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F. Gesmundo, Y. Niu, F. Viani, O. Tassa. The hot corrosion of two Fe-Al intermetallics at 600 ° C. Journal de Physique IV Proceedings, 1993, 03 (C9), pp.C9-375-C9-381. 10.1051/jp4:1993938 . jpa-00252377

HAL Id: jpa-00252377

<https://hal.science/jpa-00252377>

Submitted on 1 Jan 1993

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The hot corrosion of two Fe-Al intermetallics at 600 °C

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Abstract. — The hot corrosion of Fe₃Al and FeAl has been studied at 600 °C in combustion gases and in the presence of Na₂SO₄-NaCl and Na₂SO₄-V₂O₅ mixtures with some additional measurements with pure Na₂SO₄. Under all conditions the alloys underwent significant attack with formation of scales containing both Fe and Al. However, corrosion in Na₂SO₄ pure or mixed with NaCl slowed down significantly with time, while corrosion in Na₂SO₄-V₂O₅ mixtures was more severe, irregular and long-lasting. Except for the Na₂SO₄-NaCl mixture, Fe₃Al corroded more than FeAl. The scales consisted always of an outer layer rich in iron oxide and an inner layer containing mostly Al but also Fe and S whose actual composition differed for the two salt mixtures. The corrosion mechanism involved to a different extent mixed oxidation-sulfidation and scale fluxing.

1. Introduction.

The Fe-Al intermetallics (Fe₃Al and FeAl) have low cost, acceptable mechanical properties up to about 600-650 °C [1] and good oxidation resistance due to the formation of slowly-growing Al₂O₃ layers [2]. However, for some applications their resistance to hot corrosion (HC) is also of concern [3, 4]. Previous studies of HC of these materials at 600-800 °C with mixed (Na, K)₂SO₄ [5] or (Na, Li)₂SO₄ [6] deposits showed high corrosion rates, while no reaction occurred in their absence. Therefore the HC behavior of these materials needs to be investigated further. The present study examines the kinetics and the mechanism of HC of Fe₃Al and FeAl in combustion gases at 600 °C with different types of salt deposits.

2. Experimental.

The materials tested had the composition (wt%) 15.4 Al, 2.43 Cr, 300 ppm B (Fe₃Al) and 24 Al, 0.11 Zr, 14 ppm B, 0.023 C (FeAl), respectively. The samples (discs of 10 mm diameter) were polished down to 800 grade paper, rinsed with acetone and dried. The deposits were mixtures of Na₂SO₄ with 10 wt% NaCl (mixture 1) or 15 wt% V₂O₅ (mixture 2): pure Na₂SO₄ was also used for comparison. Coatings of about 3 mg/cm² were applied by brushing salt solutions (Na₂SO₄ or Na₂SO₄ + NaCl) or dispersions in alcohol (Na₂SO₄ + V₂O₅) on warmed samples (around 200 °C). Hot corrosion tests were performed discontinuously with a horizontal furnace at 600 °C in simulated combustion gases containing 1.0%O₂, 0.5%SO₂, balance N₂ with equilibrium $P(\text{SO}_3) = 2.48 \times 10^{-3}$ atm and $P(\text{O}_2) = 8.8 \times 10^{-3}$ atm. A Pt catalyst was used to ensure gas equilibration. The corroded samples were examined by XRD, OM, SEM and EMPA.

3. Results.

3.1 CORROSION KINETICS. — No weight gain was detected for both alloys after 4 days corrosion in combustion gases without deposits. The kinetics curves for samples coated with the two salt mixtures are shown in figure 1, while those for pure Na_2SO_4 are omitted for clarity. The corrosion rates in mixture 2 were significantly higher than in mixture 1: in addition, they were irregular with tendency to breakaway and still high up to 4 days, while those in mixture 1 slowed down significantly with reaction time, especially after 1 day. Furthermore, Fe_3Al corroded more heavily than FeAl in mixture 2 and in pure sodium sulfate, while in mixture 1 the two alloys had almost the same behavior. Finally, the corrosion rates in pure Na_2SO_4 were very similar to those in mixture 1 for Fe_3Al and slightly lower for FeAl .

Fig. 1. — Corrosion kinetics of salt-coated Fe_3Al and FeAl in combustion gases at 600°C by discontinuous measurements.

