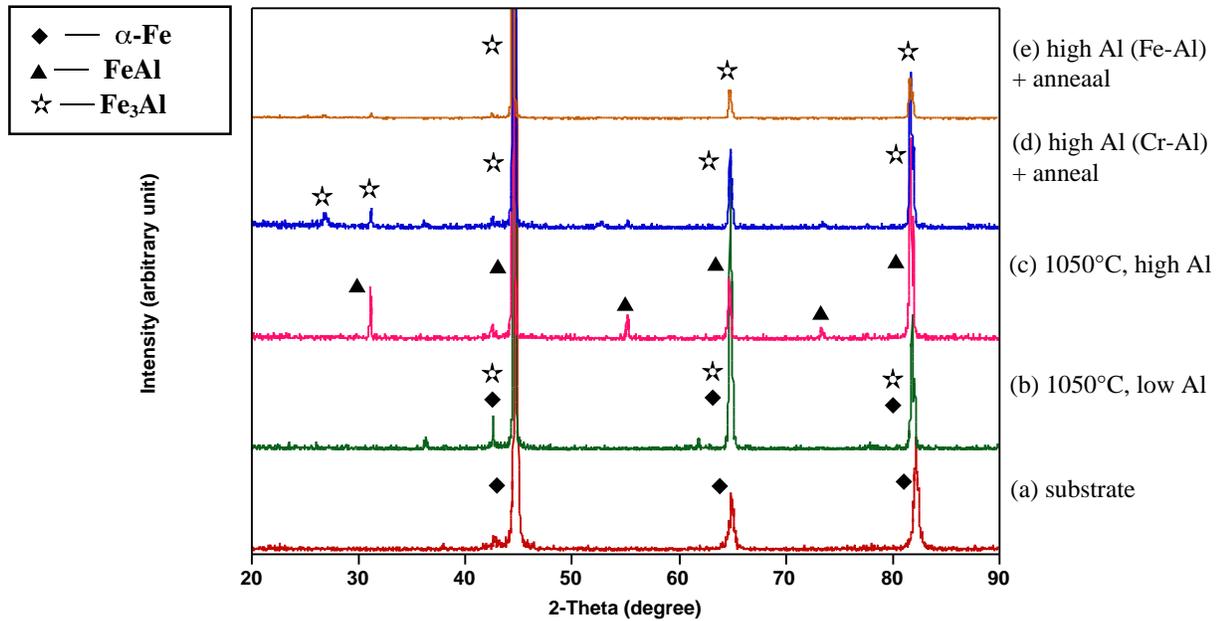
Fig. 7. XRD results of iron aluminide coatings on Fe-9Cr-1Mo: (a) Fe-9Cr-1Mo substrate, (b) 1050°C/6h (low-Al activity), (c) 1050°C/6h (high-Al activity, Cr-Al pellets), (d) 1050°C/4h coating + 2h annealing (high-Al activity, Cr-Al pellets), and (e) 1050°C/4h coating + 2h annealing (high-Al activity, Fe-Al pellets).
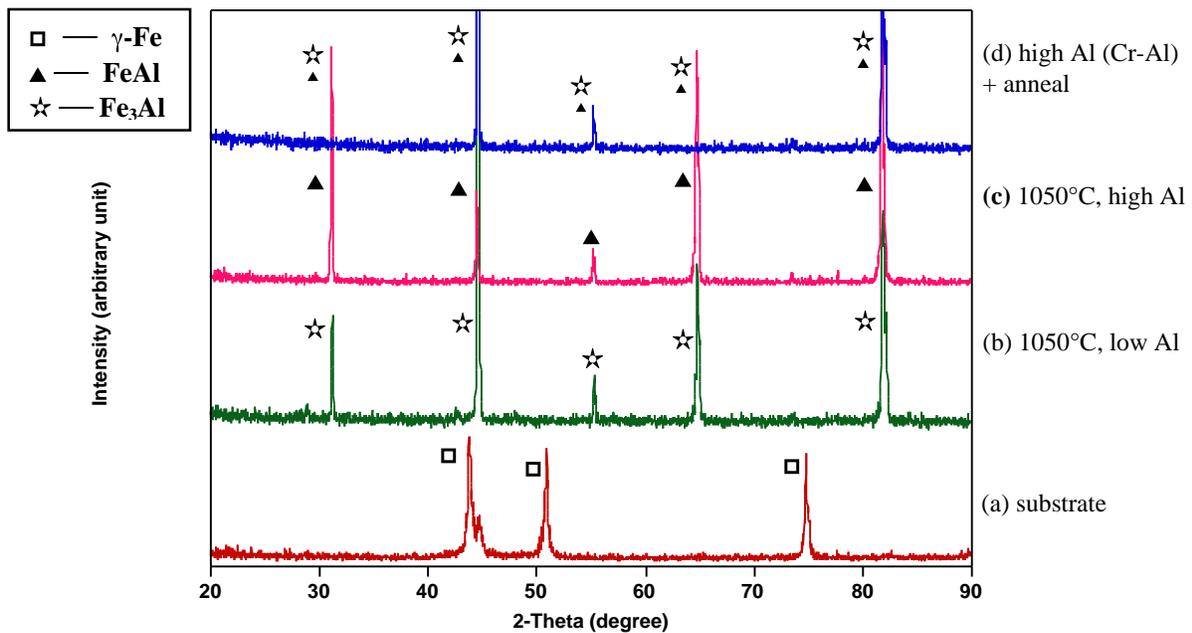

