HIGH-TEMPERATURE CORROSION BEHAVIOR OF
IRON ALUMINIDE ALLOYS AND COATINGS

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ABSTRACT

A multi-year effort has been focused on optimizing the long-term oxidation performance of ingot-processed (IP) and oxide-dispersion strengthened (ODS) Fe_3Al and iron aluminide-based coatings. Based on results from several composition iterations, a Hf-doped alloy (Fe-28Al-2Cr-0.05at.%Hf) has been developed with significantly better high temperature oxidation resistance than other iron aluminides. The scale adhesion is not significantly better; however, the α-Al_2O_3 scale grows at a slower rate, approximately a factor of 10 less than undoped iron aluminide. The benefit of Hf is greatest at 1100°-1200°C. Long-term oxidation resistance of commercially fabricated ODS Fe_3Al has been determined and compared to commercially available ODS FeCrAl. Scale spallation rates for ODS Fe_3Al are higher than for ODS FeCrAl. To complement studies of iron-aluminide weld-overlay coatings, carbon steel was coated with Fe-Al-Cr by thermal spraying. These specimens were then exposed in air at 900 and 1000°C and in air-1%SO_2 at 800°C. Most likely due to an inadequate aluminum concentration in the coatings, continuous protective Al_2O_3 could not be maintained and, consequently, the corrosion performance was significantly worse than what is normally observed for Fe_3Al.

INTRODUCTION

The good high temperature oxidation and sulfidation resistance of iron aluminides has been widely recognized and carefully studied over the past decade, e.g. Refs.1-3. However, in recent years it has been found that, relative to other alumina-forming alloys, the external alumina scale spalls more readily on iron aluminides,[4-5] even with additions of Zr,Y or Y_2O_3 which are known to improve scale adhesion.[6-7] Several attempts have been made to understand the nature of this accelerated spallation and improve the performance of iron aluminides by micro-alloying additions. Recent results are presented below.

As described previously,[2,3] the oxidation and sulfidation resistance of iron aluminides based on Fe_3Al extends to temperatures well above the point at which ingot-processed (IP) alloys have adequate mechanical strength. Consequently, oxide-dispersion-strengthened (ODS) iron aluminides are being developed to improve the strength of this alloy system while maintaining or improving corrosion resistance.[4,8,9] Data for a

commercially fabricated ODS Fe$_3$Al are presented below. Furthermore, iron aluminides could be used as coatings or claddings on higher-strength, less corrosion-resistant materials. Previous studies have focused on weld-overlay coatings.[2,10-12] This paper reports initial results for coatings produced by thermal spraying.

RESULTS & DISCUSSION

Ingot-Processed Alloys

Previous work indicated that reactive element (RE) alloy additions (Zr,Y,Hf) to a base Fe-28Al-2Cr (FAS) alloy all had a similar beneficial effect on the oxidation behavior when added at the level of approximately 0.1at.% (Ref. 5). (All compositions are listed in atomic percent and were determined by inductively coupled plasma analysis of as-cast material.) However, based on the superior performance of a 0.05% Hf addition to NiAl (Ref. 13). and the significant internal oxidation observed for FAS+0.1%Hf (Fig. 1), a lower Hf content was investigated.

The oxidation performance of FAS+0.05Hf was found to be superior to any previously studied ingot- or powder-processed iron aluminide. The lower Hf content eliminated the excessive internal oxidation observed for the higher (0.1%) Hf content (Fig. 1), which resulted in excessive weight gains at 1000 °C (Fig. 2). Due to the relatively low oxidation temperature, the benefit of 0.05%Hf was not observed relative to the more-common IP iron aluminide composition, FAL (Fe-28Al-5Cr-0.1Zr). The difference is more distinct at 1100 °C, where FAS+0.05Hf showed a lower total weight gain compared to both FAS+0.1Hf and FAL (Fig. 3). The specimen weight gain curves (dashed lines) also are plotted in Fig. 3 which indicate that the 0.05Hf addition did not eliminate scale spallation but rather reduced the scale growth rate. All of the alloys spall at 1100 °C except for FeCrAlY where the specimen and total weight gains are equal. Thus the total weight gain of FAS+0.05Hf will eventually exceed that of FeCrAlY due to scale spallation.

Similar results were observed for cyclic testing at 1200 °C, however, the optimized effect of Hf is more clearly illustrated in isothermal tests at 1200 °C (Fig. 4). Compared to undoped FAS, 0.1% additions of Hf or Zr reduce the isothermal growth rate. Multiple tests
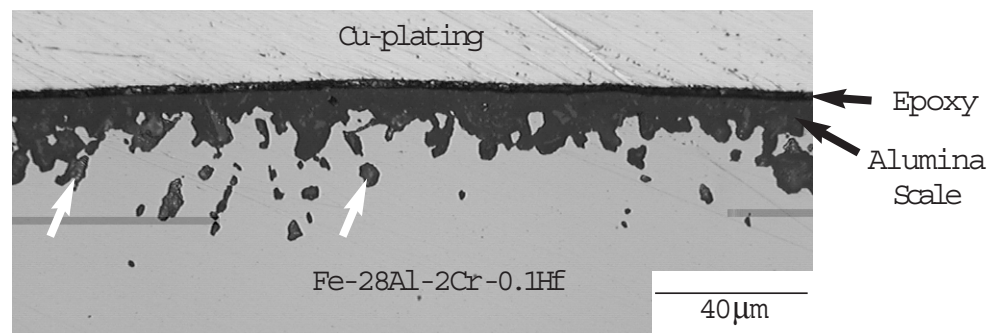