3.2 ANALYSIS OF CORRODED SAMPLES. — The scales formed by reaction with mixture 1 showed two layers of similar thickness (Fig. 2). On both alloys the inner layer (dark grey) contains practically only Al with only traces of Fe (3-4%) (all compositions in wt%) and a significant amount of S (25 to 36%). Thus, it is composed mainly of alumina mixed with an Al-S compound, probably Al_2S_3 in the inner zone but Al or mixed Na-Al sulfate close to the inner-outer layer interface, as confirmed by EMPA of spalled regions of the sample surface. The outer layer (light grey) contains a matrix of iron oxides (around 95% Fe) with some Al and S with dark islands of Na, Al and Fe sulfates with 19% Fe, 10% Na, 6% Al and 65% S. Sometimes the inner layer shows various sublayers of different composition. No evidence of the presence of NaCl (by XRD) nor of Cl (by EMPA) was obtained. In addition to iron oxides, XRD revealed also the presence of $\text{NaAl}(\text{SO}_4)_2$ and possibly gamma Al_2O_3 (weak peaks) which may only be detected after removing the outer scale layer.

Fig. 2. — SEM micrograph (BEI) of a cross section of Fe_3Al corroded for 2 days in combustion gases in the presence of Na_2SO_4 -10% NaCl deposits at 600 °C.

Cross sections of samples corroded in mixture 2 are shown in figures 3a and 3b. Fe_3Al formed multilayered scales with up to four regions (Fig. 3a). The outermost layer (light grey) contains mostly Fe (95%) with some Al (3%) and little S, V and Na (less than 1%). The intermediate layer (dark) contains mostly Al (around 50%) with Fe (30%) and some V (7%) and S (1.5%) but no Na. The following layer (middle gray) contains mostly Fe (75%) with significant Al (18%) and little S (1%), V (1.9%) and Na (0.61%). Finally, the thin innermost layer close to the alloy-scale interface contains again both Al (59%) and Fe (25%) with significant sulfur (8%) and some V (1.7%) but no Na: very likely this is a mixture of oxides and sulfides of Fe and Al. In some cases these scales contain only two main layers, with an iron-rich outer region and an inner zone of non-uniform composition containing both Fe and Al with some sulfur.

The scales formed on FeAl in mixture 2 show only two layers (Fig. 3b): the outer region (light grey) contains mostly iron oxide with some Al (1 to 9%) and islands of Na, Fe and Al sulfates. The inner region (dark grey) has a variable composition ranging from 40 to 50% Fe, 30 to 50% Al, 10 to 20% S with some V and Na (around 1%). In addition to Fe_2O_3 XRD of samples reacted with mixture 2 revealed also the presence of traces of $\text{Fe}_2(\text{SO}_4)_3$, $\text{NaAl}(\text{SO}_4)_2$, FeVO_4 and Na_3VO_4 .

In all cases the scales cracked and spalled off severely during cooling. Spallation was more severe in mixture 2 than in mixture 1 and increased with reaction time for a given alloy and salt mixture.

4. Discussion.

Two forms of hot corrosion exist, i.e. type I or high-temperature (HTHC) and type II or low-temperature (LTHC) [7, 8]. Even though they differ in many aspects, both of them require the presence of a molten salt layer. In particular, LTHC usually involves the formation of pits with little or no internal sulfidation and depletion of the reactive components in the alloy [8]: the absence of pits observed here is in agreement with previous results for the LTHC of Co-Al alloys [9, 10]. The occurrence of LTHC of the Fe-Al intermetallics at 600 °C indicates the formation of liquid solutions for all the systems examined. This aspect and the possible mechanisms for the hot corrosion of these alloys are examined in the following.

Fig. 3. — SEM micrographs (BEI) of cross sections of Fe_3Al (a) and FeAl (b) corroded for 2 days in combustion gases in the presence of Na_2SO_4 -15% V_2O_5 deposits at 600 °C.

4.1 THE FORMATION OF LIQUID SALT MIXTURES. — The LTHC of metals in the presence of alkali sulfates involves the formation of low-melting mixtures with metal sulfates, which requires high partial pressures of SO_3 [11-13]. According to recent studies, pure Fe undergoes LTHC with Na_2SO_4 deposits at 600-800 °C [13, 14] and pure Al with $(\text{Na}, \text{K})_2\text{SO}_4$ mixtures at 580 °C [15]. Thus, the two metals react with O_2 - SO_2 - SO_3 -containing gases in the presence of alkali sulfate deposits forming liquid phases containing Fe or Al sulfates. A similar behavior is then also expected for their alloys.

