Effect of Boron on the Hot Corrosion Resistance of Sprayed Fe40Al Intermetallics

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ABSTRACT

The corrosion resistance of three Fe40Al+10Al_2O_3-based sprayed intermetallic alloys with different boron contents in molten sodium sulfate (Na_2SO_4) and sodium metavanadate ($NaVO_3$) has been evaluated using the weight loss technique. Boron content was 0.1 (at.%), 0.2 and 0.4 and the temperature varied from 873 K to 973 K for $NaVO_3$, and from 1173 K to 1273 K for Na_2SO_4 at 25 K intervals. The tests were also supported by electronic scanning microscopy and microanalysis. In all cases, less corrosion resistance was obtained in the alloy with 0.4 B, whereas good corrosion resistance was found in the alloy with 0.1 B. The results were discussed in terms of dissolution of the external Al_2O_3 layer by the salt and internal sulfidation.

Key words: deposited Fe40Al, molten Na_2SO_4 and $NaVO_3$, hot corrosion.

1. INTRODUCTION

The corrosion of metallic components resulting from molten salts is a serious problem for systems using fossil fuels such as boilers, gas turbines, furnaces, etc. Fossil fuels have sulfur (S), vanadium (V) and sodium (Na) and then some low melting point compounds are formed during combustion /1/. These compounds are deposited on the hot surface of the metallic component, forming a stable electrolyte and, at high temperatures, they may lead to catastrophic corrosion. The corrosion behavior of materials in molten salts has not been widely investigated in comparison to the case in aqueous solution, but it is undoubtedly 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 molten salt with alloy, and iv) the reaction of impurities in the molten salt with the alloy /1/. In particular, the damage generated by corrosion in heat exchanger systems, incinerators and burners is considered to be, 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 (K_2SO_4) and vanadium pentoxide (V_2O_5) /2/, mixtures of sodium sulfate and vanadium pentoxide (Na_2SO_4+V_2O_5) /3/, sulfates, chlorates and carbonates /4,5/.

The melting point, characteristics and properties of intermetallics are found to differ from the original elements. Fe40Al-base intermetallics in the presence of molten salts present better corrosion resistance when compared with common alloys /6/. The corrosion of iron aluminides in molten $NaNO_3(KNO_3)$-Na_2O_2 at 973 K proceeds by oxidation, and a low release from an aluminide-rich product layer into the salt such that the compositions with higher aluminum concentrations yielded significantly better corrosion resistance /7/. The preliminary results for the FeAl in molten NaCl-Na_2CO_3 at 1173 K (used as an oxidizer for waste disposal), showed significantly better corrosion resistance than was the case with Inconel 600 /8/.

The Fe40 (at.%)Al-base intermetallics have been evaluated in a mixture of molten salts of 80mass.% V_2O_5 + 20mass% Na_2SO_4 at 873, 973 and 1073 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 /9/. The same intermetallics were evaluated in $NaVO_3$ at 898 and 973 K, where the main cause of the reduction of the corrosion rate was the fast formation of a layer of Al_2O_3 with increasing temperature /10/ and it was found that additions of 0.1at.% made the corrosion resistance still better Similar results were obtained by Tortorelli /6/ for Fe_3Al_2Cr alloy in molten Na_2SO_4 at 923 K and 973 K for the period of 800 hours.

The objective of this work is to study the corrosion resistance of atomized Fe40Al+10Al_2O_3 intermetallics with different boron contents in molten salt found in oil-fired power stations using the weight loss technique.

2. EXPERIMENTAL PROCEDURE

The materials tested in this work were prepared by atomizing Fe40(at.%)Al+10Al_2O_3 with 0.1, 0.2 and 0.4 B. A master alloy of Fe40Al was fabricated in an induction furnace under an argon atmosphere from pure iron and aluminum, both of 99.99% purity and it was cast by gravity into a cylindrical graphite mold of 40 mm in diameter. Small pieces of test specimen were cut from master alloy bar, and fed to the spray atomization and deposition system. Boron of 99.99% purity in the form of Ni_2B was used as a microalloying constituent. The commercial single crystal of α-Al_2O_3 platelet with an average diameter of 3 μm was employed as a reinforcement phase. The preparation of the Fe40Al alloy and the experimental variables used for spray atomisation and deposition were described in detail elsewhere /11/.