Figure 1. Copper-plated metallographic cross-section of the scale formed on FAS+0.1%Hf after 5000h at 1000 °C in laboratory air. Little spallation was observed but deep oxide penetrations (pegs) consisting of alumina-encapsulated Hf-rich oxide (arrows) were observed.
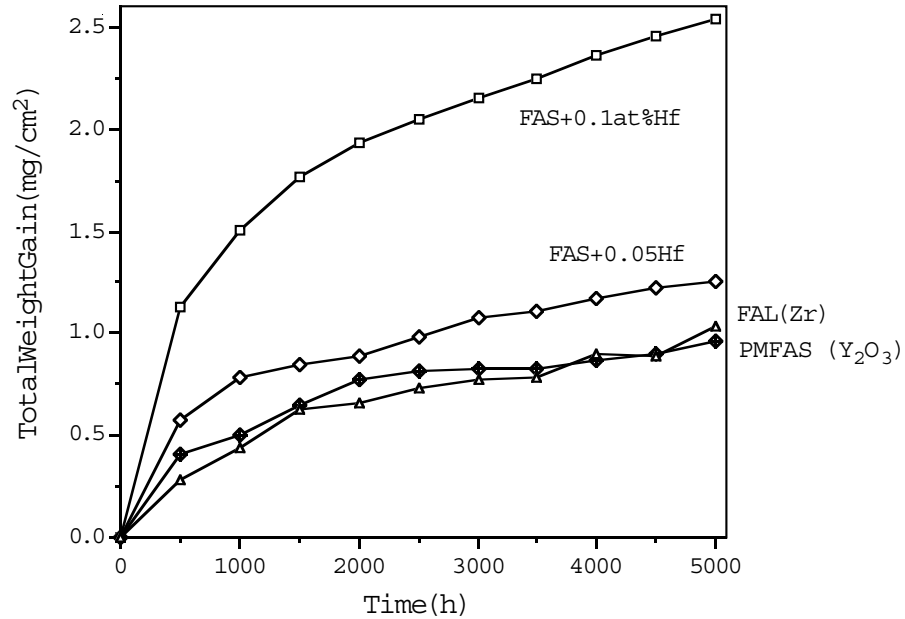
Figure 2. Total weight gain (specimen + spalled oxide) for several iron aluminides during 500h cycles at 1000 °C in laboratory air. A 0.1%Hf addition resulted in high weight gains, not due to spallation, but due to excessive internal oxidation. This problem was eliminated by reducing the Hf content to 0.05%. Specimens were contained in pre-annealed alumina crucibles.

were performed to check repeatability of this result. With the addition of 0.05%Hf, the growth rate is reduced by an order of magnitude to 1.3-1.5 x 10^{-12} g^2/cm^{4}s. (Reducing the Zr content to 0.03% did not produce a similar effect.) Thus, the principal benefit of
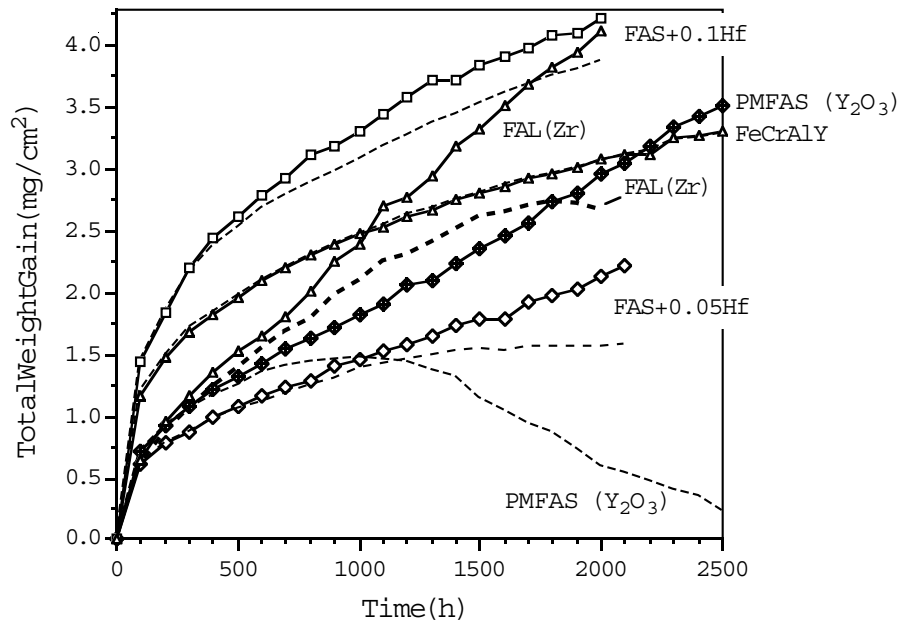

Figure 3. Total weight gain (specimen + spalled oxide) for several iron aluminides during 100h cycles in alumina crucibles at 1100 °C in laboratory air. FAS+0.05Hf shows a lower total weight gain than other IP Fe$_3$Al compositions. The dashed lines indicate specimen weight change. All of the compositions spalled except for FeCrAlY.

optimizing the Hf con[...]
preventing scale spalla[...]
spallation, the scale a[...]

