An Electrochemical Study of the Effect of B on the Corrosion of Atomized Fe40Al Intermetallics in Molten Na₂SO₄

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ABSTRACT

The hot corrosion resistance of sprayed and atomized and Fe40Al+10Al₂O₃ intermetallic materials with different boron contents (0.1, 0.2 and 0.4at.%) has been evaluated in molten Na₂SO₄ at 1173 and 1273 K using polarization curves, open circuit potential and linear polarization resistance measurements. The results are supported by electron microscopy and microchemical studies. Generally speaking, the additions of up to 0.4B were beneficial, since, for short times, they made the E_{corr} value more active but, after some hours, all the E_{corr} values became nobler, even nobler than the alloy without boron and decreased both the anodic and cathodic current density, but did not promote the formation of a passive film, at least for short times. In terms of corrosion rate, additions of boron always decreased this value as opposed to the alloy without boron, specially at 1273 K, but the corrosion rate values decreased rapidly, attaining a constant value, which was consistent with the establishment of a protective alumina, Al₂O₃ layer and promoted Al depletion on the FeAl matrix which allows internal sulfidation. It seems that the optimum amount of boron that gives the best corrosion resistance is 0.1B.

Key words: deposited Fe40Al, molten Na₂SO₄, electrochemical techniques.

1. INTRODUCTION

Corrosion in molten salts is a small factor in corrosion of aqueous systems, but without a doubt it is an important area of the corrosion in industrial fields. Molten salts can cause corrosion by i) diffusion in solution of the constituents of the structural material, electrochemical reactions, ii) mass transport due to thermal gradients, iii) the reaction of the constituents of the molten salt with the alloy, and iv) by the reaction of the impurities in the salt with the alloy /1/. In particular, the damage that is generated by corrosion in heat exchangers systems, incinerators, burners, is in great measure caused by molten salts. Several alloys and materials have been evaluated in corrosive environments at high temperatures in salts and mixtures of salts like potassium sulfate (K₂SO₄) and vanadium pentoxide (V₂O₅) /2/ mixtures of sodium sulphate and vanadium pentoxide (Na₂SO₄+V₂O₅), /3/ sulphates, chlorates and carbonates /4,5/.

Intermetallic materials have a melting point, characteristics and properties different from the original elements. Fe40Al-base intermetallics in the presence of molten salts present better corrosion resistance when comparing them with common alloys /6/. The Fe40(at.%)Al-base intermetallics have been evaluated in a mixture of molten salts of 80wt.% V₂O₅ + 20wt.% Na₂SO₄ at 873, 973, 1073 and 1273 K, and it was

concluded that the formation of an aluminum oxide (Al_2O_3) layer plays an important part in the protection against corrosion /7/ and addition of 0.1B increased the corrosion resistance. The same intermetallics were evaluated in NaVO_3 at 898 and 973, where the main cause of the reduction of the corrosion rate was the fast formation of a layer of Al_2O_3 that is increased as the temperature increases /8/. Similar results were obtained by Tortorelli /9/ for $\text{Fe}_3\text{Al}_2\text{Cr}$ alloy in molten Na_2SO_4 at 923 and 973 during 800 hours.

The corrosion of iron aluminides in molten $\text{NaNO}_3(\text{KNO}_3)\text{-Na}_2\text{O}_2$ at 923 K proceeds by oxidation, and a low release from an aluminide-rich product layer into the salt such that the compositions with higher aluminium concentrations yielded significantly better corrosion resistance /10/. The preliminary results of the exhibition of the FeAl in molten $\text{NaCl-Na}_2\text{CO}_3$ at 1173 K (used as an oxidiser for waste disposal), showed significantly better corrosion resistance of this aluminide than that for Inconel 873 K /11/.

The objective of this work was to study the corrosion resistance of atomized Fe40Al intermetallics with different boron contents in sodium sulfate (Na_2SO_4) since addition of 0.1B increased its corrosion resistance using and this element improves its ductility /12/. Since a molten salt acts as an electrolyte, electrochemical techniques such as potentiodynamic polarization curves, open circuit potential and linear polarization resistance (LPR) measurements can be used.