Standard weight loss measurements (gravimetric) were carried out after exposing the rectangular specimens with 10 mm long, 8 mm width and 3 mm thick for the period of 10 days. The working salts were of analytical grade Na_2SO_4 and $NaVO_3$. The testing temperatures were chosen from 898 K to 973 K for $NaVO_3$ and from 1173 K to 1273 K for Na_2SO_4 at intervals of 25 K. In addition to these tests, 4 tests at 873 K and 973 K for $NaVO_3$, and at 1173 K and 1273 K for Na_2SO_4, in which one specimen was taken out every 24 hours, were carried out. The corrosion products were removed before the final weighing by immersing the specimen in 15(mass%) ammonium citrate at 343 K. Scanning electronic microscopy studies as well as x-ray mappings were also carried out on selected specimens. For this purpose, the specimens were mounted in cross section, metallographically polished and analyzed in an energy dispersive X-ray (EDX) attached to a scanning electronic microscope (SEM) system. The amount of molten salt in each run was 5×10^{-1} mg/m^2 in a furnace with a capacity up to 1373 K for all experiments.

3. RESULTS AND DISCUSSION

The change of weight loss of three alloys in $NaVO_3$ at 898 K are shown in Fig. 1 as a function of time and the results at 973 K are shown in Fig. 2, respectively. In both cases a monotonic increase with time is observed, but after 216 hours (approximately 9 days) this weight gain increases abruptly. The final weight loss at 973 K is almost twice as high as the case at 898 K (note: the melting point for this compound is around 873 K). This suggests the so-called incubation time before catastrophic corrosion takes place. The increase in weight loss with time at 973 K during incubation time is distinct, in comparison with that of 898 K.

As shown in the results of Figs. 3 and 4, a similar change in weight loss was found in Na_2SO_4 at 1173 and 1273 K. However, the following observation is considered to be worthy of note. Except for the alloy containing 0.1B, no appreciable increase in weight loss at 1173 K was observed during the first 216 hours, but beyond that time an abrupt increase is observed. This is attributed to the fact that the melting point of Na_2SO_4 salt is 1168 K. Since this salt is completely melted at 1273 K, the weight loss at 1273 K given in Fig 4 increases more rapidly with time. The final value (0.6×10^4 mg/m^2) of weight loss is higher than that obtained at

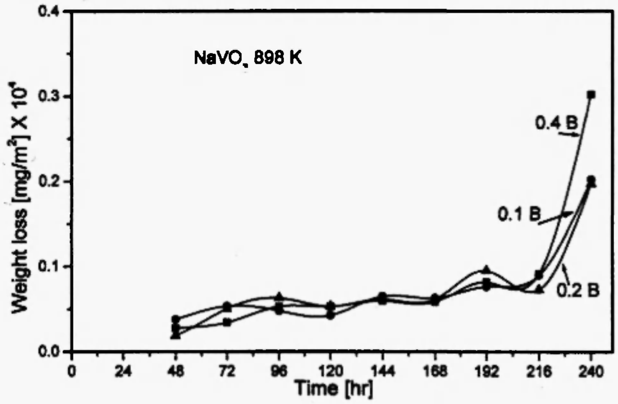

Fig. 1: Effect of B contents on the change of weight loss with time for Fe40Al alloy corroded in NaVO$_3$ at 898 K.

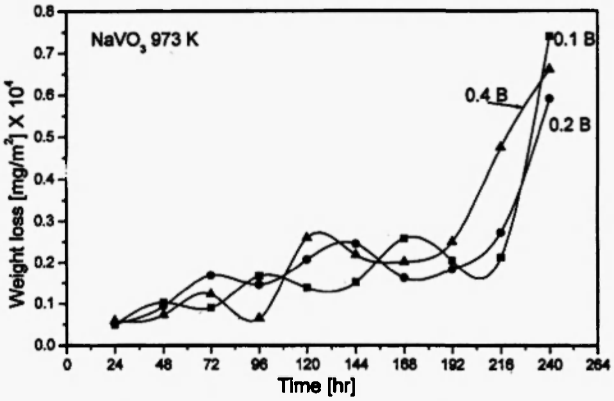

Fig. 2: Effect of B contents on the change of weight loss with time for Fe40Al alloy corroded in NaVO$_3$ at 973 K.

