

Short communication

Effect of heat treatment and chemical composition on the corrosion behavior of FeAl intermetallics in molten (Li + K)carbonate

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Abstract

The corrosion performance of various Fe–Al alloys in 62 mol. %Li₂CO₃–38 mol.%K₂CO₃ at 650 °C has been studied using the weight loss technique. Alloys included FeAl with additions of 1, 3 and 5 at.% of either Ni or Li with or without a heat treatment at 400 °C during 144 h. For comparison, 316L type stainless steel was also studied. The tests were complemented by X-ray diffraction (XRD), scanning electronic microscopy and microchemical studies. Results showed that FeAl base alloy without heat treatment had the highest corrosion rate but by either heat treating it or by adding either Ni or Li the mass gain was decreased. When the FeAl base alloy was heat treated and alloyed with either 5Ni or 1Li the degradation rate reached as low values as those found for 316L stainless steel which had the lowest degradation rate. Both Ni and Li improved the adhesion of external protective layer either by avoiding the formation of voids or by lowering the number of precipitates and making them more homogeneously distributed.

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1. Introduction

Conventional molten carbonate fuel cells (MCFC) operate at 650 °C and consist of several cells made of a porous, lithiated NiO cathode, a molten (Li,K)₂CO₃ electrolyte in a LiAlO₂ ceramic matrix and a porous Ni anode [1,2]. Austenitic stainless steels such as 310S, 316 or 316L are typically used for cathode current collectors and bipolar separator plates [3–6]. Corrosion of these components still represents a serious technological item that may adversely affect the useful lifetime of the fuel cell [7–10]. The corrosion resistance of stainless steels and Ni-based alloys in these environments is, thus, limited. Several efforts have been undertaken recently to overcome this problem. Perez et al. [11] for instance, protected 310S type stainless steels and TA6V titanium alloy by slurry aluminides and used electrochemical impedance spectroscopy to characterize their

corrosion resistance. They found that a slurry aluminide coating was able to improve the stainless steel corrosion behaviour in molten carbonate. Aguero et al. [12] used the thermal spray coating technique to deposit NiAl, AlCoFeCr and FeCrAl coatings onto 310 type stainless steel. Results showed that FeCrAl exhibits a higher molten salt corrosion resistance than aluminide coatings whereas NiAl was attacked at the beginning of the test. Frangini and Masci [13] used the electrospark technique to deposit FeAl based coatings onto 316L type stainless steel. They found that the corrosion resistance of electrospark coatings is comparable to that of ion deposition technique coating and higher than uncoated stainless steel.

FeAl type intermetallics are widely used for their high temperature oxidation resistance due to their ability to develop an Al₂O₃ protective layer, which also provides corrosion resistance in molten salts [14,15]. However, one of the main drawbacks for these aluminides is their poor ductility. Salazar et al. [16] found that by alloying with either Li or Ni results in the improvement of their ductility as measured in their compressive ductility, and this improvement was increased if the specimens were annealed

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at 400 °C during 120 h. The aim of this work is, thus, to evaluate the effect of small additions of Li and Ni together with a heat treatment on the corrosion resistance of FeAl in molten (Li,K)₂CO₃ at 650 °C and compare them with that for 316L type stainless steel, a commonly used material in bipolar plates in MCFC.

