

HIGH TEMPERATURE OXIDATION PERFORMANCE OF ALUMINIDE COATINGS

B. A. Pint, Y. Zhang,[†] J. A. Haynes and I. G. Wright

Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

[†]Department of Mechanical Engineering
Tennessee Technological University
Cookeville, TN 38505-0001

INTRODUCTION

Coatings are required in many high temperature applications to protect high strength or low cost structural alloys that do not have sufficient inherent oxidation resistance. Aluminide (Fe_3Al or FeAl) coatings are of interest for many environments, because of the formation of a highly stable, external alumina scale.¹⁻⁶ For Fe-base alloys, aluminide coatings can be protective in sulfidizing environments.^{2,5,6} Environments containing water vapor (steam, exhaust gas) also are of particular interest because of the accelerated attack observed on Fe-base alloys⁷⁻¹² associated with volatile chromium hydroxide formation. Alumina is more stable in such environments¹³ and alumina-forming coatings provide excellent protection.^{5,14,15} Recent long-term results on representative CVD aluminide coated ferritic (Fe-9Cr-1Mo) and austenitic (type 304L stainless steel) substrates in humid air showed coating failure and substrate attack after 2,000h at 700°C when the specimens were cycled every hour.^{14,15} Very little Al was lost to the substrates, due to interdiffusion after this exposure. The coating failure was attributed to thermal fatigue cracking due to the difference in coefficient of thermal expansion (CTE) between the substrate and coating.⁵ The current work is continuing to examine this type of failure, by examining the performance of (1) thinner coatings under the same conditions, where less strain would be expected in the coating layer, (2) similar coatings in 100h cycles (i.e. fewer thermal cycles), and (3) similar coatings on impurity controlled substrates. In addition to the oxidation experiments, 10,000h diffusion experiments are being conducted to assist in the development of a coating lifetime model.¹⁶ An additional issue for the model is the critical Al content of the coating needed for protection in humid environments. This issue is being addressed by testing model alloys and by accelerated testing of coatings at 800°C.

DISCUSSION OF CURRENT ACTIVITIES

EXPERIMENTAL PROCEDURE

The substrates used in this study were commercial Fe-9Cr-1Mo, commercial type 304L stainless steel (Fe-18Cr-9Ni nominally) and laboratory castings of 304L with controlled impurity contents. The laboratory-scale CVD reactor and coating process for low-activity (thin coatings) and high-activity (thick coatings) have been described elsewhere.^{5,15,17} Coatings made by CVD have been used in this work in order to

have a well-controlled, high purity coating for long-term testing. It is anticipated that similar aluminide coatings could be made by a higher-volume, commercial process, such as pack cementation. Characterization of the as-deposited coatings has been described elsewhere.¹⁶⁻¹⁹

The oxidation testing focuses on 700°C, where the substrate alloys are adversely affected by environmental effects, but some strength is retained. Some tests were conducted at 800°C in order to accelerate interdiffusion with the substrate. Cyclic oxidation testing in air with 10±0.5vol.%H₂O was conducted two ways: (1) in a vertical, automated test rig with the specimens suspended from alumina rods using Pt-Rh wire and a cycle consisting of 1h at temperature and 10min cooling at room temperature, or (2) in a horizontal tube furnace with the specimens in an alumina boat, the cycle consisting of 100h at temperature with the specimens cooled and weighed after each cycle. In each case, both ends of the high-purity alumina reaction tube were closed and the addition of water vapor was controlled in the carrier gas by a water injection system described elsewhere.¹¹ Humid air produces similar reaction products as steam environments.^{9,12}

Before and after exposures, specimens were weighed on a Toledo-Mettler model AG245 balance. Selected specimens were examined by light microscopy, field emission gun, scanning electron microscopy (SEM) equipped with energy dispersive x-ray analysis (EDXA) and electron probe microanalysis (EPMA) using wavelength dispersive x-ray analysis. For cross-sections, the surface reaction product was protected by Cu-plating the specimen prior to mounting in epoxy.