Figure 5.   Total weight gain (specimen + spalled oxide) for several iron aluminides during 100h
cycles in alumina crucibles at 1200 °C in laboratory air   FAS+0.05Hf shows a lower initial total

Cu-plating

Epoxy

Fe-28Al-2Cr-0.1Hf

40μm

Alumina Scale

Cu-plating
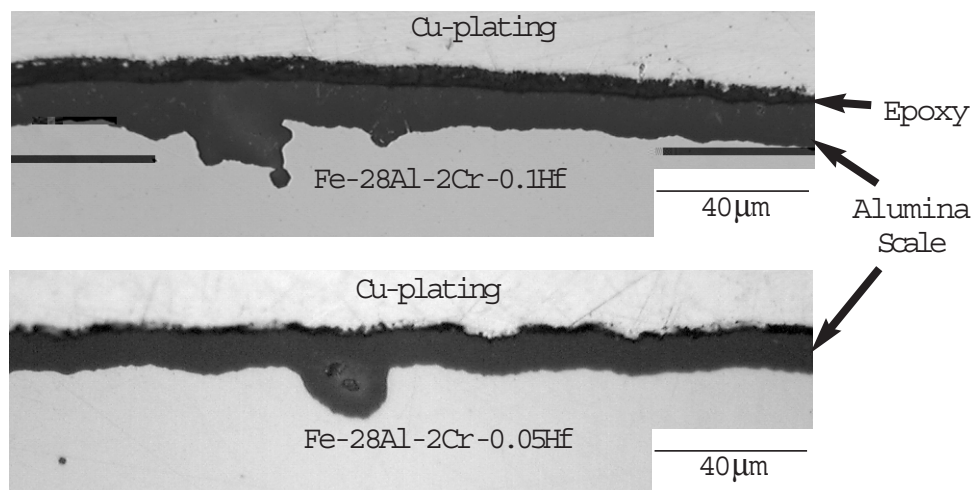
Fe-28Al-2Cr-0.05Hf

40μm

Figure 6.   Copper-plated metallographic cross-sections of the scale formed after 100h at 1300 °C on (a) FAS+0.1%Hf and (b) FAS+0.05%Hf. Under these conditions, changing the Hf content of the alloy had little effect.

for this alloy. This is also apparent in 100h cycles at 1200 °C (Fig. 5) where FAS+0.05Hf has a lower weight gain initially but, due to its linear increase, it soon exceeds the weight gains of more adherent (but faster-growing) FeCrAlY and ODS FeCrAl substrates.   At 1300 °C, the detrimental effect of 0.1%Hf in FAS was not observed, thus lowering the Hf content did not result in any improvement.   The scales on the 0.05 and 0.1Hf FAS alloys after 100h at 1300 °C were very similar (Fig. 6). As in the case of Hf-doped NiAl, it is not clear why Hf in FAS is more effective than Zr in reducing the alumina scale growth rate. Higher rates with Y are attributed to the formation of Y-rich precipitates which internally oxidize, thereby increasing the total weight gain.   However, Y additions are much more effective than Hf in improving scale adhesion in NiCrAl or FeCrAl.[14] One possibility is that, when segregated to α-Al$_2$O$_3$ grain boundaries,[7] Hf has a higher effective ionic radii than other dopants and thus is able to inhibit the rate-limiting diffusion along these pathways.

A sample of FAS+0.05Hf was included in a hot corrosion test using 1h cycles in flowing O$_2$ at 950 °C. Specimens were coated with 1.0mg/cm^2 Na$_2$SO$_4$ prior to testing and recoated every 100h.   While catastrophic oxidation was not observed (unlike NiAl+Hf), the weight gains were substantially higher than observed for NiCoCrAlY (Fig. 7) and much higher than those observed in air at 1000 °C (Fig. 2). However, similar weight changes to FeCrAlY with 20%Cr (rather than 2% in FAS) were observed.   This is different than with Ni-base alloys, where increasing the Cr content improved resistance to hot corrosion.[15]