2. Experimental procedure

Intermetallic Fe₅₀Al₅₀ alloy were melted in an induction furnace using silicon carbide crucibles. Pure Li and Ni elements with 1, 3 and 5 at.%, respectively were added to the AlFe intermetallic compound. All elements were 99.9% of purity. In order to avoid the specimens machining procedure the ingots were obtained with ending dimensions according to the E800b ASTM standard. Cylindrical specimens dimensions were 0.5 in. diameter × 2 in. length in the test section and 2.5 in. for the final section. The ingots were homogenized to minimize the thermal vacancy effects by heat treating them (HT) at 400 °C during 120 h under an argon atmosphere. The corrosive agent used in the tests was synthetic potassium carbonate (K₂CO₃) and pure lithium carbonate (Li₂CO₃) with the composition 62 mol. %Li₂CO₃-38 mol.%K₂CO₃ at 650 °C. All the reagents were analytical grade. Before corrosion tests the specimens (30 mm × 20 mm × 1 mm) were cleaned with acetone and dried and then packed in the mixture of salts in porcelain crucibles with 500 mg cm⁻² of the synthetic salt. Coupons were completely immersed in the carbonate salt. The corrosion tests were carried out in electric furnaces in a static air during 100 h. After the corrosion tests, the corrosion rate was measured as weight loss. Three specimens of each condition test were decaled and chemically cleaned according to ASTM G1 81 standard. One of each heat was mounted in bakelite in cross section and polished to analyze the subsurface corrosive attack using a scanning electron microscopy (SEM) aided with energy dispersive spectroscopy (EDX) to carry out micro chemical analysis. Finally, the corrosion products of some specimens were analyzed in a Phillips X-ray diffractometer.

3. Results and discussion

Fig. 1 shows the mass loss of the different materials after exposure beneath a molten (Li,K)₂CO₃ deposit during 100 h at 650 °C. It can be seen that the FeAl base alloy without heat treatment suffers the greatest mass loss, whereas 316L stainless steel and the heat treated alloy containing 5Ni had the lowest. By heat treating the FeAl base alloy decreased the mass gain for more than 50%, but it was still higher than 316L stainless steel. If the FeAl alloy without heat treatment was alloyed with either Ni or Li in any quantity, the corrosion rate was decreased, especially with 3%, where the improvement in the corrosion rate was the highest, i.e. 10 times. Heat treated FeAl with either 1Li or 5Ni had low corrosion rates too, very similar to the 316L stainless steel. It can be said that for unalloyed FeAl intermetallic, a decrease in the mass loss was obtained either by heat treating it or by additions of less than 5% of Ni or 1Li, but additions of 5% of this element increased the mass loss.

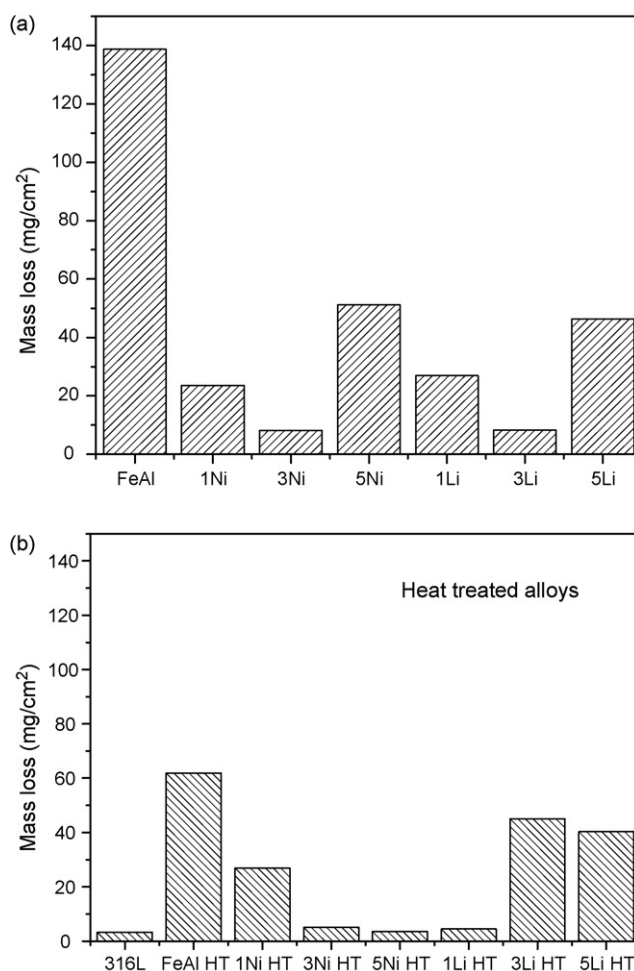


Fig. 1. Effect of Ni and Li contents on the mass loss in a 62 mol. %Li₂CO₃-38 mol.%K₂CO₃ mixture at 650 °C for (a) alloys without heat treatment and (b) alloys with heat treatment.

