MECHANICALLY RELIABLE SCALES AND COATINGS

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ABSTRACT

As the first stage in examining the mechanical reliability of protective surface oxides, the behavior of alumina scales formed on iron-aluminum alloys during high-temperature cyclic oxidation was characterized in terms of damage and spallation tendencies. Scales were thermally grown on specimens of three iron-aluminum compositions using a series of exposures to air at 1000°C. Gravimetric data and microscopy revealed substantially better integrity and adhesion of the scales grown on an alloy containing zirconium. The use of polished (rather than just ground) specimens resulted in scales that were more suitable for subsequent characterization of mechanical reliability.

INTRODUCTION

In many high-temperature fossil energy systems, corrosion and deleterious environmental effects arising from reactions with reactive gases and condensible products often compromise materials performance and, as a consequence, degrade operating efficiencies. Protection of materials from such reactions is best afforded by the formation of stable surface oxides (either as deposited coatings or thermally grown scales) that are slowly reacting, continuous, dense, and adherent to the substrate. However, the ability of normally brittle ceramic films and coatings to provide such protection has long been problematical, particularly for applications involving numerous or severe high-temperature thermal cycles or very aggressive (for example, sulfidizing) environments. A satisfactory understanding of how scale and coating integrity and adherence are improved by compositional, microstructural, and processing modifications is lacking. Therefore, to address this issue, the present work is intended to define the relationships between substrate characteristics (composition, microstructure, and mechanical behavior) and the structure and protective properties of deposited oxide coatings and/or thermally grown scales. Such information is crucial to the optimization of the chemical, interfacial, and mechanical properties of the protective oxides on high-temperature materials through control of processing and composition and directly supports the development of corrosion-resistant, high-temperature materials for improved energy and environmental control systems.

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The work described in this paper is being conducted at Oak Ridge National Laboratory (ORNL) in collaboration with work sponsored by the Department of Energy's Office of Fossil Energy at Argonne National Laboratory (ANL)¹ and Lawrence Berkeley Laboratory (LBL)² and in concert with directly related activities that are part of the Office of Basic Energy Sciences' Center of Excellence for the Synthesis and Processing of Advanced Materials. These cooperative efforts allow the integration of several advanced and, in some cases, unique characterization, modeling, and coating/deposition techniques so as to systematically investigate the relationships among corrosion performance, bulk composition, and surface oxide chemistry, structure, adherence, and elastic and plastic properties. However, in order to effectively pursue these types of study, it is necessary to first determine the effects of alloy composition, microstructure, surface condition, etc. on high-temperature oxidation behavior and associated scale integrity and spallation tendencies for a particular system. This paper presents initial results in this regard with respect to alumina scales on iron-aluminum alloys using thermal cycling under oxidizing conditions to gauge scale integrity in terms of gravimetric data and microstructural characterization. A similar characterization effort will then be conducted for as-deposited alumina on similar substrates.²

This work will ultimately include several model material systems, which are defined as ones that develop, upon oxidation, slowly growing, chemically stable surface oxides that offer the potential for protection of the metal from rapid reaction at high temperatures and show a substantial sensitivity to small additions of certain alloying elements. Alumina on iron-aluminum alloys appeared to satisfy these criteria³ and this system was chosen as the initial one for study.

EXPERIMENTAL PROCEDURES

Three iron aluminides were studied. Their compositions and common designations are listed in Table 1. Ingots of these alloys were prepared by arc melting and casting. These were then rolled to a final thickness of between 0.8 and 1.3 mm. Rectangular specimens (typically 12 x 10 mm) were prepared from these sheets. The surface finish was either as-ground (600 grit, SiC paper) or polished (0.3 or 1 μ m, alumina paste).

Gravimetric measurements under thermal cycling conditions were used to establish overall corrosion behavior at 1000°C. These cyclic oxidation experiments were conducted in static air by exposing coupons in individual pre-annealed alumina crucibles to a series of (typically) 24-h exposures. At the end of each exposure period, the crucibles were taken

Table 1. Compositions of iron-aluminum alloys used in this study.

Alloy Designation	Concentration ^a (at. %)				
	Al	Cr	Zr	Nb	Other
FA186	28	5			
FA129	28	5	-	0.5	0.2 C
FAL	28	5	0.1	-	0.05 B

^a Balance is Fe.

from the furnace hot zone into the ambient atmosphere in about 2 min. Both the weight of the specimen, W_s , and that of any spalled scale, W_o (as collected in the crucible holding the coupon), were measured prior to the start of each experiment and after every thermal cycle. In this way, the total reacted mass due to oxidation, W_t , where

$$W_t = \Delta W_s + \Delta W_o, \quad (1)$$

could be measured as a function of oxidation time. Several of the oxidized coupons were examined by scanning electron microscopy (SEM). Two plan-view scale specimens for transmission electron microscopy were prepared from cyclically oxidized FAL and FA129.