2. EXPERIMENTAL PROCEDURE

The materials tested here were atomized Fe-40at.%Al+10 Al_2O_3 , with and without boron (B) 0.1(at.%), 0.2 and 0.4. A master alloy of Fe40Al was fabricated employing iron and aluminium, both of 99.99% purity. The alloy was cast in an induction furnace under an argon atmosphere and it was poured by gravity into a cylindrical graphite mold of 4 cm diameter. Small pieces were cut of master alloy bar, and fed to the spray atomization and deposition system. Boron with a purity of 99.99% in the form of Ni_2B was used as a microalloying constituent. The reinforcement phase was commercially pure (99.99%) single crystal $\alpha\text{-Al}_2\text{O}_3$ platelets with an average diameter of 3 μm . The

synthesis of the Fe40Al alloy and experimental variables used for spray atomisation and deposition are described elsewhere /12/. Electrochemical techniques included potentiodynamic polarization curves and LPR measurements. Details of the experimental set-up for the electrochemical cell used in this work are given elsewhere /7/. The body of the cell was a 15 ml silica crucible. The most important elements are: a reference electrode, made of 0.5 mm diameter platinum wire inside a mullite tube and filled with a refractory cement (Fig.1). In order to check if it was stable, another platinum electrode was immersed in the working salt and the potential of the first electrode was monitored with time once the temperature was stabilised. This potential at beginning was 30 mV more noble than the second platinum electrode, but after 40-50 min. this difference was very stable, having a fluctuation of ± 2 mV. As an auxiliary electrode, another platinum electrode was used, exactly the same as the reference electrode, and as working electrode, a cylindrical piece of the intermetallic material having 3 mm length and 8 mm in diameter inside a mullite tube and filled with the

Fig. 1: Schematic diagram showing the experimental set up.

same cement. The amount of molten salt in each run was $5 \times 10^3 \text{ g/m}^2$. The electrical contact was made by welding an 80 mass % Cr – 20 Ni (Nicomel) wire to the specimen. A tube furnace with capacity up to 1373 K was used for all the experiments. An automated potentiostat was used for all the electrochemical measurements.

The working salt was analytical grade Na_2SO_4 . Prior to use, the specimens were polished with 1200-grade emery paper, washed with distilled water and degreased with acetone. All the experiments were performed in static air. The tests lasted 5 days, and the LPR measurements were taken every 30 min. The specimens were polarized at $\pm 10 \text{ mV}$ with respect to the free corrosion potential (E_{corr}) at a scan rate of 1 mV/s ; the same rate was used in the polarization curves. The testing temperatures were 1173 and 1273 K. Energy dispersive of X-ray (EDX) studies were obtained from mounted and polished specimens using a scanning electronic microscope (SEM)/EDX system.

3. RESULTS

The stability of a platinum reference electrode was measured by measuring its free corrosion potential versus another identical platinum reference electrode and the results are shown in Fig. 2. We can see that during the first ten minutes the potential value increases

Fig. 2: Potential fluctuations of a platinum reference electrode versus another platinum reference electrode.

up to 55 mV more positive, but after this, the potential value drops and reaches a more or less stable value after approximately one hour or so.

Potentiodynamic polarization curves for the three intermetallic materials in Na_2SO_4 are observed in Fig. 3. At 1173 K, the alloy without boron had a much higher, almost 600 mV, free corrosion potential, E_{corr} value, whereas the E_{corr} value of the alloy with 0.4B was located very close to the value of the 0.2B containing alloy laid around -1100 mV. The Fe40Al+0.1B alloy exhibited the most active E_{corr} value, approximately -1200 mV. The anodic current densities were higher for the alloy without B by almost two orders of magnitude, followed by the 0.1B alloy, whereas the other two alloys had very similar current density values. At 1273 K, Fig. 4, the behavior was very similar, but the alloy with 0.4B contents has now the most active E_{corr} value, around -1500 mV, whereas the alloy with 0.1B has now the most noble E_{corr} value, -1100 mV, still more active than the alloy without boron, which again had the highest anodic and cathodic current densities values. Apparently the alloys did not show a passive behavior at this stage of the tests.

The changes of the open circuit potential values, E_{corr} , with time for the three alloys at 1173 K are shown in Fig. 5. It can be seen that at the beginning the base material, the alloy without boron, had more noble E_{corr} values, but after a few hours, the E_{corr} values of all the

Fig. 3: Polarization curves of Fe40Al-base intermetallics in Na_2SO_4 at 1173 K.

Fig. 4: Polarization curves of Fe40Al-base intermetallics in Na₂SO₄ at 1273 K.

Fig. 5: Change of E_{corr} with time for Fe40Al-base intermetallics in Na₂SO₄ at 1173 K.

alloys moved towards more noble values, especially the alloys with 0.1 and 0.2B, which even had more noble E_{corr} values than the base alloy. The alloy with 0.4B showed an irregular behavior, since the E_{corr} value also moves towards more noble values, it decreases towards more negative, active values, and, finally, it remains in more active values. The most noble value was for the alloy with 0.2B, very close to that for the alloy with 0.1B, and the most active value was for the 0.4B containing alloy. The difference between the initial and final values is for up to 1000 mV.