An SEM micrograph of the 3Li containing alloy without heat treatment is given in Fig. 2, showing the corrosion products layer. An EDX spot analysis done in point (a) and shown in Fig. 3 revealed that this point consisted of C, O Fe and some Al. XRD of the corrosion products showed the presence of the FeAl aluminate phase together with LiFeO₂, Fe₂O₃ and LiAlO₂ oxides, Fig. 4. LiAlO₂ has been reported to give some corrosion protection in molten carbonate mixtures [12,13] It was not detected the presence of a protective Al₂O₃ which maybe was consumed by the eutectic (Li,K)₂CO₃ deposit, and it was transformed in to LiAlO₂ and something similar occurred to the Fe₂O₃ deposit, which was converted in to LiFeO₂.

An SEM of the corroded surface of the heat treated alloy containing 3Li is shown in Fig. 5. A spot EDX analysis to the interface metal/deposit, point (c), revealed that it is rich in C, O and Al with some traces of Fe, Fig. 6. On the other hand, punctual EDX analysis in the middle of the deposit and in the outer part of the deposit showed that the content of C and O is similar to that found at the metal/deposit interface but the content of Al is much lower, which may indicate that at this interface there is some Al₂O₃ which has not been dissolved by the (Li,K)₂CO₃ deposit, although the XRD analysis did not reveal its presence,

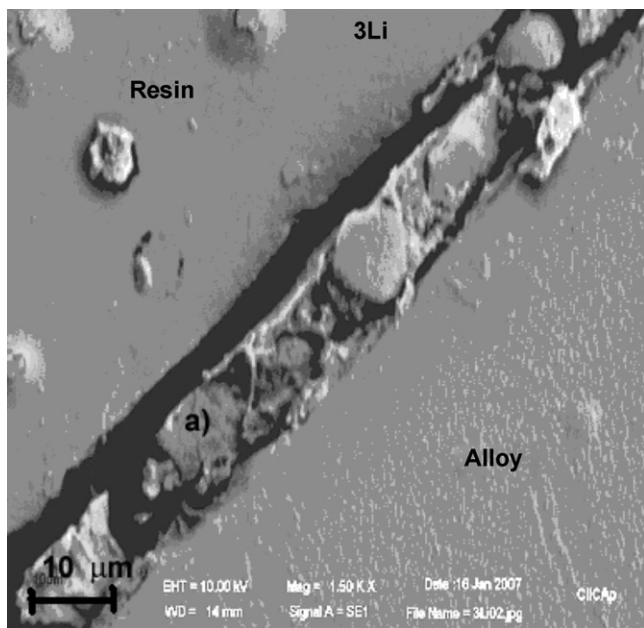


Fig. 2. Micrograph of FeAl+3Li corroded in 62 mol. %Li₂CO₃-38 mol. %K₂CO₃ at 650 °C showing in point (a) the corrosion products.

maybe because it was localized at this point only. The corrosion products consisted, again, of LiFeO₂, Fe₂O₃ and LiAlO₂ oxides and the FeAl phase, as shown in Fig. 7.

A cross section of the corroded surface for heat treated alloy containing 3Ni is shown in Fig. 8. This figure shows the presence of some pits, whereas a punctual EDX analysis done in points 1 and 2 revealed that they consisted of C, O and some Al, as shown in Fig. 9. The XRD analysis of the corrosion products consisted of the same phases found in the other specimens, i.e.