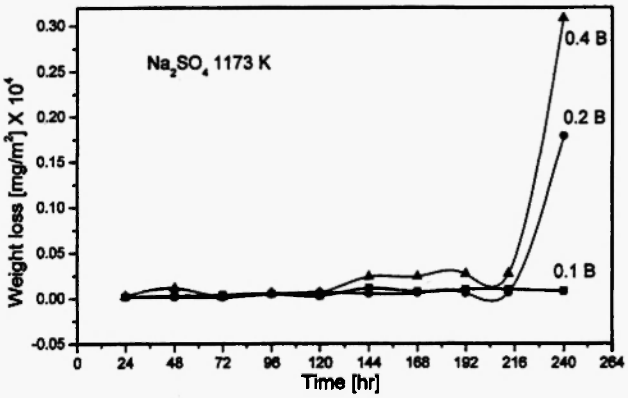

Fig. 3: Effect of B contents on the change of weight loss with time for Fe40Al alloy corroded in Na$_2$SO$_4$ at 1173 K.

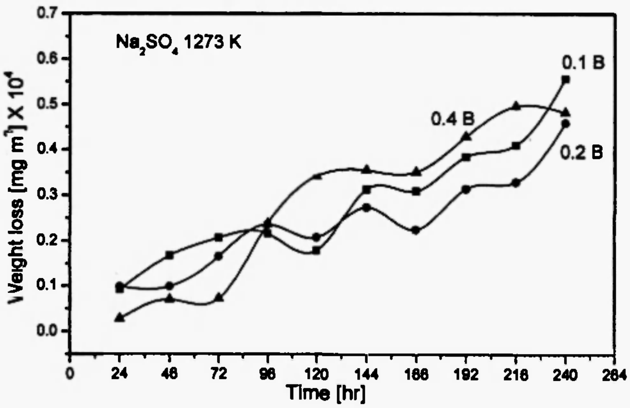

Fig. 4: Effect of B contents on the change of weight loss with time for Fe40Al alloy corroded in Na$_2$SO$_4$ at 1273 K.

1173 K (0.30×10^4 mg/m^2). It is worth mentioning that the final values of weight loss obtained in the tests at lower temperature with NaVO$_3$ salt are found to be very similar to the case with Na$_2$SO$_4$ salt. In the tests at higher temperature, an almost identical conclusion is obtained.

The change in weight loss of alloys with three different B contents after 10 days in NaVO$_3$ is given in Fig. 5 as a function of temperature. The weight loss is not detected at 898, 923 and 948 K for three alloys. However, an abrupt increase is observed for three alloys at 973 K. The amount of weight loss is found to increase with increasing boron content. Similar behavior was obtained in the Na$_2$SO$_4$ case, as shown in Fig. 6. It is again worth mentioning that better corrosion resistance of the alloy containing 0.1 B in comparison with alloys containing 0.2 and 0.4 B.

The cross sections of the Fe40Al-10Al$_2$O$_3$-0.2B and Fe40Al-10Al$_2$O$_3$-0.1B intermetallic alloys corroded in NaVO$_3$ at 973 K are presented in Figs. 7 and 8 respectively together with their X-ray mappings of Al and V. These results clearly indicate that an external layer containing Al is formed in the corrosion products. The presence of V component is also shown in these layers. This indicates that the corrosive salt uniformly degraded the alloy and no further attack is then detected in the specimens.

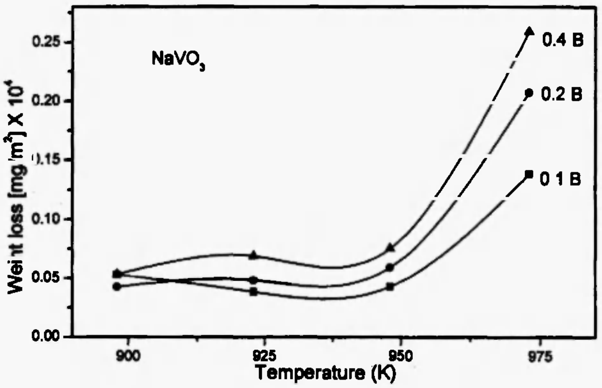

Fig. 5: Effect of B contents on the change of weight loss with temperature for Fe40Al alloy corroded in $NaVO_3$ during 10 days.