RESULTS AND DISCUSSION

Effect of Coating Thickness on Performance in 1h Cycles at 700°C

Previous experimental results suggested a role of the coating-substrate thermal expansion mismatch. Additional experiments are being conducted to explore the role of CTE mismatch on coating performance. If the CTE difference leads to coating failure, then coating thickness could play a role. The stress on cooling is proportional to the CTE difference and is independent of coating thickness. However, the strain generated on cooling should increase with coating thickness. Previous work on thin CVD aluminide coatings, with a 5µm Al-rich outer layer, did not show significant degradation after 1,000, 1h cycles at 700°C in air + 10vol.%H₂O.¹⁹ Without a coating, 304L and Fe-9Cr-1Mo were severely attacked after short exposures in this environment, Figure 1. After 1,000 cycles, the coated specimens were sectioned for metallographic analysis.¹⁸ However, thicker coatings (40µm Al-rich outer layer) made by a high activity CVD process did not show complete penetration until after 2,000 1h cycles. In order to clarify the role of coating thickness, a new set of thin CVD coatings was made and testing is in progress, Figure 1. In general, there is good agreement for the mass gain of these new thin coated samples with the previous results for thin coatings. For the coating on 304L, the mass gain for the thin and thick coatings were similar after 1,600h. However, for the coating on Fe-9Cr-1Mo, the mass gain was lower for the thin coatings. This suggests that coating thickness may be more of a factor on coatings on ferritic substrates than on 304L. The new specimens with thin coatings will be characterized after completing 2,000 1h cycles to compare their performance to the thick coatings.

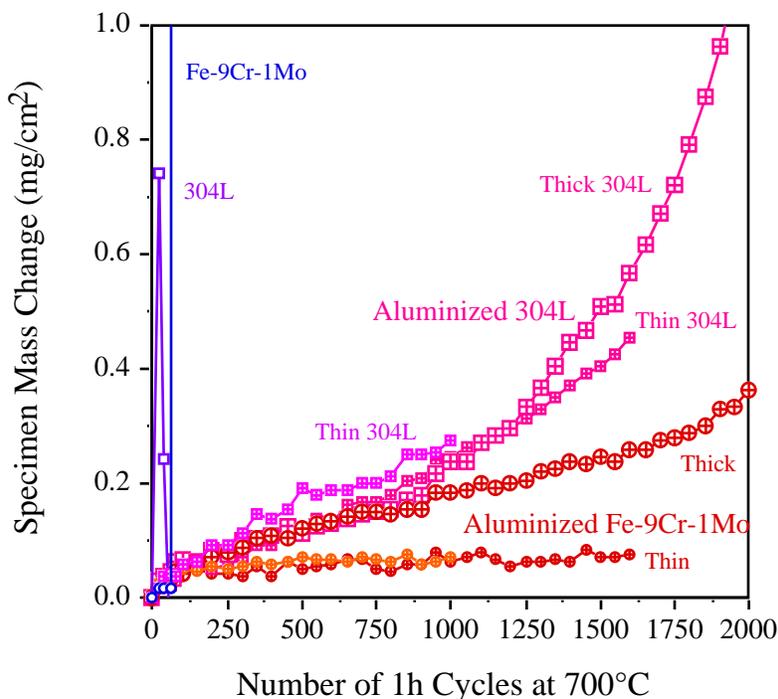


Figure 1. Specimen mass changes during 1h cycles at 700°C in air+10% H_2O . Results are shown for specimens coated with both the high (larger symbol) and low (smaller symbol) Al activity processes to yield thick and thin aluminide coatings, respectively.