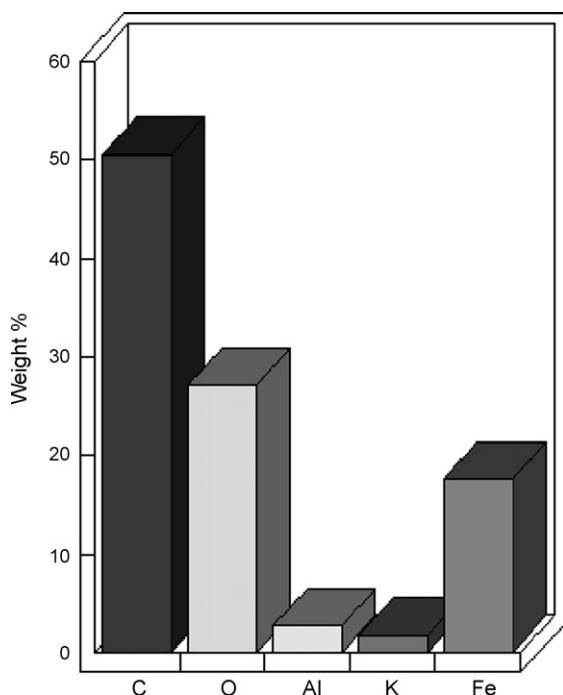


Fig. 3. EDX analysis for point (a) on Fig. 2.

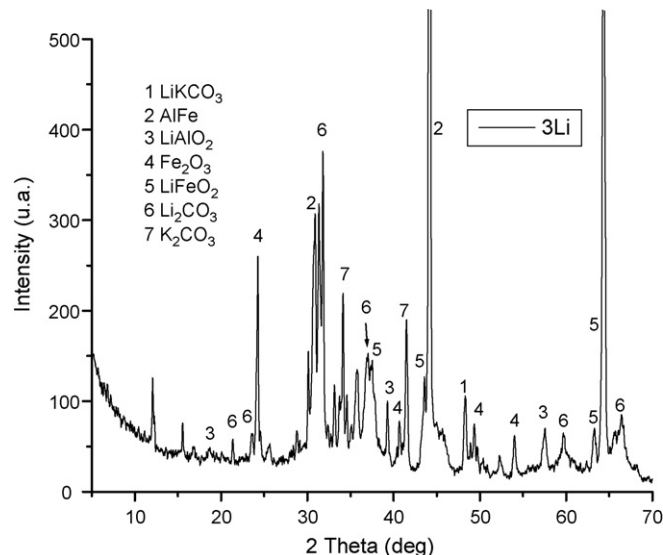


Fig. 4. XRD pattern for corrosion products found on FeAl+3Li.

LiFeO₂, Fe₂O₃ and LiAlO₂ oxides and the FeAl phase, as can be seen in Fig. 10.

Finally, a cross section of corroded 5Ni containing FeA alloy with X-ray mappings of C, Al, K, and O is shown in Fig. 11. It can be seen that the presence of aluminum together with oxygen outside the alloy suggests the formation of the protective alumina, Al₂O₃ layer. Also, we can see that elements of the molten salt, such as C and K, are not only outside the alloy, but they have penetrated and dissolved the Al₂O₃ layer, being present inside the alloy, which is evidence of the dissolution of the underlying alloy once the protective oxide, e.g. Al₂O₃ layer has been dissolved by the melt.

Nishima et al. [17] have shown that the first stage of the reduction of O₂ in the melt resulted in a CO₂ production with the reaction:

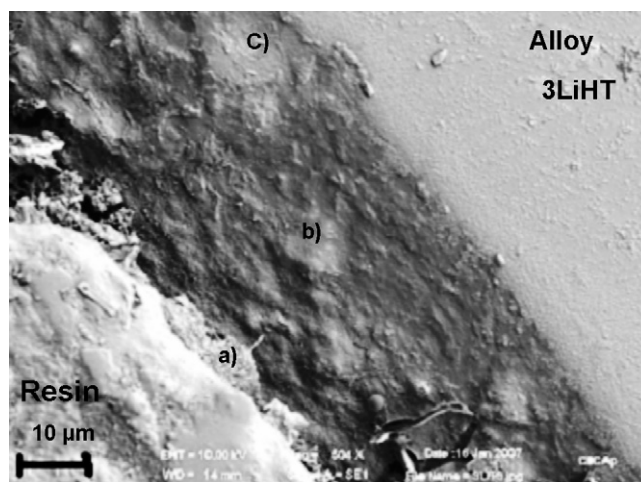


Fig. 5. Micrograph of heat treated FeAl+3Li corroded in 62 mol. %Li₂CO₃-38 mol. %K₂CO₃ at 650 °C showing in point (a) the molten salt, in point (b) the corrosion products and in point (c) the alloy-corrosion products interface.

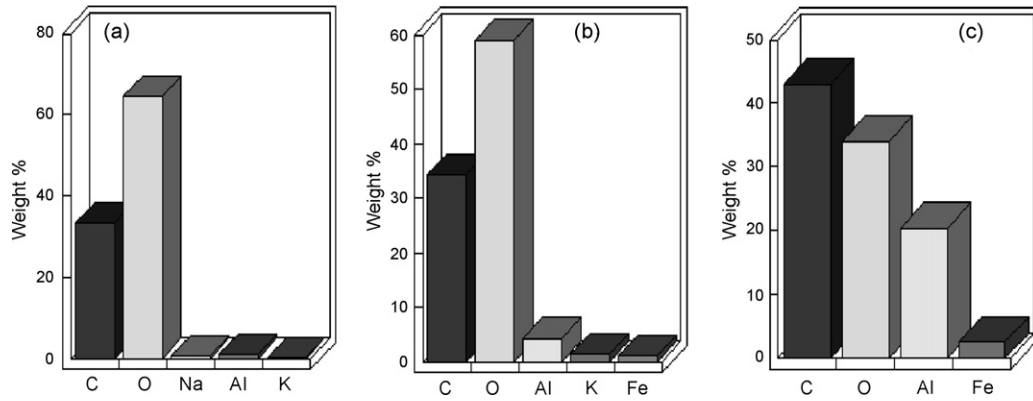


Fig. 6. EDX analysis of points (a), (b), and (c) on Fig. 5.

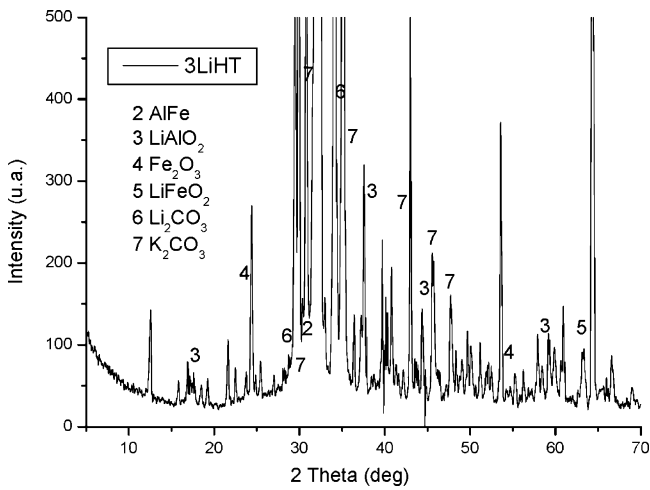
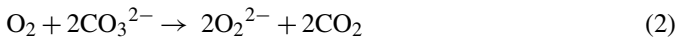


Fig. 7. XRD pattern for corrosion products found on heat treated FeAl + 3Li.