NaCl takes commonly part in the formation of deposits leading to HC, especially for gas turbines operating in marine environments: when added to Na_2SO_4 it tends to accelerate hot corrosion [16]. A first effect of NaCl is to lower the melting point of sodium sulfate since the pure compounds melt at 884 °C (Na_2SO_4) and 798 °C (NaCl), respectively, while their eutectic melts at about 625 °C [17]. In addition, above 300 °C NaCl reacts with SO_3 in the gas forming sodium sulfate and releasing Cl_2 . In particular, a mixture of Fe_2O_3 and NaCl

exposed to an O_2 - SO_2 mixture forms liquid solutions very corrosive for both low-alloyed and stainless steels even at 300 °C, as reported recently [18]. Moreover, Cl_2 can induce scale cracking and spalling, possibly followed by penetration of salt down to the metal surface [16]. Finally, the formation of both gaseous Cl_2 and volatile metal chlorides can result in the growth of porous non-protective scales [17].

Vanadium is also often present in deposits formed by burning low-quality liquid fuels [17] and accelerates the HC attack [19]. During combustion it first forms V_2O_4 and later V_2O_5 [20] which then reacts with Na_2SO_4 to yield various low-melting Na-V compounds [19]: their mixtures with Na_2SO_4 may have even lower melting points. Their chemistry has been rationalized recently [7] in terms of only three species, i.e. V_2O_5 , Na metavanadate $NaVO_3$ and Na_3VO_4 (orthovanadate), whose equilibria in Na_2SO_4 depend on the local salt basicity. Under very acid conditions V_2O_5 prevails, which transforms gradually into $NaVO_3$ and then into Na_3VO_4 as the salt basicity increases [7]. Thus, even if the initial deposit contains only V_2O_5 , its equilibrium composition will depend on the local melt acidity and therefore change with the distance from the salt-gas interface and may include also Na vanadates. Thus, the reaction between sodium sulfate and V_2O_5 produces SO_3 especially under conditions of low acidity, i.e. close to the scale-salt interface, where SO_3 is needed to support corrosion. Moreover, sodium vanadates increase the acid and especially the minimum solubility of the metal oxides, as revealed recently for a number of compounds [7]. These factors may contribute to accelerate HC if scale fluxing plays an important role.

4.2 THE REACTION MECHANISMS. — According to Stringer [20] three main processes are involved in HC, i.e.: 1) mixed attack with simultaneous sulfidation and oxidation as a result of the penetration of sulfur through the inner oxide scale; 2) penetration of the liquid salt through the scale to react with the alloy as described above; and 3) fluxing of the protective oxides with subsequent formation of porous, non protective scales within the salt layer. The large rates of HC are due to a combination of fast transport of oxidants through the molten salt and of the formation of porous oxides in the outer layer and of rapidly-growing oxides-sulfides mixtures in the inner layer [7, 8, 20]. Other negative effects due to sulfidation have been examined by Stringer [20]: in particular, the reaction may become catastrophic if a liquid sulfide of the base metal (especially Ni) forms in contact with the alloy.

The LTHC of the two Fe-Al intermetallics in the present salt mixtures appears to involve a combination of the previous mechanisms whose relative importance changes according to the salt deposit. In particular, scale fluxing with formation of metal sulfates is necessarily involved because otherwise hot corrosion could not occur, at least with pure Na_2SO_4 , since it melts only at 884 °C.

According to Rapp and Goto [7, 21] continued oxide dissolution at the scale-salt interface requires a negative solubility gradient at this site. The sign of this gradient depends on the shape of the oxide solubility curve vs. melt basicity and on the melt basicity at this interface [7, 21]. For LTHC the salt must be quite acidic due to the high SO_3 pressures required to stabilize the melt [22]. This corresponds to the acid side of the solubility curve for basic oxides (NiO and CoO), which then cannot fulfill Rapp-Goto's criterion [22]. A similar situation exists for Fe_2O_3 , whose solubility curve is intermediate between those of basic (NiO, CoO) and acid (Cr_2O_3 and Al_2O_3) oxides [7]. However, other mechanisms have been proposed to explain the dissolution-precipitation of CoO in these conditions, which are not expected to apply for Cr_2O_3 and Al_2O_3 [23]. Thus, LTHC of Co-Cr or Co-Al alloys has been attributed to a fast CoO dissolution which prevents the growth of a continuous layer of protective oxides at their surface [23]. However, according to recent measurements of LTHC of pure Al around 600 °C [15] Al_2O_3 may be fluxed by alkali sulfates: thus, the same conclusions should also

apply to the LTHC of alumina-forming alloys.