Effect of Cycle Frequency on Coating Performance at 700°C

A second method for testing the role of CTE is to change the cycle frequency of the test. In the case of the CTE difference between an alumina-forming alloy and the alumina scale, decreasing the cycle frequency generally results in less scale spallation.²⁰ Previously, results from exposures using 100h cycles at 700°C in air + 10vol.% H_2O have been reported to 2,000h.¹⁴ Figure 2 shows the continuation of this test past 6,000h with relatively low mass gains for both coated substrates and no indication of coating failure as was observed in 1h cycles. Also shown in Figure 2 are the results for uncoated 304L and Fe-9Cr-1Mo substrates in 100h cycles. After less than 1000h, both substrates experienced accelerated attack, similar to that observed in 1h cycles. Figures 3a and 3b show the type of macroscopic degradation observed on the edges of coated specimens after 2,000, 1h cycles.^{14,15} In contrast, only minor cracking was observed on coated 304L after 60, 100h cycles (arrows in Figure 3c). Figure 3d shows virtually no cracking in the coating at the edge of the Fe-9Cr-1Mo substrate after 6,000h. While there was much less macroscopic damage observed in the coatings exposed in 100h cycles, some damage is developing with time. Figures 4a and 4b show the coating surfaces after 40, 100h cycles at 700°C. After 60, 100h cycles, there was some increase in the number of cracks observed on the specimen surfaces, Figure 4c and 4d, with more cracks observed on the 304L substrate. Without stopping the test and sectioning the specimens, it is not possible to determine the depth of these cracks. However, based on the low mass gains (Figure 2) these cracks are unlikely to have breached the coating. Thus, by reducing the cycle frequency, coating performance was improved, supporting a detrimental role of substrate-coating CTE mismatch.

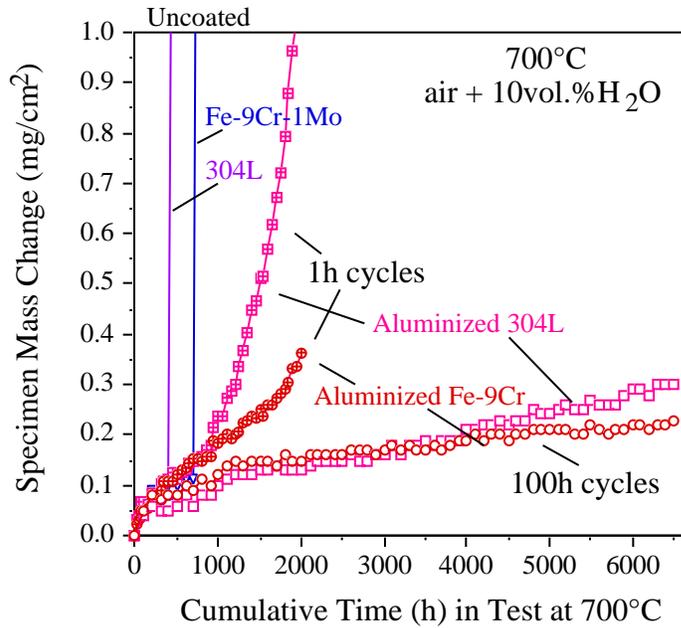


Figure 2. Specimen mass changes during 1h cycles at 700°C in air+10% H_2O . Results are shown for specimens coated with both the high (larger symbol) and low (smaller symbol) Al activity processes.

Effect of Substrate Impurities on Coating Performance

Characterization of the coatings on commercial substrates showed AlN particles in both the as-deposited and exposed coatings.¹⁶ The source of the nitrogen was determined to be the substrate and initially, laboratory castings of 304L and Fe-9Cr-1Mo compositions were made with lower nitrogen contents: 300ppmw in 304L compared to 800ppm in commercial material and 200ppm in Fe-9Cr-1Mo compared to 475-575ppm in commercial heats. However, coatings on these laboratory cast substrates did not have significantly fewer precipitates nor did they perform significantly better than coatings on commercial alloy