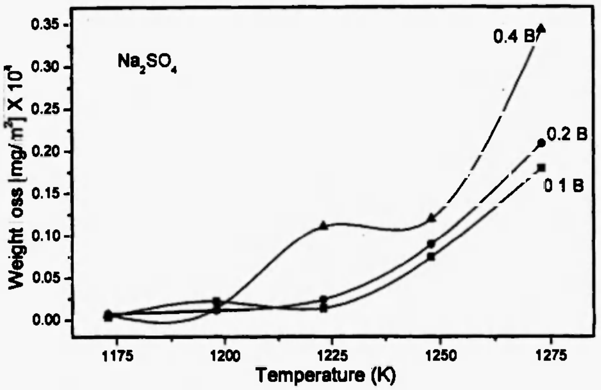

Fig. 6: Effect of B contents on the change of weight loss with temperature for Fe40Al alloy corroded in Na_2SO_4 during 10 days.

On the other hand, Figs. 9 and 10 show the cross sections of Fe40Al-10Al_2O_3-0.2B and Fe40Al-10Al_2O_3-0.4B corroded in Na_2SO_4 at 1273 K respectively together with their X-ray mappings of Al, and S. In this case, the external layer is considered to consist mainly of Al and S, but some internal sulfidation is observed in the Fe40Al-10Al_2O_3-0.2B alloy. It is very likely that sulfur penetrates into the alloy through the layer containing Al, by dissolving and attacking the substrate. No attack, however, was found on the grain boundaries, like in some other alloys such as the Cr-containing alloy

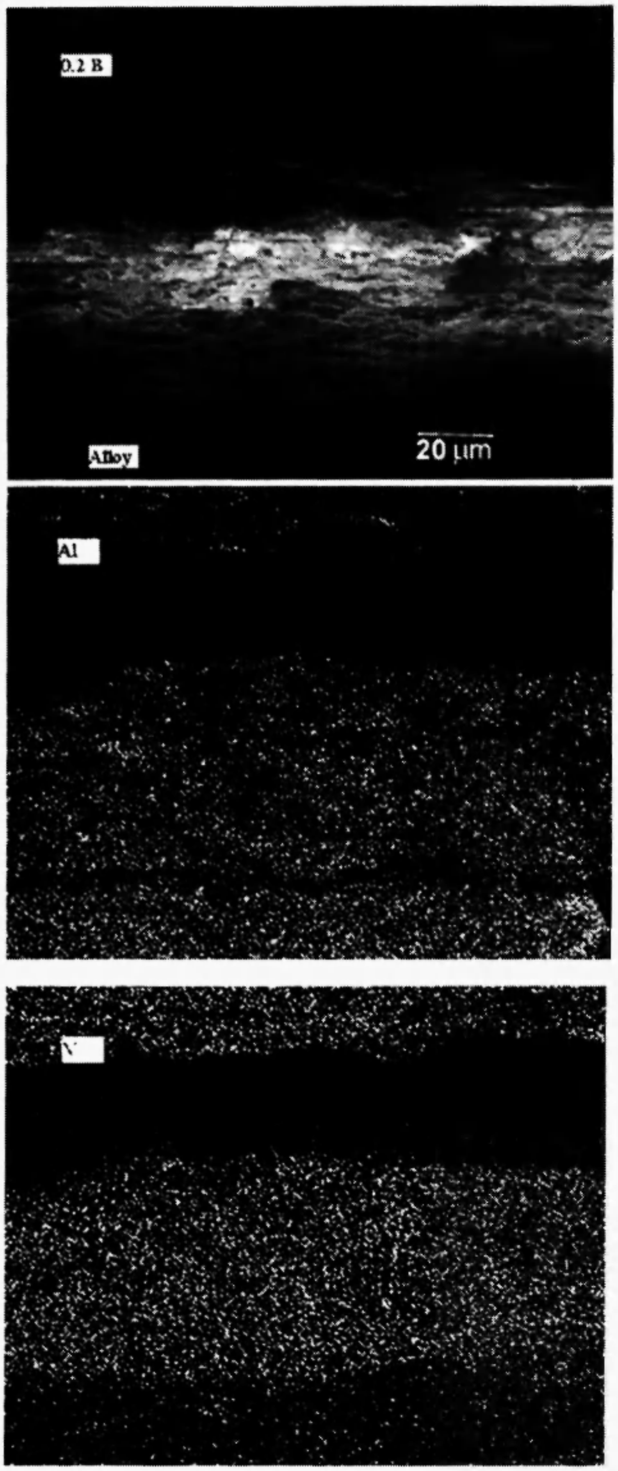

Fig. 7: Cross section of Fe40Al-10Al_2O_3-0.2B corroded in $NaVO_3$ at 973 K. and X-ray mappings of Al, and V.