Oxide-Dispersed Fe$_3$Al Alloys

Long-term testing has been nearly completed on commercially-produced ODS Fe$_3$Al (PMFAS). At 1000 °C, the scale growth rate is very similar to that observed for FAL and other alumina-forming alloys (Fig. 2). In a similar manner to lab-produced ODS FAS, spallation problems began at 1100 °C and continued at higher temperatures. A comparison of PMFAS performance at 1100 °C to several commercial ODS FeCrAl alloys [Y$_2$O$_3$-
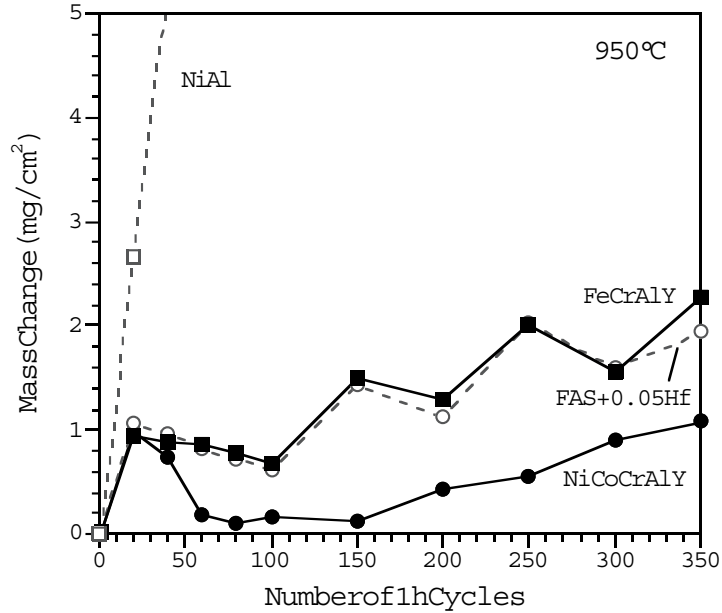
Figure 7. Specimen mass change for several alumina-forming alloys during hot corrosion testing in 1h cycles at 950 °C. Specimens were coated with 1.0mg/cm^2 Na$_2$SO$_4$ prior to testing and recoated every 100h. After 350h, weight gains were higher than those observed after 5000h at 1000 °C in air, indicating significant accelerated attack due to the salt.

dispersed FeCrAl made by Inco (MA956), Dour Metal (ODM751) and Plansee (PM2000) and ZrO$_2$-dispersed FeCrAl, Kanthal APM] is shown in Fig. 8. The higher total weight gain for PMFAS is a direct result of the scale spallation noted by the specimen weight loss
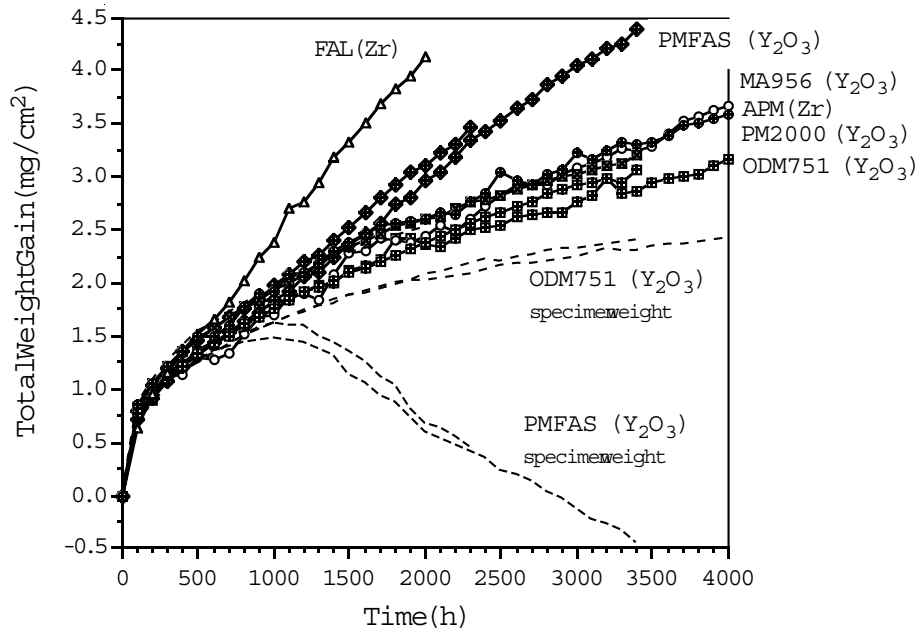

Figure 8. Total weight gain (specimen + spalled oxide) for several ODS alloys during 100h cycles in alumina crucibles at 1100 °C in laboratory air. The dashed lines indicate specimen weight change. PMFAS shows higher total weight gains because of excessive scale spallation compared to the ODS FeCrAl alloys. ODM751 (FeCrAl+Y$_2$O$_3$) only has scale spallation at the specimen edges.

(dashed lines). ODS FeCrAl alloys also show some spallation (as illustrated for ODM751) but this loss is relatively minor and involves mostly spallation at specimen edges. These tests will continue to 10,000h. Testing with 100h cycles at 1200°C has been completed to 5000h for a number of different materials with very similar performance observations (Fig. 5). These higher temperature data give confidence to long-life predictions at lower temperatures. Very similar behavior is observed for very long times.