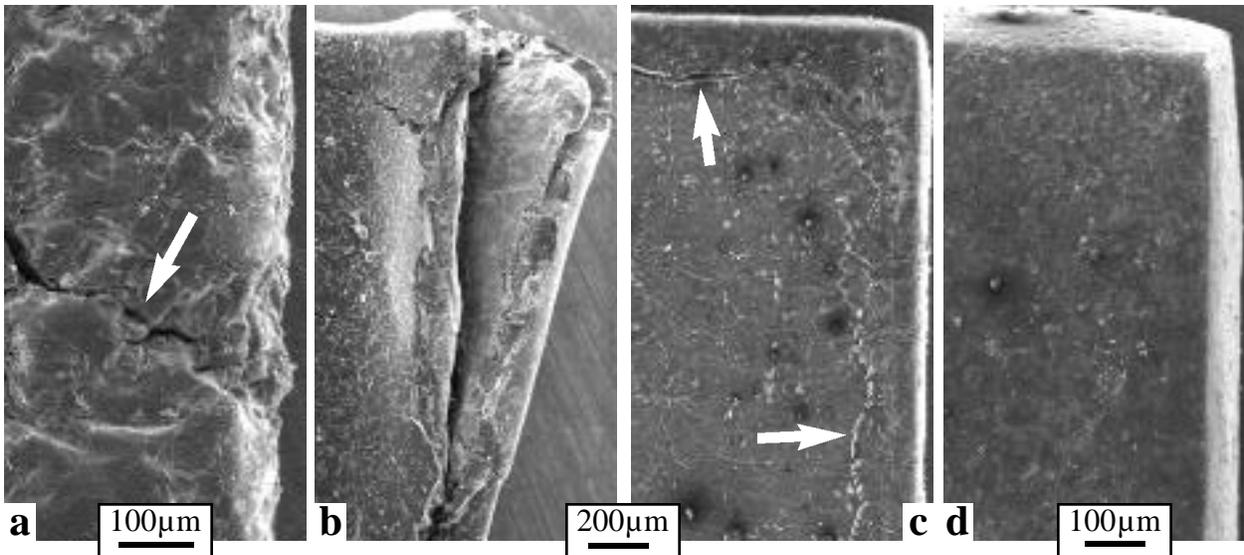


Figure 3. SEM secondary electron plan-view images of coated specimens exposed at 700°C in humid air; (a) Fe-9Cr-1Mo after 2000, 1h cycles, (b) 304L after 2000, 1h cycles, (c) 304L after 60, 100h cycles and (d) Fe-9Cr-1Mo after 60, 100h cycles. Arrows point to cracks in the coating.