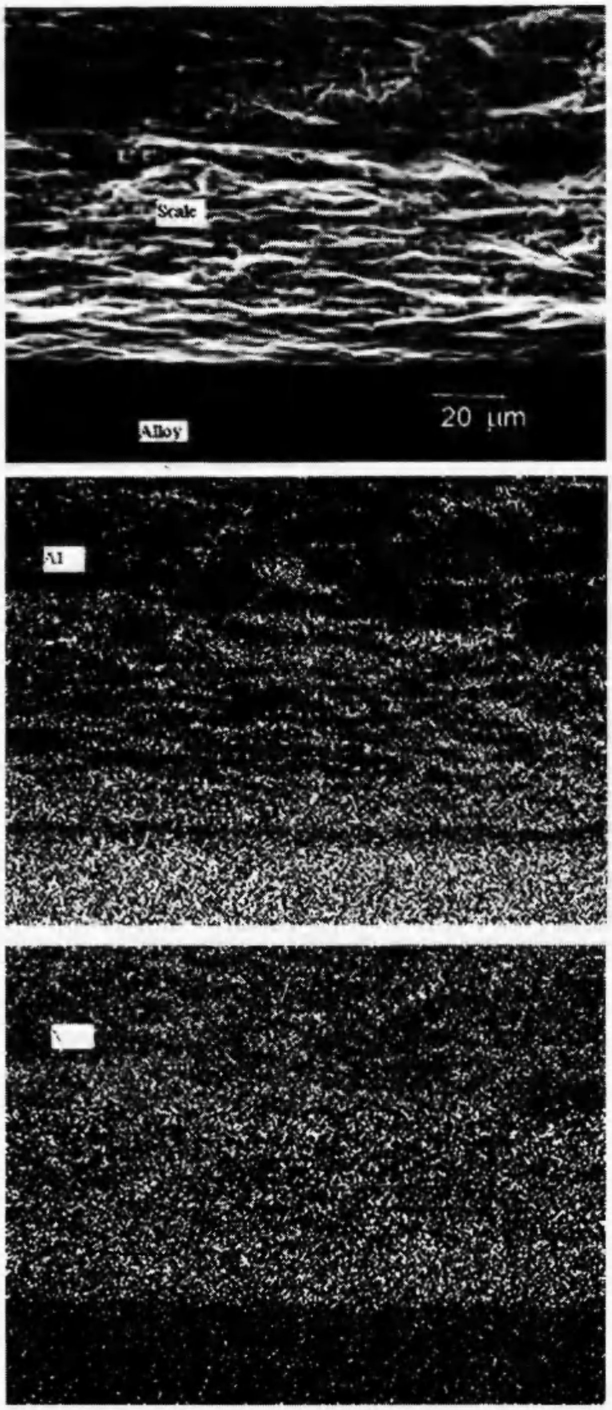

Fig. 8: Cross section of Fe-40Al-10Al_2O_3-0.1B corroded in $NaVO_3$ at 973 K. and X-ray mappings of Al, and V.