At 1273 K (Fig. 6) a similar behavior was observed,

the E_{corr} values move towards more noble values, this time for more than 1000 mV, although the value for the 0.1B containing alloy remained constant after an initial shift towards more positive values. This time the most active value was for the alloy with 0.2B whereas the noble one was the one containing 0.4B. This shift towards more noble E_{corr} values is related to the formation of a passive, protective, film, and, in the case of Al-containing alloys, to the presence of an external, protective alumina, Al₂O₃ film.

Fig. 6: Change of E_{corr} with time for Fe40Al-base intermetallics in Na₂SO₄ at 1273 K.

Polarization curves are important because from them the anodic (b_a) and cathodic (b_c) slopes can be used to calculate the corrosion current density (I_{corr}) in terms of the polarization resistance, R_{lp} obtained from the LPR experiments according to the Stern-Geary equation [13]:

$$I_{corr} = \frac{B}{R_{lp}} \quad (1)$$

where

$$B = \frac{b_a \cdot b_c}{2.303(b_a + b_c)} \quad (2)$$

The values of I_{corr} obtained from the LPR tests are shown in Figs. 7 and 8. At 1173 K, all the alloys, although initially showed high I_{corr} values, specially the base alloy, very soon reached very similar, constant, I_{corr} values. Apparently, within the experimental error, the

Fig. 7: Change in I_{corr} with time for Fe40Al-base intermetallics in Na_2SO_4 at 1173 K.

Fig. 8: Change in I_{corr} with time for Fe40Al-base intermetallics in Na_2SO_4 at 1273 K.

alloy most resistant was the one with 0.4B and the least resistant was the one without B. At 1273 K, however, the base material had higher corrosion rates, Fig. 8, and, although the alloy with 0.4B had initially high I_{corr} values, the three alloys with boron had very constant corrosion rate values, close to each other, being the alloy without B again the least corrosion resistant followed by the one with 0.4B, whereas the one with 0.1B was the most resistant. It seems that the optimum addition of B which gives the best corrosion resistance is 0.1, since additions of either 0.2 or 0.4% increase the corrosion rate values.

A cross section of the intermetallics freely corroded in Na_2SO_4 at 1173 and 1273 K during five days and their X-ray mappings of Al, and S are presented in Figs. 9 and 10 respectively. In both cases, the external layer consisted mainly of Al and S. Sulfur penetrated into the alloy through the Al-containing layer, dissolving it and corroded the substrate. The presence of S on the grain boundaries in high concentrations obtained is a characteristic of internal sulfidation generated by sulfates [1]. Some dark particles are also seen, and an EDX analysis showed that they contained Al and O, which means that they were alumina particles. In the indications observed at 1173 K on the iron aluminides, they contained aluminium and sulphur (Figs. 9 and 10), under a layer of external aluminium oxide which is probably in the form of Al_2O_3 [14]. Sulfur moves from the oxide/ molten-salt interface towards the metal/oxide interface by diffusion, or infiltration of the melt through the structure defects of the scale, and there preferably reacts with the aluminium (of more activity) to form aluminium and sulphur compounds, presumably Al_2S_3 [15]. Sodium was related neither in the protective scales nor inside the pits. At 1173 K the three alloys developed a protective layer of Al_2O_3 , which maintained the corrosion rate values at lower levels in relation to those obtained at 1273 K.

The chemical analysis done on the Fe40Al+10Al₂O₃+0.1B alloy did not show Na as a component on the scale. This can be an indication of the lower corrosion rate exhibited by this material during the first 50 hours of testing, which was due to the basic character of the salt. The sulfidation could be due to the presence of SO_3 from the decomposition of Na_2SO_4 , taking a sour and aggressive gradient on the interface metal/scale, and a preferential attack in the grain boundaries of the alloy. On the same form, the external layer is rich in Al and was related with S. The scale was detached from the alloy due to the infiltration of the molten Na_2SO_4 that is in contact with the alloy, and that might be the reason why that material presented high corrosion values. The elements present in the materials corroded at 1273 K showed important contents of Al and S, and the depletion of Fe in these areas is evident, which could happen because it diffuses towards the scale and later on into the molten salts.

(a)

(b)

(c)

Fig. 9: (a) Photomicrograph of Fe40Al+10Al₂O₃+0.1B alloy freely corroded in Na₂SO₄ at 1173 K during 5 days and chemical mappings of b) Aluminum and c) Sulfur.

(a)

(b)

(c)

Fig. 10: (a) Photomicrograph of Fe40Al+10Al₂O₃+0.2B alloy freely corroded in Na₂SO₄ at 1273 K during 5 days and chemical mappings of b) Aluminum and c) Sulfur.