RESULTS

Cyclic oxidation results for duplicate FAL specimens with 600 grit surface finishes are shown in Fig. 1. Both ΔW_s and ΔW_o (filled and open symbols, respectively) are plotted versus time; each data point represents one thermal cycle. Note that the weight of spalled material was usually small. In contrast, significant amounts of spalled material were measured for cyclically oxidized FA129 (Fig. 2) and FA186 (Fig. 3). For both of these alloys, ΔW_o was consistently greater than ΔW_s . Comparing Figs. 2 and 3 with Fig. 1, and referring to eq. 1, the total reacted mass due to oxidation (W_t) is therefore significantly greater for FA129 and FA186, as shown in Fig. 4.

Distinct differences in the surface appearance of the respective oxidized iron-aluminide alloys were observed. Visual examination revealed a uniformly dark gray product on the FAL and a lighter, powdery scale on the FA129 and (based on substantially fewer observations) FA186. As typified by the representative SEM micrographs in Fig. 5, the oxidized ground FA129 surfaces exhibited areas of bare metal from where the oxide product had completely spalled and fragmented, loosely-adherent pieces of scale. In contrast, the

Fig. 1. Weight change versus time for FAL specimens cyclically oxidized in air at 1000°C. Each point represents one thermal cycle. Closed and open symbols represent weight changes of the specimen and spalled material, respectively. The specimens had a 600 grit surface finish.

Fig. 2. Weight change versus time for FA129 specimens cyclically oxidized in air at 1000°C. Each point represents one thermal cycle. Closed and open symbols represent weight changes of the specimen and spalled material, respectively. The specimens had a 600 grit surface finish.

Fig. 3. Weight change versus time for FA186 specimens cyclically oxidized in air at 1000°C. Each point represents one thermal cycle. The triangles are for a specimen that was exposed for one 96-h cycle. Closed and open symbols represent weights of the specimen and amount of spalled material, respectively. The specimens had a 1 μ m surface finish. The specimens represented by the circles and triangles were in the as-rolled condition prior to exposure. The squares indicated an annealed condition.

Fig. 4. Total weight change (weight of specimen plus that of spalled material) versus time for FAL, FA129, and FA186 specimens cyclically oxidized in air at 1000°C. Each point represents one thermal cycle.

(a) (b)
Fig. 5. SEM micrographs of ground iron-aluminum alloys that were oxidized for 48 h in air at 1000C. (a) FA129 (b) FAL

(a) (b)
Fig. 6. SEM micrographs of polished (0.3 μm) iron-aluminum alloys that were oxidized for 48 h in air at 1000C. (a) FA129 (b) FAL

surface oxides grown on ground FAL were nodular and adherent. In this case, oxide appeared to nucleate along grinding marks - see Fig. 5b. These macro- and microscopic differences were observed regardless of exposure time. The surfaces resulting from cyclic oxidation exposures with specimens that first were polished to a finish of either 0.3 or 1.0 μm showed scale characteristics somewhat different from those observed for the ground specimens. As shown in Fig. 6, there was some, albeit small, areas of adherent scale on FA129, and a finer, less nodular, adherent surface oxide on FAL. Transmission electron microscopy of plan-view scales formed on FAL and FA129 showed very fine-grained oxides (approximately 200 nm) in both cases (Fig. 7).

Weight change measurements for polished specimens of FAL are compared to those for ground surfaces in Fig. 8. The ground specimens had slightly higher specimen weight gains, but all the mass changes shown in Fig. 8 are relatively small. With either type of surface finish, the weights of spalled material were substantially less than the respective changes in specimen weight. For FA129, the ΔW_o of a polished specimen was less than those of the ground ones (Fig. 9), which is consistent with the microscopy results described above. Polished specimens of FA186 were exposed in as-rolled and annealed (1000°C, 1 h) conditions. As shown in Fig. 3 (circles and triangles - as-rolled, squares - annealed), the differences in the gravimetric data due to starting microstructural condition was negligible.

Figure 8 also shows that the gravimetric data for FAL is cycle independent. Two FAL specimens with a 1 μm surface finish that were exposed for 96 h had identical weight changes despite the fact that one had four thermal cycles (square with cross symbols) and the other just one (filled square). In contrast, as shown in Fig. 3, the weight change data for FA186 did depend on the number of cycles - a specimen that was exposed for 96 h prior to cooling to room temperature (triangles) showed substantially different ΔW_s and ΔW_o than those measured for specimens of this alloy that underwent four 24-h thermal cycles from 1000°C (circles and squares).

DISCUSSION

Referring to eq. 1, the principal difference between FAL and the other two iron aluminides was in the weight of spalled scale, ΔW_o . Alloys FA129 and FA186 showed substantial scale spallation during cooling from the oxidation temperature at the end of most exposure periods. On the other hand, W_o for FAL was usually negligible (Fig. 1). These results, which were replicated for several specimens of each composition, are consistent with

Fig. 8. Specimen weight change versus time for FAL cyclically oxidized in air at 1000°C. Each point represents one thermal cycle. The specimens had either ground (600 grit) or polished (0.3 or 1 μm) starting surfaces as indicated.