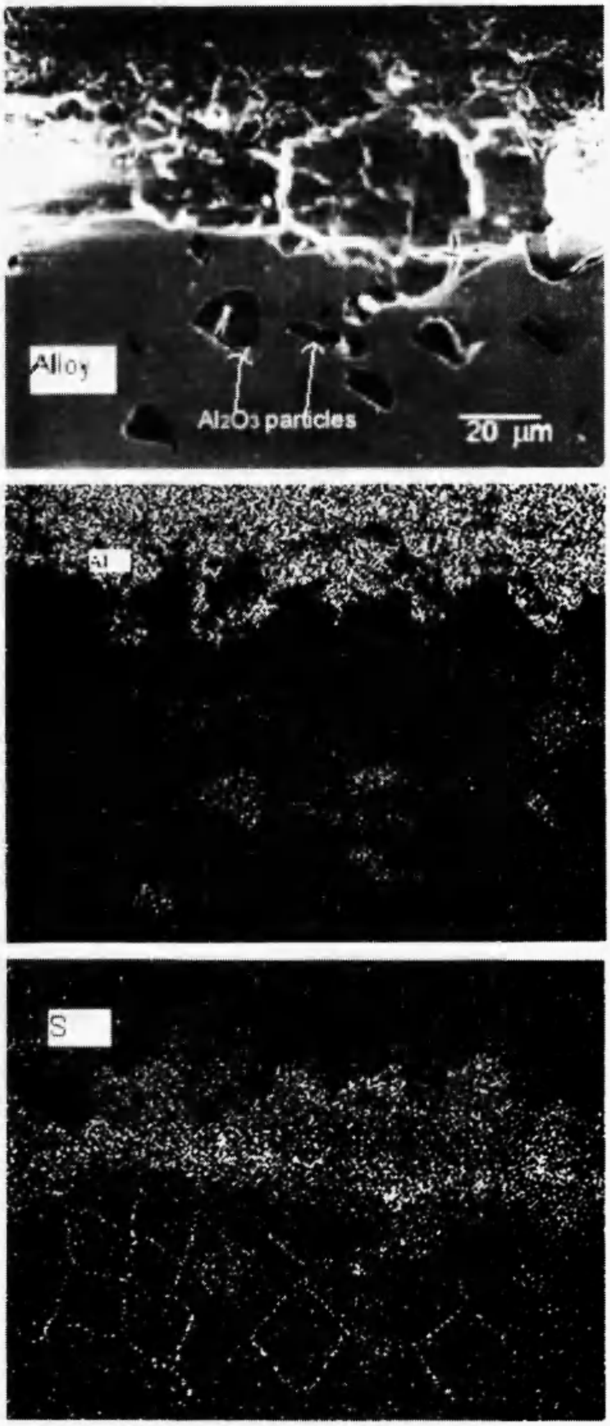

Fig. 9: Cross section of Fe-40Al-10Al_2O_3-0.2B corroded in Na_2SO_4 at 1273 K. and X-ray mappings of Al, and S.

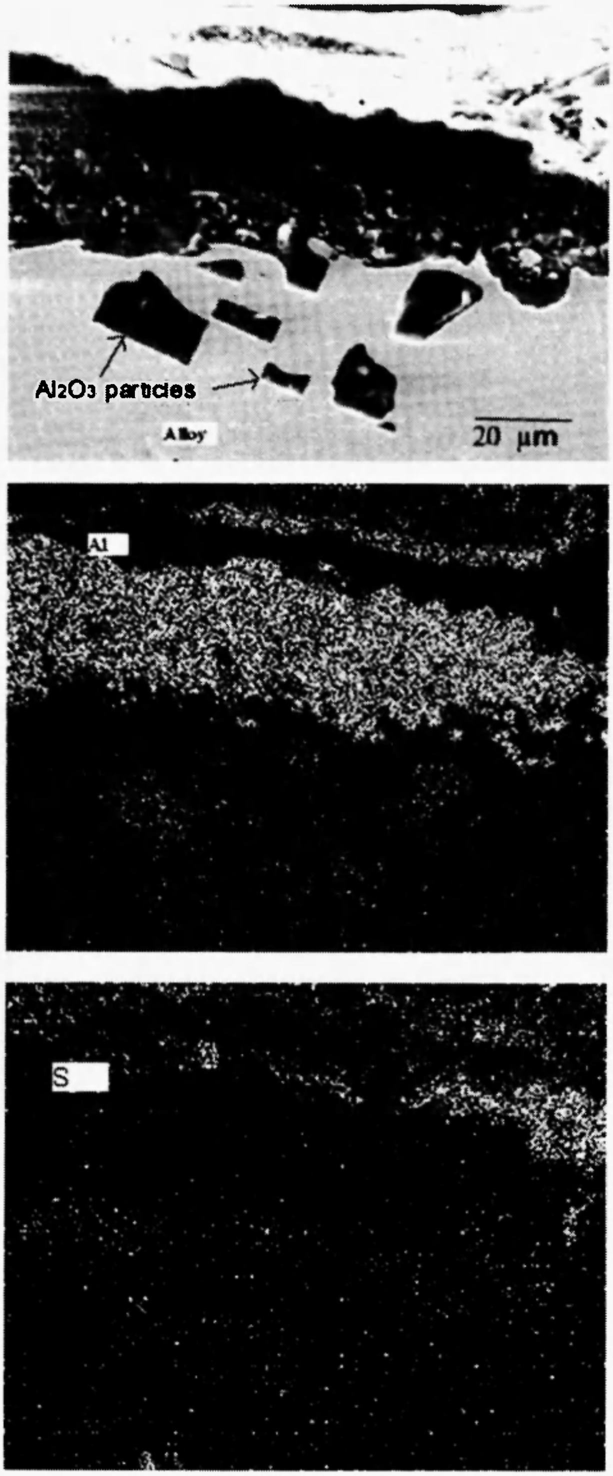

Fig. 10: Cross section of Fe-40Al-10Al_2O_3-0.4B corroded in Na_2SO_4 at 1273 K. and X-ray mappings of Al, and S.