Tests at 1200°C also included 1h cycles (Fig. 9). PMFAS (1.5mm thick) has completed 2250, 1h cycles. At this point, its weight change is similar to that for ODS FeCrAl (PM2000) and FeCrAl. However, without total weight gain data, it is difficult to predict the relative lifetimes of these materials. A 1mm thick undoped FAS specimen had a lifetime of 1800, 1h cycles. The effect of cycle time has been investigated at 1200°C (Fig. 10). The time to first spallation decreases with increasing cycle frequency.[16] More difficult to explain is the observation that the weight loss does not continue linearly, as for Ni-base alumina-formers,[17] and can actually show weight increases for both 1h and 100h cycles. Weight gains are associated with macroscopic specimen deformation and thick, convoluted, non-protective oxides on the surface.[16]

Several attempts have been made to improve the oxidation performance of ODS FAS including varying the type and amount of oxide dispersion. PMFAS contains an optimized amount of Y_2O_3 (0.2%Y), as determined for lab-processed ODS FAS.[4] One further approach was to de-sulfurize PMFAS, which has been shown to improve the oxidation performance of Ni-base superalloys[18] and FeCrAl.[19] The de-sulfurization was performed at NASA, Cleveland, OH and the specimens were tested in 100h cycles at 1100°C (Fig. 11) and 1h cycles at 1200°C (Fig. 12). In both cases, the de-sulfurized PMFAS performed slightly better than the nominal material, but no dramatic improvement in
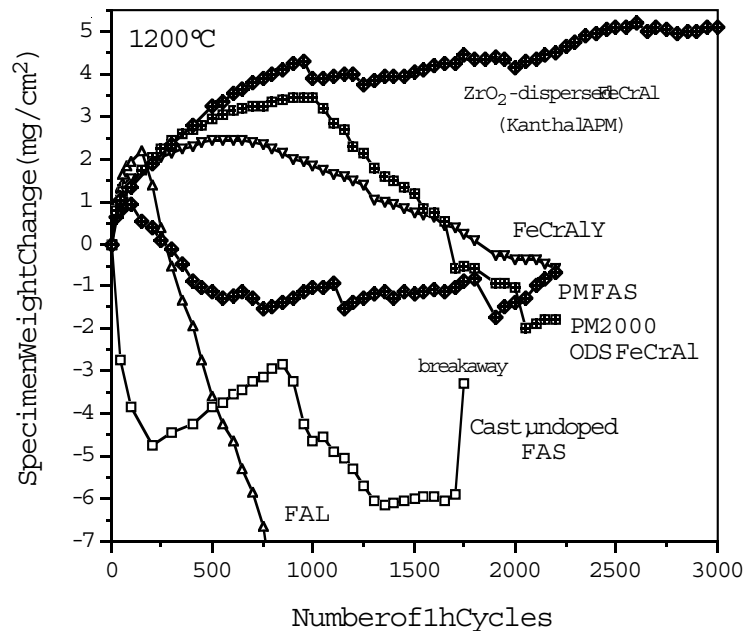

Figure 9. Specimen weight change for several alumina-forming alloys during 1h cycles at 1200°C in dry flowing O_2. PMFAS began spalling relatively quickly but did not continue to lose weight like FAL. With only specimen weight change, it is difficult to predict lifetime in this test.
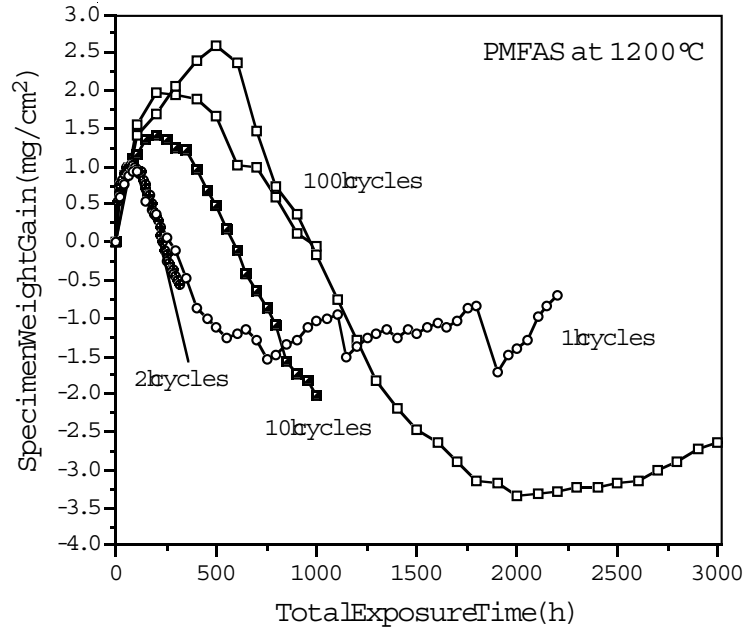
Figure 10. Specimen weight change for PMFAS with different cycle times at 1200 °C plotted versus time at temperature. Shorter cycles decreased the time to initial spallation (downturn in the mass). At longer times, the rate of weight loss decreased and begins to increase slightly for both 1h and 100h cycles.