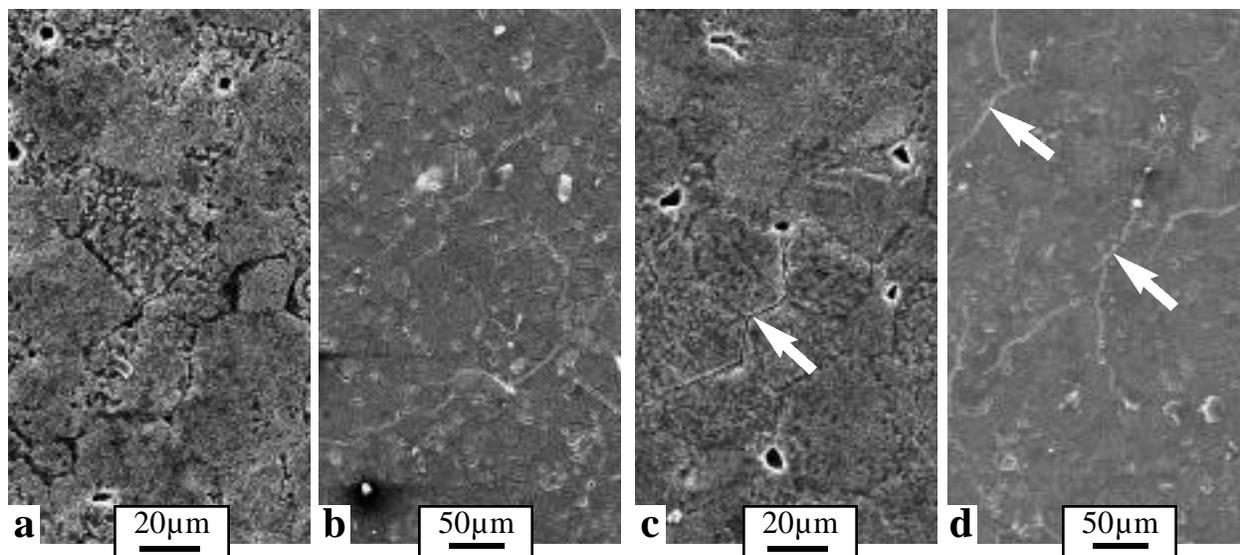


Figure 4. SEM secondary electron plan-view images of coated specimens exposed in 100h cycles at 700°C in humid air; (a) Fe-9Cr-1Mo after 40 cycles, (b) 304L after 40 cycles, (c) Fe-9Cr-1Mo after 60 cycles and (d) 304L after 60 cycles. Arrows point to cracks in the coating.

substrates. A subsequent group of alloys was made with very low N contents. High activity CVD coatings on laboratory-cast, low N 304L, exhibited no nitride precipitates in the coating and fewer voids.¹⁶ Testing has begun to determine if the precipitate-free coatings on this substrate have superior performance to those on commercial 304L substrates. Figure 5 shows the current results of that test in humid air using 1h cycles at 700°C. After 600 cycles, the coating on laboratory 304L shows a similar mass gain to the coatings on commercial 304L substrates. This test will be continued to determine if low substrate nitrogen levels affect coating performance.

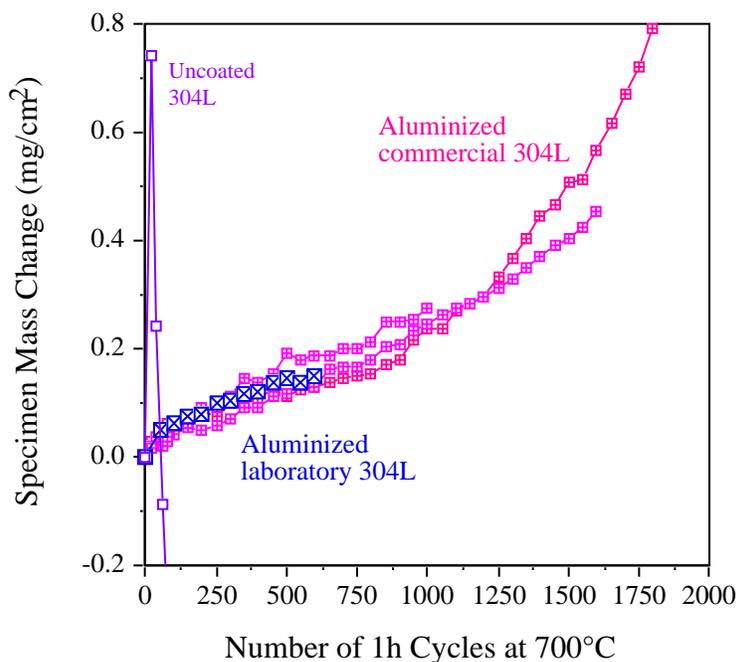


Figure 5. Specimen mass changes during 1h cycles at 700°C in air+10% H_2O for coatings on commercial 304L and laboratory-cast, low N 304L.