Scale fluxing for these alloys may also involve a synergistic effect producing faster dissolution of both Fe_2O_3 and Al_2O_3 , as already reported for a mixture of Fe_2O_3 and Cr_2O_3 in sodium sulfate melts [7]. The same effect is possible also for the simultaneous fluxing of Fe_2O_3 and Al_2O_3 because the acid-base behaviour of Al_2O_3 and Cr_2O_3 are very similar [7]. In any case, iron is always located mainly in the outer region of the scales formed on the two Fe-Al intermetallics, suggesting a larger solubility and/or a faster diffusion than Al through the liquid phase.

The presence of large S concentrations in the inner scale region indicates that an oxidation-sulfidation mechanism, more important for mixture 1 than for mixture 2, is also operating. The growth of mixed oxide-sulfide scales is generally associated with fast corrosion, especially if channels or networks of interconnected sulfide particles form within the oxide matrix [12, 24]. However, the corrosion rate in the two salt deposits is surprisingly more affected by the presence of iron than by that of sulfur in the inner scale region. A mixture of Al oxide and sulfide with little Fe such as observed after reaction with mixture 1 slows down HC significantly, effectively hindering iron diffusion through the inner layer.

The higher reaction rates of the two alloys with mixture 2 are not only a result of the factors considered earlier, i.e. the production of SO_3 within the salt and the increase of oxides solubility due to the presence of vanadium, but also of possible modifications in the transport of oxidants through the molten salts as well as of the presence of iron, salt and porosity in the inner scale region. In fact, oxidants transport through the liquid layer may be accelerated by a counterflow of V^{+4} and V^{+5} ions [7, 21]. Moreover, the presence of vanadium in the inner scale region shows that the salt penetrates to some extent through cracks or pores; this may also be responsible for the tendency to breakaway. Finally, the inner region of scales formed by LTHC in mixture 2 contains less S but much more Fe than in the previous case. This may contribute significantly to yield high corrosion rates by allowing Fe to diffuse through the inner region and migrate in the outer layer, while Al, which is also corroded, remains in the inner region.

The corrosion rates in Na_2SO_4 -NaCl mixtures are similar to those observed in pure Na_2SO_4 , especially for Fe_3Al . Apparently Cl_2 is not able to induce scale cracking with subsequent salt penetration. Also the formation of porous scales due to the development of Cl_2 and metal chlorides seems to play an insignificant role.

The Al content of both alloys is higher than required to afford complete protection against oxidation [2], but not against HC. However, higher Al contents should increase also the corrosion resistance to this attack due to a greater tendency of alloys to form alumina scales. This is in agreement with the results concerning pure Na_2SO_4 and mixture 2, while corrosion in mixture 1 is not affected by the Al content of the alloy.

Finally, the corrosion resistance of these alloys may be significantly lowered if they are exposed to thermal cycling, especially in the presence of continued salt deposition, due to the tendency of the scales to spall extensively upon cooling. In fact, this enhances the ability of salt to penetrate within the inner scale region and perhaps down to the alloy surface, producing heavy corrosion, especially in the case of mixtures containing vanadium compounds.

5. Conclusions.

Both Fe_3Al and FeAl undergo hot corrosion attack in the presence of various salts at 600 °C, in spite of their high Al content. The scales show two main layers: the outer zone contains mostly iron oxide, while the inner zone is a mixture of Al oxide and sulfide with some Fe. Corrosion in pure Na_2SO_4 and in Na_2SO_4 -NaCl mixtures slows down significantly after an initial

stage, while corrosion in $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$ mixtures is long-lasting. The corrosion mechanism is complex and involves to a different extent mixed oxidation-sulfidation, oxides fluxing and scale penetration by molten salts. Due to extensive cracking and spalling of the scales during cooling these alloys are expected to corrode heavily under thermal cycling conditions.

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