These reactions are governed by the acidity of the melt and, in the less acidic melts which correspond to our conditions, the reaction in Eq. (2) prevails, including a more important CO₂

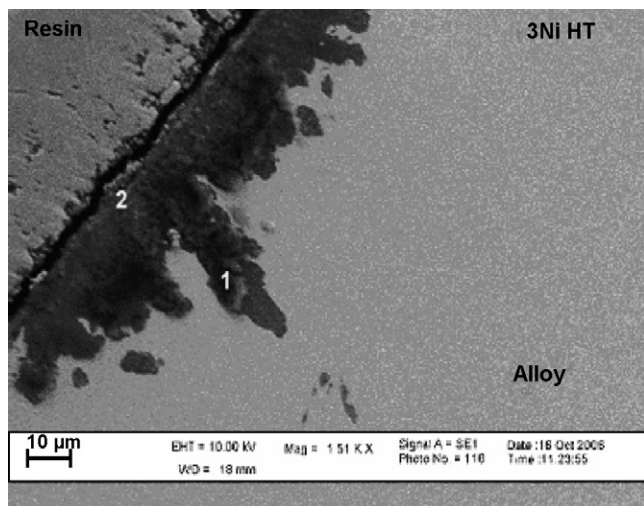


Fig. 8. Micrograph of heat treated FeAl + 3Ni corroded in 62 mol. %Li₂CO₃-38 mol. %K₂CO₃ at 650 °C.

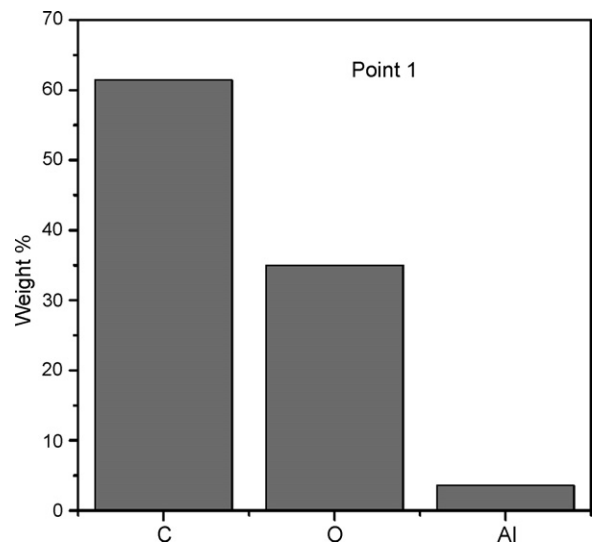


Fig. 9. EDX analysis of points 1 on Fig. 8.

formation in the melt. In the case of immersion of Al-rich alloys in molten carbonate, the following electrochemical reactions would take place:

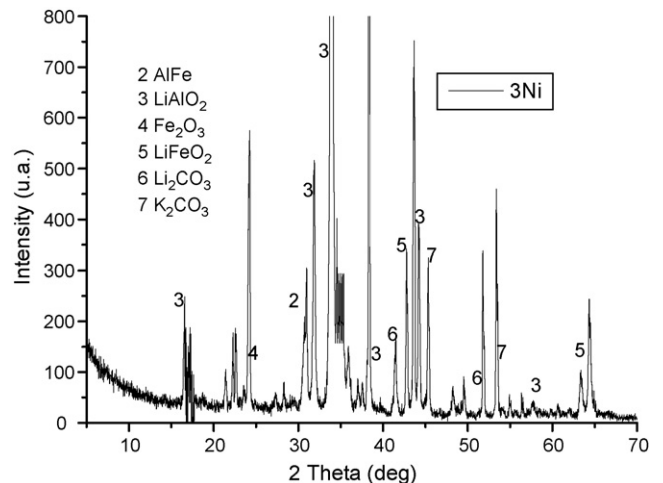
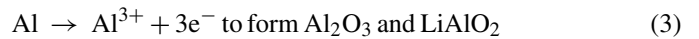


Fig. 10. XRD pattern for corrosion products found on heat treated FeAl + 3Ni.