DETERMINATION OF THE CRITICAL Al CONTENT FOR COATING FAILURE

A further issue that needs to be resolved for the development of a coating lifetime model is the critical Al content at failure, i.e., the amount of Al remaining at the coating surface when the coating is no longer protective. Initially, this issue was studied using model binary Fe-Al alloys.^{5,19,21} However, it was suspected that Cr in the coating also would have a significant effect on the critical Al content and thus model Fe-Al-Cr alloys were fabricated. Figure 6 shows a summary of these results. Binary Fe-Al alloys require 20at.%Al in order to prevent FeOx formation during 100, 1h cycles at 700°C in humid air.^{19,21} However, when Cr was added, protective behavior was observed for Fe-13Al-10Cr and Fe-20Cr-10Al (FeCrAl). The protective alloys were tested to 1,000 1h cycles and continued to form a thin, protective alumina scale. Initial work showed that Hf added to these model alloys played a significant role. The mass gain for Fe-15Al was much higher for the Hf-free alloy. However, there was less difference for Fe-17Al with and without Hf and protective behavior was observed for FeCrAl with and without Hf. To continue this work, additional Fe-Al-Cr model alloys could be fabricated with lower Al contents to determine a critical Al level when 10%Cr was present. However, prior work on low alloyed Fe-Al-Cr alloys showed a significant role of alloy grain size in this temperature range, with fine grained alloys forming protective scales where coarse-grained alloys did not.²² Given the large difference in grain size between coatings (50µm) and cast alloys (1-2mm), the results from cast alloys may not be representative of coating performance.

A second set of experiments is being conducted to provide more information about the critical Al content for these coatings. By accelerating the test temperature to 800°C, the loss of Al to the substrate by interdiffusion should be significantly increased, thereby reducing the time to failure. A CVD-coated (high activity) specimen of commercial Fe-9Cr-1Mo has been tested for over 2,000h in humid air at 800°C in 100h cycles, Figure 7a. As at 700°C, an uncoated Fe-9Cr-1Mo specimen begins accelerated attack in less than 500h in these conditions while the coated specimen continues to show a low mass gain. A prior diffusion anneal showed that the surface Al content of the aluminide coating decreased to 12%Al after a 2,000h isothermal exposure at 800°C. Exposure of the coated specimen will continue until the coating is

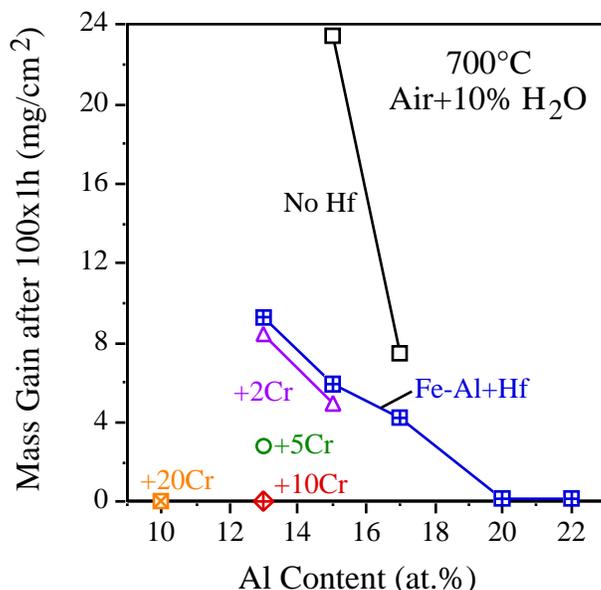


Figure 6. Summary of mass gains for cast Fe-Al-Cr alloys after exposure for 100, 1h cycles at 700°C in air + 10 vol.%H₂O.