Fig. 8. XRD results of iron aluminide coatings on 304L: (a) Fe-9Cr-1Mo substrate, (b) 1050°C/6h (low-Al activity), (c) 1050°C/6h (high-Al activity, Cr-Al pellets), and (d) 1050°C/4h coating + 2h annealing (high-Al activity, Cr-Al pellets).

Preliminary Work on Pt Plating for Task II

A platinum plating system (Fig. 9) was set up at TTU in order to (1) provide an avenue to carefully control the Pt plating process, and (2) study the effect of Pt content on oxidation behavior of (Ni,Pt)Al coatings. Figure 9(a) shows the whole plating system, which includes a polyvinylidene fluoride (PVDF) plating tank (14" x 10" x 10"), a Teflon immersion heater, an in-tank filter system, and a DC power source supplied by a rectifier with 3 amps and 18 volts DC output. A close-up view of the plating tank in Fig. 9(b) shows the anode and cathode bars. The plastic balls floating on top of the solution are to prevent evaporation of the plating solution during plating. A Cu coupon was plated using Pt20-Q electrolyte [19] ("Q" salt, Johnson Matthey) at 90-95°C with solution pH of 10-10.5 and Pt concentration greater than 10 g/l. The Pt thickness was ~2.5 µm after 15 min plating based on the mass gain. The surface morphology and microstructure of the Pt layer are currently being characterized. The next step is to plate Pt on Ni-base superalloy coupons and further characterize the coating composition and microstructure.
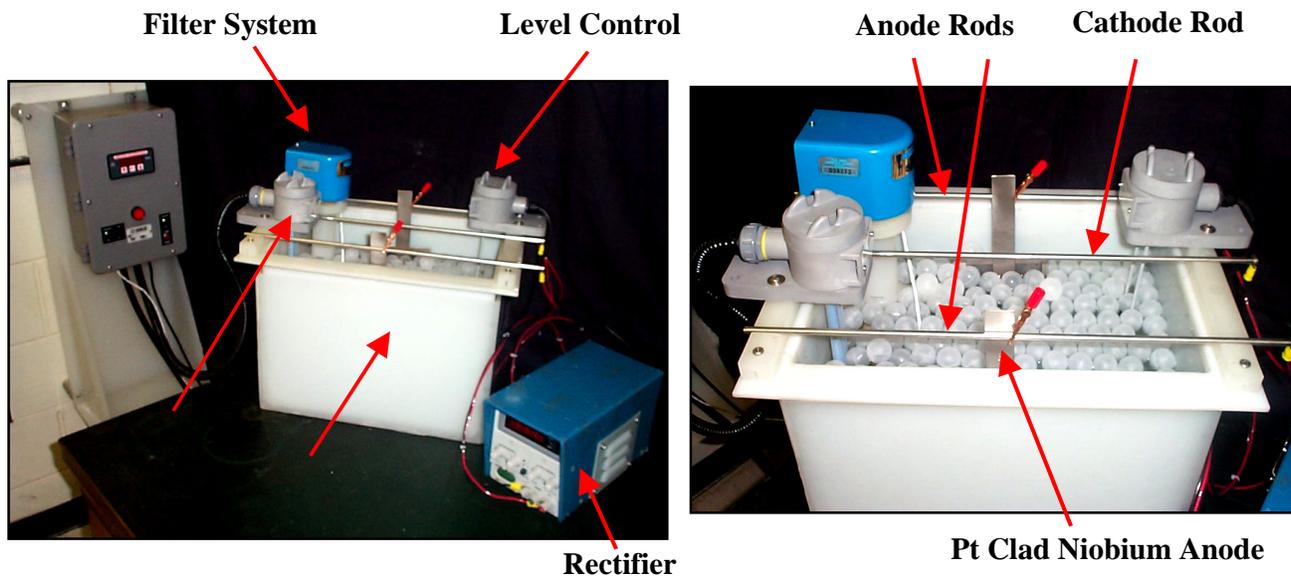