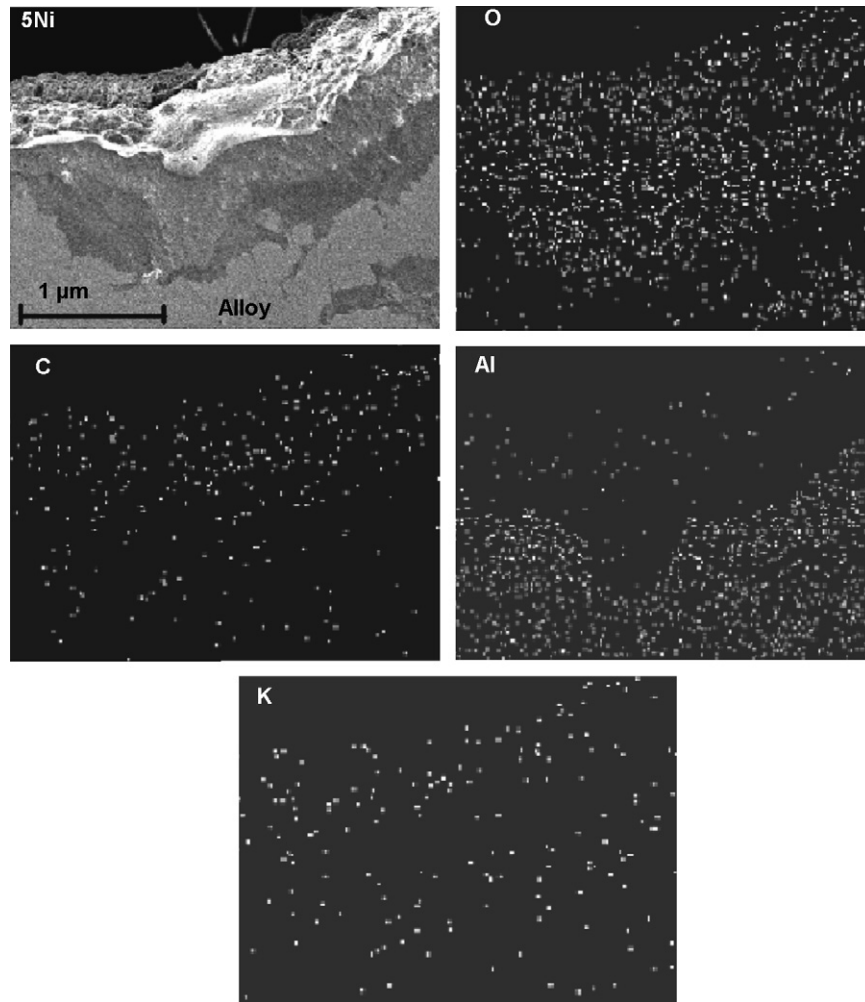
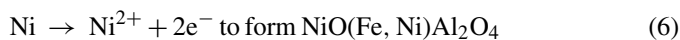
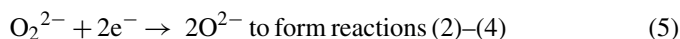
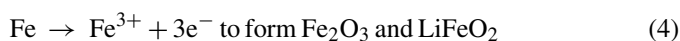


Fig. 11. Micrograph of FeAl + 5Ni corroded in 62 mol. %Li₂CO₃-38 mol.%K₂CO₃ at 650 °C together with X-ray mappings of O, C, Al and K.



but, since the amount of Ni present in the alloy is little, lower than 5 at.%, corrosion products given by reaction (6) were not detected neither by EDX nor by XRD analysis. The corrosion protection of an alloy against salt melt attack depends on the chemical stability of both the kind of metal and their compounds such as oxides, carbonates, etc . . . In fact, a breakdown of the protective oxide readily occurs by dissolution into the melt, and the degradation rate can be specially fast if the oxide has a high solubility. With the establishment of the Al₂O₃ layer, the corrosion rate decreases. The predominant surface product that forms between 600 and 800 °C has been reported to be α-Al₂O₃ [18] but it is quite possible for γ-Al₂O₃ or θ-Al₂O₃ to exist in this temperature range [19]. These forms of alumina are faster growing, more voluminous, more porous and less protective than α-Al₂O₃ [20]. The temperature at which there is a transition from other types of alumina to the slower growing α-Al₂O₃ appears to be 900 °C [20]. In the FeAl base alloy, the alumina whisker cannot