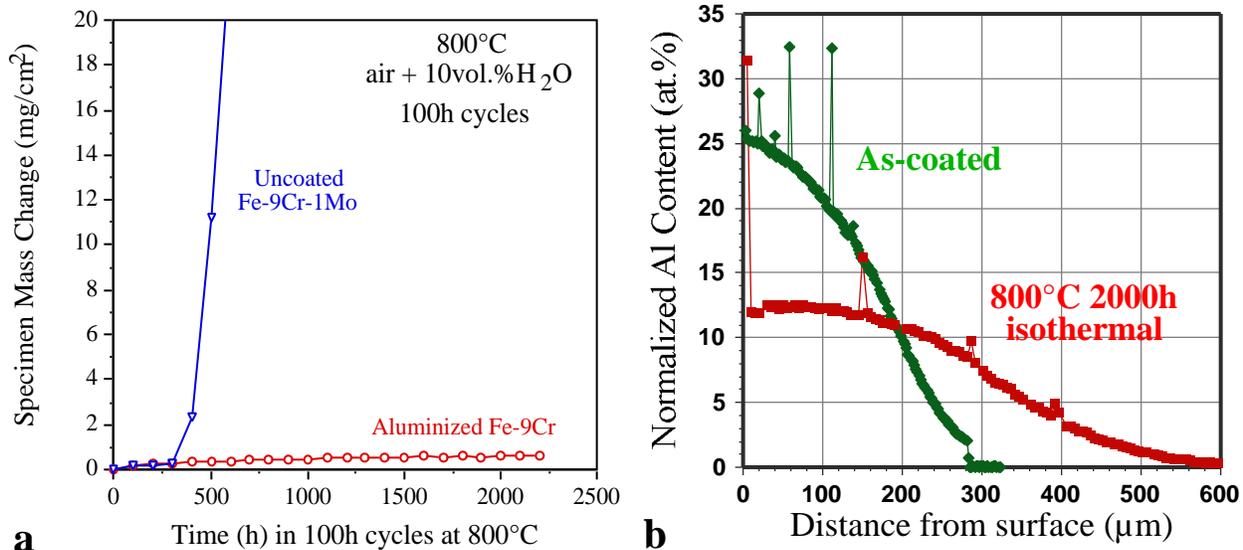


Figure 7. (a) Specimen mass changes during 100h cycles at 800°C in humid air for coated and uncoated commercial Fe-9Cr-1Mo. (b) EPMAAl profiles before and after a 2000h, 800°C isothermal anneal.

breached. At that point, the remaining Al content will be measured. Results from these tests may provide a more accurate value of the critical Al content. A coated 304L specimen also will be tested in these conditions.

SUMMARY

Long-term testing of CVD aluminide coatings on one ferritic (Fe-9Cr-1Mo) and one austenitic (304L) Fe-base substrate is being conducted in air+10% H₂O, where these substrates are readily attacked when not coated. The role of the coating-substrate thermal expansion mismatch is being studied by changing the coating thickness and the test cycle frequency. Increasing the cycle time from 1h to 100h, significantly increased the coating lifetime and reduced cracking in the coating at 700°C. The role of substrate impurities also is being evaluated. Reducing the N content in 304L produced a coating with fewer voids and AlN precipitates. The performance of the reduced defect coating is being evaluated. To complete a coating lifetime model, testing is under way to determine the critical Al content in these coatings. Initial work focused on results from model alloys. However, accelerated testing of the coatings at 800°C in 100h cycles may provide more accurate values, because of differences in the grain size between coatings and castings.

An unresolved issue is the more severe thermal cycling damage on 304L substrates compared to Fe-9Cr-1Mo. Several hypotheses have been suggested but none have been confirmed. One explanation is that 304L retains more strength at the 700°C test temperature than the ferritic alloy: a weaker substrate may allow more stress relaxation in the coating at temperature. A second explanation is that the diffusion of Al into the 304L substrate should cause the inner coating layer to become ferritic. This would result in three zones with different CTE's in the coating-substrate system resulting in the generation of more strain during each cycle. In the case of the coating on Fe-9Cr-1Mo, both the substrate and the inner coating layer would remain ferritic. Only the thinner, outer aluminide layer would have a CTE mismatch in this system.