Fig. 9. Weight change versus time for FA129 specimens cyclically oxidized in air at 1000°C. Each point represents one thermal cycle. The specimens had either ground (600 grit) or polished (0.3) starting surfaces as indicated. Closed and open symbols represent weight changes of the specimen and spalled material, respectively.

earlier, preliminary studies showing that zirconium had a beneficial effect on the adherence of scales grown on Fe_3Al alloys at both higher (1300°C)⁴ and lower (900°C)⁵ temperatures. Zirconium is known to also have a positive effect on scale adherence in other alumina-forming alloys systems (see, for example, ref. 6), but the mechanism by which it provides a beneficial influence in iron aluminides has not been demonstrated. There is some electron microscopy evidence that zirconium ions accumulate in the alumina scale,⁷ but these observations do not definitively prove any one particular model for the effect of this element on scale adherence. As the initial transmission electron microscopy revealed that the surface oxides on both FAL and FA129 were fairly fine grained (Fig. 7), the effect of zirconium does not appear to be due to a major modification of the bulk scale microstructure. However, this result is preliminary; the influence of zirconium on scale and interface characteristics will be investigated in more detail using microscopy and other analytical techniques available at ORNL, ANL and LBL.

For spallation-resistant alloys, there should be little influence of cycle frequency on weight-change measurements unless substantial scale cracking occurs. Therefore, the finding that the measured weight changes of FAL undergoing cyclic oxidation at 1000°C are not frequency dependent (Fig. 8) is consistent with the lack of any observations of spallation or visible scale cracking. On the other hand, because of the spallation susceptibilities of FA129 and FA186, the gravimetric results for these alloys do show a dependence on the number of thermal cycles for a given oxidation period (see, for example, Fig. 3). Most of the scale damage is due to thermal cycling; in Fig. 3, W_0 is about the same regardless of whether the first cycle was after 24 or 96 h of exposure.

As mentioned above, the present work represents the initial stage in defining the fundamental correlations among properties, structure, and mechanical reliability of the surface oxides as they relate to corrosion performance. This first step includes determination of the effects of starting alloy microstructure, composition, and surface finish on high-temperature cyclic oxidation behavior and associated scale integrity and spallation susceptibility. The results of this work are being used to prepare suitable thermally grown oxides on iron-aluminum alloys for examination by a variety of characterization techniques, including analytical electron microscopy, SEM observation of cracking behavior using a bending stage, and nanoindentation (to determine elastic and plastic properties as well as fracture toughness). In this regard, the oxidation results described above have important implications for the use of these alloys as model materials for such a comprehensive study of the microstructure and properties of alumina scales. The use of polished (rather than just

ground) surfaces on the specimens of FAL results in a more uniform scale upon oxidation such that these characterization techniques can be facilitated. Furthermore, whereas the scales formed on FA129 with a 600 grit surface finish (Fig. 5a) were wholly unsuitable for such analyses, there appears to be some possibility in obtaining information from the pieces of sound, adherent oxide remaining on polished surfaces of this alloy (see, for example, Fig. 7a). This could be a key part of subsequent study as it may be just as crucial to obtain information from spallation-prone scales (in this case, those formed on FA129 and FA186) as it is for adherent surface oxides (such as those grown on FAL). As such, these results may well prove to be an important step in specifying the microstructural, chemical, and mechanical differences of scales exhibiting different degrees of adherence to their alloy substrates.

The present findings on scale damage resulting from cyclic oxidation represent the traditional way of assessing corrosion performance and the mechanical reliability of scales. Because of this, they provide the means of linking oxidation performance of this system with the results forthcoming from use of the characterization techniques listed above. In addition, this study of alumina scales grown on iron-aluminum alloys will form the basis for comparison with results from similar work with as-deposited alumina on the same substrates.

SUMMARY AND CONCLUSIONS

As a part of the initial effort in defining the fundamental relationships among properties, structure, and mechanical behavior of surface oxides that provide corrosion protection at high temperatures, the integrity of alumina scales formed on iron-aluminum alloys during cyclic oxidation was characterized by gravimetric measurements and microscopy. Specimens with ground or polished surface finishes were prepared from three iron-aluminum compositions. Scales were thermally grown using a series of (typically) 24 h exposures to air at 1000°C. Gravimetric data and scanning electron microscopy revealed little scale damage and substantially better adhesion of the alumina grown on the alloy containing zirconium. Thermal cycling caused extensive disruption and spallation of the scales formed on the other two alloys. Transmission electron microscopy showed that scales grown on spallation-resistant and spallation-susceptible iron-aluminum alloys were both fine-grained. Use of polished (rather than just ground) specimens resulted in scales that were more amenable to characterization.

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