4. DISCUSSION

The degradation of the Fe40Al base intermetallics can be explained based on its electrochemical mechanism. In general, any process of corrosion to high temperature depends on two electrochemical reactions, that is to say, the oxidation of the metal, which can take the place of an anode to form metal ions,

and the reduction of the species oxidizers in the cathode taking to the reduction of species,

These two reactions can be measured by using the corrosion current density. During the corrosion process, all the electrons are given of the anodic reactions and they are consumed by the cathodic reactions. As a result, the system of the electrode will have mixed potentials in its potential of corrosion. At this potential, the reaction of the anodic process is similar to the cathodic reaction. The current density corresponding to this reaction regimen can be examined by electrochemical methods as it is the method of LPR. The corrosion current measured can be converted this way to instantaneous corrosion rate measurements of the material.

With the establishment of the Al_2O_3 layer, the corrosion rate decreases. The predominant surface product that forms between 873 and 1273 K has been reported to be $\alpha-Al_2O_3$, /16/, but it is quite possible for $\gamma-Al_2O_3$ or $\theta-Al_2O_3$ to exist in this temperature range /17/. These forms of alumina are the fast growing, more voluminous, more porous and less protective than $\alpha-Al_2O_3$ /18/. The temperature at which there is a transition from other types of alumina to the slower growing $\alpha-Al_2O_3$ appears to be 1173 K /19/. On the other hand, the formation of Al_2O_3 consumes a certain quantity of Al, reducing its activity and partial pressure of the oxygen. This causes a relative increase in the activities of the Fe and the S, driving them to react with the molten mixture and to obtain a compound such as FeS.

The corrosive activity of a mixture depends on its

electric conductivity. As is to be expected, as the temperature is increased, the mobility of the ions of the salt is increased, and thus also the conductivity. Zheng /14/ found that the conductivity of a mixture of Na_2SO_4 -(mass.% 0-30) $NaVO_3$ was increased with the temperature in a range from 1150 to 1220 K. Another important characteristic of the molten salts was their character acid-basic, where the $SO_3(g)$ is the sour component in the sulphates. These characteristics, based on the concept of their ability to donate load or to accept it electronically, suggest that, for example in the molten Na_2SO_4 , it has the following balance:

and the activity parameters and partial pressure are:

$$\begin{aligned} \log a_{Na_2O} + \log P_{SO_3} &= \Delta G_2^\circ / 2.303RT \\ &= -16.7 \text{ at } 1200 \text{ K.} \end{aligned} \quad (6)$$

where the parameter $-\log a_{Na_2O}$ can be taken as a measure of the salt basicity. In accordance with the previous expressions, is obvious to consider to $-\log a_{Na_2O}$ (basicity) and $\log P_{SO_3}$ (acidity) for Na_2SO_4 , besides the partial pressure of the SO_3 in balance with Na_2SO_4 fixed the activity of Na_2O or the melting basicity /19-21/. Keeping in mind that balance in the molten salt, the following reactions can be presented in the metallic interface:

which generates the conditions for reaction carried out:

and in the oxide/molten salt interface the basic dissolution for reaction occurs /17/:

The hot corrosion in molten salts usually exhibits selective attack and internal oxidation. The scale dissolution in a melt, in terms of the acidity or basicity of the salt, results in the film becoming less protective, and the corrosion rate is increased. In addition to the

dissolution of the protective scales, there appeared to be a dissociation of the Na_2SO_4 , increasing the concentrations of Na_2O in the melt, and later on, with diffusion of Na and S, an increase of these elements in the metal/scale interface. This caused the detachment and cracking of the protective scale, allowing the corrosion of the material. This phenomenon was equally observed on the other intermetallic materials at 1273 K which presented high corrosion rates and a significant metal degradation. This explains the values of the anodic current density values that were observed in Figs. 3 and 4.

5. CONCLUSIONS

The results of exposing atomized Fe40Al-base intermetallics to molten Na_2SO_4 have shown that, at both 1173 and 1273 K, the Fe40Al+10Al₂O₃ material exhibited a higher corrosion rate than those alloyed with boron. The additions of up to 0.4B, for short times made the E_{corr} value more active but after some hours, all the E_{corr} values became more noble, even nobler than the alloy without boron. None of the alloys showed a passive region, at least at short times. In terms of corrosion rate, additions of boron always decreased this value as opposed to the alloy without boron, especially at 1273 K, but the corrosion rate values decreased rapidly, attaining a constant value, which was consistent with the establishment of a protective alumina, Al₂O₃ layer, and promoted an Al depletion on the FeAl matrix which allowed internal sulfides formation.. It seems that the optimum amount of boron that gives the best corrosion resistance is 0.1B

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