case, as a result of sensitization /8/. Some dark particles are also seen, and an EDX analysis shows the presence of Al and O, indicating alumina particles. Thermal gradients in the melt can provide an opportunity for metal dissolution in hot spots and metal deposition in cold spots. The result is very similar to the galvanic corrosion in aqueous solution systems and a continuous electric path may be given among the hot and cold areas. Corrosion has been observed by cavities because the attack in the interface lines due to oxygen is not very common in the metal/molten-salt/air interface /1/.

In the specimens tested at 1273 K there is aluminum and sulfur found in an external layer 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. Sulfur preferably reacts with aluminum (of more activity) to form a compound, presumably Al_2S_3 /14/. On the other hand, sodium was not related to the protective scales. At 1173 K three alloys with a protective layer of Al_2O_3, show the relatively lower corrosion rate in comparison with the case at 1273 K

Because the corrosion reaction in molten salts is known to be controlled by a process of oxidation of metal as well as its reduction, information of the relative activity of molten salts with metal is important. It is also noted that the corrosion potential of metal frequently depends on the impurities in molten salt or gas phase, which increase the rate of cathodic reaction and influence the change of the basicity or acidity of molten mixture /1/. These factors could bring about the dissolution of metals and such dissolution can take place by two mechanisms, the local dissolution or the selective dissolution of the different components of oxide. In the first case, the growth rate of the protective oxide layer will be smaller than the gas corrosion case /15/. On the other hand, when the selective dissolution takes place, structural stability of the scale is no longer maintained by losing some elements or components and this induces cracking and spalling of the scale.

At 1273 K the iron aluminides show severe corrosion and this is particularly true in the case of Fe40Al+0.4B. As shown in the results of Figs. 9 and 10, sulfur was infiltrated in the Fe40Al alloys under the external aluminum oxide, which was thicker than the layers observed at 1173 K. The higher concentrations of Al and S observed inside the alloy may be characterized by internal sulfidation generated by sulfates /1/. This sulfidation could be described by 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 alloys. Sodium was also detected in the scale in the experiments with two salts and its distribution is found to be in the metal/scale interface, similar to the case with sulfur. The scale was detached from the alloy by infiltration of molten Na_2SO_4 and this might be one reason for severe corrosion in this case. The scale dissolution is likely to be related to the acidity or basicity of molten salt and it results in decreased protection of the scale and an increase in corrosion rate. Additional important factors may be given as follows: the dissociation of Na_2SO_4 increasing the Na_2O concentration in the melt, diffusion of the components such as Na and S and their increase in the metal/scale interface. These factors cause the detachment and cracking of the protective scale, and then the degradation is considered to start with the alloy oxidation as well as formation of an external oxide layer (or mixture of oxides, i.e. Fe_2O_3 and Al_2O_3). After this, the oxide layer is dissolved by molten salt so as to contact directly the reactive elements (V, S, etc.) with other components. Some elements such as sulfur also start to penetrate into the alloy, causing catastrophic corrosion.

4. CONCLUSIONS

The corrosion rate in molten salts of atomized $Fe40Al+10Al_2O_3$ with different boron content of 0.1, 0.2 and 0.4 at % has been examined using the weight loss technique and the following conclusions were obtained.

1. In two salts of $NaVO_3$ and Na_2SO_4, the corrosion rate of alloys always increased with increasing boron content and such behavior is found with increasing temperature.
2. The so-called incubation period, at which catastrophic corrosion was clearly detected, was found in all cases with three alloys and two salts, and such severe corrosion was observed in specimens after 9 days test, regardless of the chemical composition or temperature.
3. The critical temperatures, at which the corrosion rate abruptly increased, were also found and they were 948 K for $NaVO_3$, and 1248 K for Na_2SO_4.
4. In both salts, the corrosion process was attributed to the dissolution of the external oxide layer by salt. In the case of Na_2SO_4, however, the corrosive salt could penetrate underneath such an oxide layer, and this resulted in the internal sulfidation.

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