performance was observed, in contrast to what is found for Ni-base superalloys. It is likely that the Y_2O_3 addition is sufficient to inhibit any detrimental role of indigenous S in PMFAS. Further reducing the S content in the alloy provides no additional benefit.
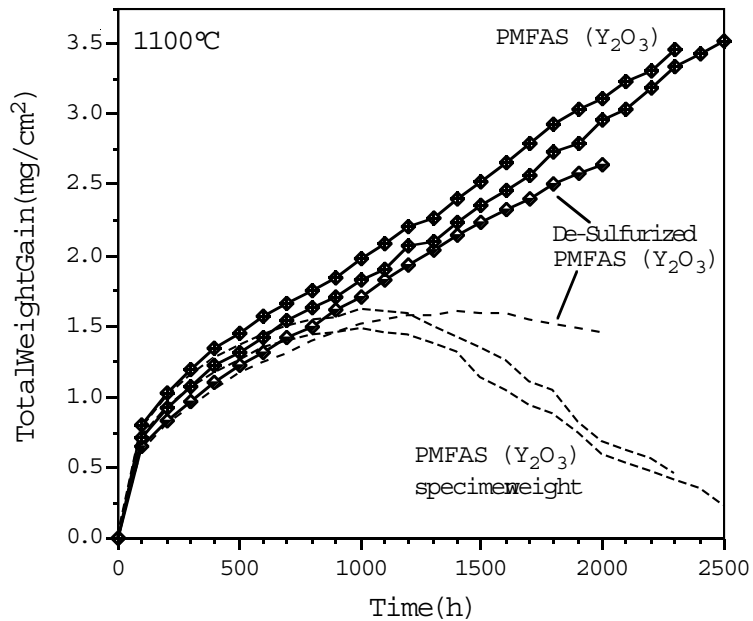

Figure 11. Total weight gain (specimen + spalled oxide) for PMFAS during 100h cycles in alumina crucibles at 1100 °C in laboratory air. De-sulfurizing PMFAS produced only a minimal improvement in performance with a slightly reduced amount of spallation.
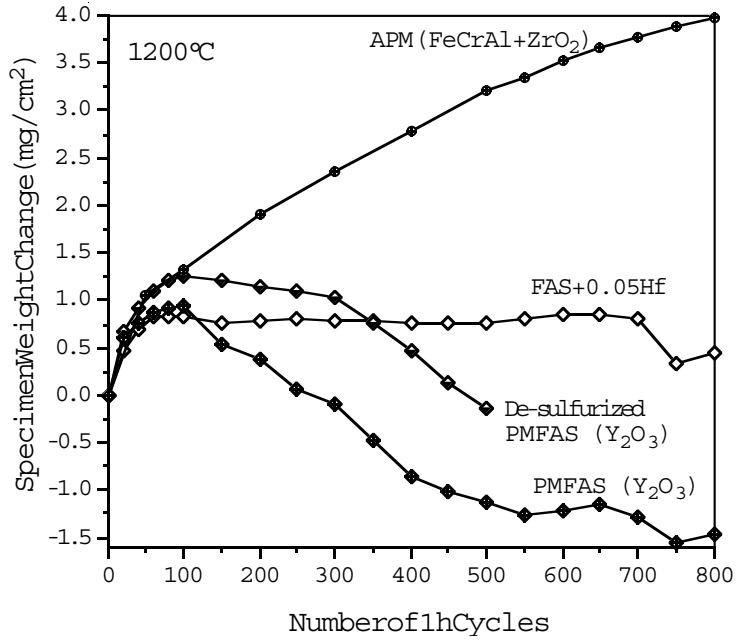
Figure 12. Specimen weight change for several alumina-forming alloys during 1h cycles at 1200 °C in dry flowing O_2. De-sulfurizing PMFAS slightly reduced the amount of spallation but is unlikely to significantly extend the lifetime to breakaway in this test.

Thermally-Sprayed Fe-Al Coatings

As a complement to research on weld overlays of iron aluminides,[2,10-12,20-21] a first attempt was made to fabricate thermal-sprayed coatings and qualitatively evaluated their high-temperature corrosion behavior by simple gravimetric measurements. Using wire produced for gas metal arc deposition of weld-overlay coatings as the feedstock,[10] coatings of Fe-Al-Cr were deposited by thermal spray onto carbon steel substrates made from round stock and machined to have hemispherical ends (see Fig. 13a). The coated specimens were then exposed in individual alumina crucibles to air at 900 and 1000 °C and to air - 1% SO_2 at 800 °C.
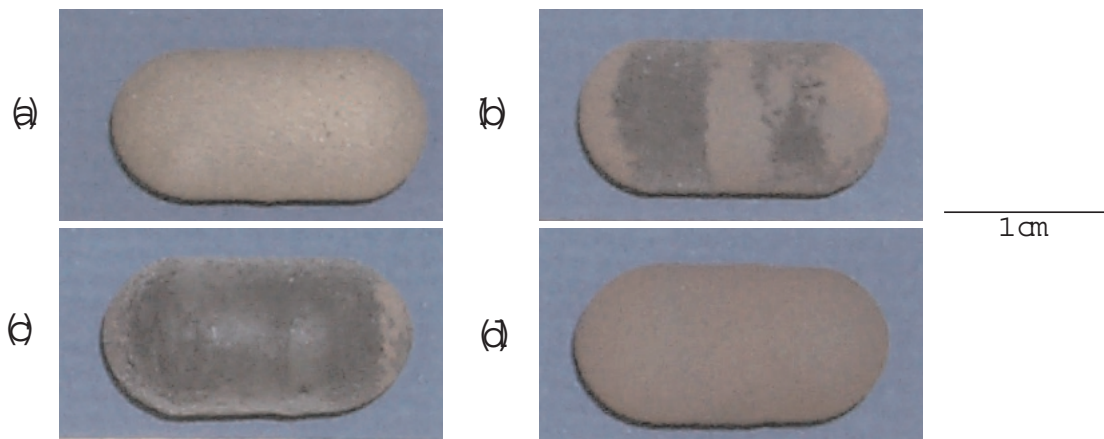