form a protective layer, which cannot provide an effective barrier to stop the diffusion of Fe and the diffusion to the interface of the oxygen, and this can be seen on the results obtained by the FeAl alloy which is higher than those obtained by the rest of the alloys (Fig. 1). On the other hand, the formation of Al₂O₃ consumes certain quantity of Al, reducing its activity and partial pressure of the oxygen. This causes a relative increase in the activities of the Fe driving it to react with the molten mixture and to obtain the compound such as LiFeO₂.

Frangini and Masci [13] have shown that additions of some ternary elements to FeAl intermetallics such as Cr or Ti improve the Al₂O₃ protectiveness by suppressing spalling of these scales. Additionally, they showed that, if Ni is added, there will be some diffusion of Ni outwards rather than diffusion inwards of Al, thus, preventing the formation of voids on the surface that could lead to a scale spalling. Normally, additions of Ni have been reported to increase the corrosion resistance of iron-base alloys in molten salts [15]. This corrosion resistance has been reported to be due to the establishment of a more stable passive layer in addition to the formation of voids as explained above.

It was shown elsewhere [16] that by adding Li, the precipitates present in the FeAl-base alloy were drastically lowered. In

unalloyed FeAl intermetallic there were elongated Fe₃AlC particles inside the grain boundaries together with Al₂O₃ particles along the grain boundaries. When Li was added, the amount of the precipitates was decreased, and they were spherical and homogeneously distributed. This more homogenous distribution of these particles could serve for a better anchoring of the protective external Al₂O₃ layer. In the same work, it was shown that by annealing the specimens, the formation of thermal vacancies was minimized, thus, if there were now less vacancies on the surface, the adhesion or anchoring of the protective alumina layer is now improved.

The scale cracking, spalling or dissolution in a melt, gives as a result that the film becomes less protective and, thus, the corrosion rate is increased. Additionally to the dissolution of the protective scales, the dissociation of the (Li,K)CO₃ allowed the diffusion of Li and K, and 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. Incorporation of ions such as Ni²⁺ and Li⁺ into the scale could improve the resistance of the oxide layer to the dissolution by the melt, and, thus, decrease the corrosion rate, as evidenced by Fig. 1 This explains the values of the corrosion rates that were observed in Fig. 1 for the FeAl + Li and FeAl + Ni alloys.

4. Conclusions

A study on the effect of heat treatment and additions of 1, 3 or 5 at.% of either Ni or Li on the corrosion performance of FeAl intermetallic alloy in molten 62 mol. %Li₂CO₃-38 mol.%K₂CO₃ at 650 °C has been carried out using the weight loss technique. Results showed that the FeAl base alloy showed the highest degradation rate whereas 316L type stainless steel had the lowest one. When the FeAl intermetallic alloy was heat treated at 400 °C during 144 h the corrosion rate was decreased by more than 50% but it was still much higher than the corrosion rate exhibited by the stainless steel. If the base alloy without heat treatment was alloyed with either Li or Ni the weight loss was decreased up to 10 times, reaching values close to those for 316L type stainless steel, especially with 3%. Finally, when the base alloy was heat treated and alloyed either with 5Ni or 1Li,

the degradation rate reached the lowest values, similar to those for 316L type stainless steel. This was because by adding Ni, the adhesion of external protective layer was improved by avoiding the formation of voids on the surface. Addition of Li, on the other hand, decreased the corrosion rate because it reduced the amount of particles precipitated and they were more homogeneously distributed, thus, a better anchoring of the external protective layer was promoted. Thermal annealing helped to reduce the corrosion rate by minimizing thermal vacancies and reducing the number of voids.

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