ACKNOWLEDGMENTS

The authors would like to thank K. Cooley, L. D. Chitwood, G. Garner, K. S. Reeves and H. Longmire at ORNL for assistance with the experimental work and M. P. Brady and P. F. Tortorelli at ORNL for manuscript comments. This research was sponsored by the U.S. Department of Energy, Fossil Energy Advanced Materials Research Program under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

REFERENCES

1. P. F. Tortorelli and K. Natesan, *Mater. Sci. Eng.*, A258 (1998) 115.
2. P. F. Tortorelli, I. G. Wright, G. M. Goodwin, and M. Howell, in: *Elevated Temperature Coatings: Science and Technology II*, Eds. N. B. Dahotre and J. M. Hampikian; TMS, Warrendale, PA, 1996, p.175.
3. F. D. Geib and R. A. Rapp, *Oxid. Met.*, 40 (1993) 213.
4. M. Zheng and R. A. Rapp, *Oxid. Met.*, 49 (1998) 19.
5. B. A. Pint, Y. Zhang, P. F. Tortorelli, J. A. Haynes and I. G. Wright, *Mater. High Temp.*, 18 (2001) 185.
6. P. F. Tortorelli, G. M. Goodwin, M. Howell and J. H. DeVan in: *Heat Resistant Materials II*, Eds. K. Natesan, P. Ganesan and G. Lai; ASM International, Materials Park, OH, 1995, p.585.
7. G. C. Wood, I. G. Wright, T. Hodgkiess, D. P. Whittle, *Werk. Korr.*, 21 (1970) 900.
8. J. Shen, L. Zhou and T. Li, *Oxid. Met.*, 48 (1997) 347.
9. H. Nickel, Y. Wouters, M. Thiele and W. J. Quadackers, *Fresenius J. Anal. Chem.*, 361 (1998) 540.
10. H. Asteman, J.-E. Svensson, L.-G. Johansson and M. Norell, *Oxid. Met.*, 52 (1999) 95.
11. B. A. Pint and J. M. Rakowski, NACE Paper 00-259, Houston, TX, presented at NACE Corrosion 2000, Orlando, FL, March 2000.
12. S. Henry, A. Galerie and L. Antoni, *Mater. Sci. Forum*, 369-372 (2001) 353.
13. E. J. Opila and N S Jacobson in: *Fundamental Aspects of High Temperature Corrosion*, Eds. D A Shores, R A Rapp, and P Y Hou; Proc. Vol.96-26, Electrochemical Society, Pennington, NJ, 1996, p.344.
14. B. A. Pint, Y. Zhang, J. A. Haynes and I. G. Wright in: *Proc. Seventeenth Annual Conf. Fossil Energy Materials*, R. R. Judkins (comp.), U. S. Department of Energy, 2003.
15. Y. Zhang, B. A. Pint, G. W. Garner, K. M. Cooley and J. A. Haynes, *Surf. Coat. Tech.*, in press (2004).
16. Y. Zhang, B. A. Pint, J. A. Haynes, K. M. Cooley and I. G. Wright, in: *Proc. Eighteenth Annual Conf. Fossil Energy Materials*, R. R. Judkins (comp.), U. S. Department of Energy, 2004.
17. Y. Zhang and B. A. Pint in: *Proc. Sixteenth Annual Conf. Fossil Energy Materials*, R. R. Judkins (comp.), U. S. Department of Energy, 2002.
18. Y. Zhang, B. A. Pint, J. A. Haynes, K. M. Cooley and I. G. Wright, in: *Proc. Seventeenth Annual Conf. Fossil Energy Materials*, R. R. Judkins (comp.), U. S. Department of Energy, 2003.
19. B. A. Pint, Y. Zhang, P. F. Tortorelli, J. A. Haynes and I. G. Wright in: *Proc. Sixteenth Annual Conf. Fossil Energy Materials*, R. R. Judkins (comp.), U. S. Department of Energy, 2002.
20. B. A. Pint, P. F. Tortorelli and I. G. Wright, *Oxid. Met.*, 58 (2002) 73.
21. B. A. Pint and I. G. Wright, *Mater. Sci. Forum*, in press (2004).
22. M. J. Maloney and G. J. Yurek, in: *Composites/Corrosion-Coatings of Advanced Materials*, Eds. S. Kimura, A. Kobayashi, S. Umekawa, K. Nii, Y. Saito and M. Yoshimura, Proc. Vol. IMAM-4, Materials Research Society, Pittsburgh, PA, 1989, p.383.