Fig. 13. Carbon steel coated with Fe-Al-Cr by a thermal spray process. (a) as-deposited. (b) 1000 °C, two 24-h cycles in air, total weight gain of 13.1 mg/cm². (c) 1000 °C, two 24-h cycles in air, total weight gain of 45.3 mg/cm². (d) 900 °C, two 24-h cycles in air, total weight gain of 3.6 mg/cm².
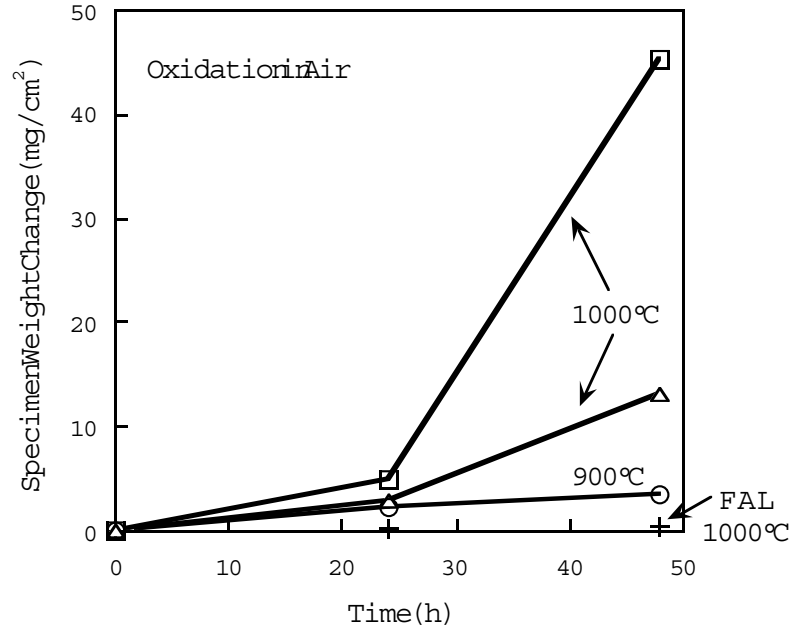
Fig. 14. Specimen weight changes versus time for thermally-sprayed coatings of Fe-Al-Cr on carbon steel substrates exposed to air at 900° and 1000 °C (same specimens as shown in Fig.13). Similar data for IP FAL also are shown.

Large mass gains were measured for all the exposed specimens. As shown in Fig. 14, these weight gains are much larger than for IP FAL exposed under similar conditions. Furthermore, at 1000 °C, the weight gains over the second 24-h exposure period were substantially larger than those measured for the initial 24h of oxidation. Such behavior indicates that a second, less protective corrosion product was starting to form. Visual examination of the specimens indicated that a darker (gray-dark blue) product had formed on the specimens exposed at 1000 °C, in addition to a medium-gray scale, and that it was more prevalent on the specimen with the higher weight gain (Fig. 13). Only the medium-gray product was observed after 48 h at 900 °C. It appeared that this gray scale (presumably containing some Al) was the initial product to form (albeit at a rate faster than normally observed for alumina on Fe_3Al – see the FAL data in Fig. 14 as well as ref. 1), but that, within 48 h at 1000 °C, it yields to an even faster growing product because most of the available aluminum must have already been consumed by reaction (as observed in breakaway oxidation[22]). Accordingly, a similar transition to a higher rate of weight gain would be expected at 900 °C when sufficient oxidation has occurred to deplete the aluminum in the coating (estimated from the data in Fig. 14 to occur when a mass increase of approximately 4–5 mg/cm^2 is reached). The coated specimen exposed at 800 °C in air-1%SO_2 had a significant weight gain (~6 mg/cm2) and showed both gray and reddish-brown (iron oxide) corrosion products after 100 h.

Given the very high weight gains observed in the initial experiments with the thermal spray coatings and the observation of corrosion products that are visibly different from protective alumina, it wasn't deemed necessary to conduct microstructural analyses of the specimens. Obviously, in the present case, this thermal-spray process produced coatings either not fully dense or with low Al levels such that a continuous protective alumina scale

could not be maintained for even relatively short periods of time. This could be due to loss of Al by oxidation during the thermal spraying itself and may require even higher aluminum concentrations in the feedstock or the use of low-pressure thermal spraying to prevent the oxidation of Al during spraying. Previous limited results from spray coatings of iron aluminides (using powder) also showed high corrosion rates.[23] A more extensive effort will thus be required to produce uniform iron-aluminide coatings with sufficient aluminum concentration to proffer adequate oxidation and sulfidation protection.