Fig. 9. The platinum plating system: (a) overview and (b) close view of the plating tank.

DISCUSSION

The current research effort has clearly demonstrated the feasibility of fabricating a model Fe-Al coating with suitable thickness and composition using a well-controlled laboratory CVD process. If the aluminide coating growth is predominantly controlled by solid-state diffusion, raising the aluminizing temperature generally increases the coating thickness, as observed for most CVD nickel aluminide coatings.[20] However, as shown in Fig. 2 raising the CVD aluminizing temperature from 900°C to 1050°C only increased the thickness of the inner interdiffusion layer of iron aluminide coatings while the Al-rich outer layer remained nearly unchanged. On the other hand, increasing Al activity in the CVD process successfully increased the outer coating thickness on both ferritic and austenitic alloys. Some CVD aluminizing processes reported in the literature have used molten Al to raise Al activity.[20-21] Al-containing metal pellets (e.g., Cr-Al or Fe-Al pellets [8]) seemed to yield the same effect in the present study while liquid metal handling was avoided. Although coatings with thicker outer layers were obtained with increased Al activity, the aluminide coating on 304L spalled after CVD processing when cooled to

room temperature. The disparity in thermal expansion coefficient between coating and substrate and/or brittleness of the Fe-Al coating might exacerbate with increasing Al content, and thus increase the likelihood of crack formation on cooling. Similar cracks were reported on iron aluminide coatings made by pack cementation which typically contain more Al than CVD aluminide coatings.[22-23] An *in-situ* post-coating annealing was used after CVD aluminizing to improve coating adhesion by allowing some interdiffusion between coating and substrate. The XRD results shown in Figs. 7 and 8 are consistent with this treatment as surface Al concentration is reduced after annealing. However, this *in-situ* annealing treatment is not practical for traditional pack cementation aluminizing processes.

In general there are fewer published studies on diffusion aluminide coatings on ferrous systems than on Ni-base superalloys.[24-27] For nickel aluminide coatings, high or low Al activity is mainly determined by the location of the original substrate surface after aluminization (inward or outward growth).[28] It is not yet clear how the concept of inward and outward aluminide coating types should be applied to Fe-base alloys. As reported for earlier pack aluminide coatings on Fe-base alloys, most processes are essentially inward-growth and aluminide coatings consist of either an Al-enriched ferrite surface layer or external phases of FeAl or $FeAl_2$.[29] In the present study, the CVD aluminizing process with Al-containing pellets in the reactor was simply defined as high-Al activity, which does not necessarily indicate a change in the growth direction as it does for Ni-base alloys.

SUMMARY

The present work has used a CVD process to produce model coatings that are amenable to corrosion and diffusion studies aimed at examination of key issues associated with Fe-Al coatings. By raising the Al activity in the CVD aluminization process, a model iron aluminide coating with suitable coating thickness for high-temperature oxidation and corrosion testing was produced. *In-situ* coating annealing is helpful in improving coating adhesion to substrate alloys. Initial Pt-plating experiments have been conducted for future coating work on Ni-base alloys.

ACKNOWLEDGEMENTS

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