SUMMARY

An Fe-28Al-2Cr alloy with an optimized Hf concentration (0.05%) has shown significantly better high-temperature oxidation resistance than other iron aluminide compositions. Its improved performance is mainly related to a slower isothermal α-Al$_2$O$_3$ scale growth rate and is observed mainly at 1100°-1200°C. Long-term oxidation resistance of a commercially fabricated ODS Fe$_3$Al (dispersed with Y$_2$O$_3$) has been studied. It spalled more readily than ODS FeCrAl for exposures at 1100° and 1200°C but overall showed relatively good oxidation resistance. De-sulfurization of ODS Fe$_3$Al had little additional benefit on oxidation performance. Preliminary results for thermal-sprayed Fe-Al coatings on carbon steel showed that corrosion resistance was poor, most likely due to insufficient Al in the as-deposited coating. A continuous protective alumina layer was not maintained even after relatively short exposures at 900° and 1000°C.

REFERENCES

1. P.F.Tortorelli and J. H. DeVan, Mat. Sci. and Eng. A153 (1992) 573-7.
2. P.F.Tortorelli, B. A. Pint, and I. G. Wright pp. 235-46 in Proc. Eleventh Annual Conf. Fossil Energy Materials, R. R. Judkins (comp.), U. S. Department of Energy, December, 1997.
3. P.F.Tortorelli and K. Natesan, Mater. Sci. and Eng. A258 (1998) 115-25.
4. B. A. Pint, P.F.Tortorelli and I. G. Wright, Mater. and Corr. 47 (1996) 663-74.
5. B. A. Pint, P.F.Tortorelli and I .G. Wright, Mater. High Temp. in press (1999).
6. A. Strawbridge and P.Y. Hou, Mater. High Temp. 12 (1994) 177-81.
7. B. A. Pint, Oxid. Met. 45 (1996) 1-37.
8. I. G. Wright, C. G. McKamey, E. K. Ohriner, and B. A. Pint, paper 4.1 in Proc.

Twelfth Annual Conf. Fossil Energy Materials, U. S. Department of Energy, September, 1998.

9. I.G. Wright, C. G. McKamey, B. A. Pint, and P. J. Maziasz, these proceedings.

10. G. M. Goodwin, pp. 381-92 in Proc. Tenth Annual Conf. Fossil Energy Materials, N. C. Cole and R. R. Judkins (comp.), U. S. Department of Energy, August 1996.

11. P.F.Tortorelli, J. H. DeVan, G. M. Goodwin, and M. Howell, pp. 203-12 in Elevated Temperature Coatings: Science and Technology I, N. B. Dahotre, J. M. Hampikian, and J. J. Stiglich (eds.), TMS, Warrendale, PA, 1995.

12. K. Natesan and R. N. Johnson, pp. 591-99 in Heat-Resistant Materials II, K. Natesan, P. Ganesan, and G. Lai (eds.), ASM International, Materials Park, OH, August 1995.

13. B. A. Pint, I. G. Wright, W.Y. Lee, Y. Zhang, K. Prüßner and K. B. Alexander, Mater. Sci. and Eng. A245 (1998) 201-11.

14. B. A. Pint, P.F.Tortorelli and I. G. Wright, Oak Ridge National Laboratory, unpublished research 1999.

15. C. Leyens, I. G. Wright and B. A. Pint, pp.79-90 in Elevated Temp. Coatings: Sci. and Tech. III, J. M. Hampikian and N. B. Dahotre eds., TMS, Warrendale, PA, 1999, p.79-90.

16. B. A. Pint, P. F. Tortorelli and I. G. Wright, submitted to the European Federation of Corrosion International Workshop on Cyclic Oxidation, Feb. 1999, Frankfurt, Germany.

17. J. A. Nesbitt, E. J. Vinarcik, C. A. Barrett, and J. Doychak, Mater. Sci. Eng., A153 (1992) 561-6.

18. J. L. Smialek, D. T. Jayne, J. C. Schaeffer and W. H. Murphy, Thin Solid Films 253 (1994) 285-92.

19. G. H. Meier, F. S. Pettit and J. L. Smialek, Werk. Korr. 46 (1995) 232-40.

20. S. W. Banovic, J. N. DuPont, and A. R. Marder, paper 4.3 in Proc. Twelfth Annual Conf. Fossil Energy Materials, R. R. Judkins (comp.) U. S. Department of Energy, September 1998.

21. P.F.Tortorelli, B. A. Pint, and I. G. Wright, paper 2.8 in Proc. Twelfth Annual Conf. Fossil Energy Materials, R. R. Judkins (comp.) U. S. Department of Energy, September 1998.

22. P. Kofstad, High Temperature Corrosion, Elsevier Applied Science, London, 1988.

23. P.F.Tortorelli, Oak Ridge National Laboratory, unpublished research, 1995.