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NICKEL FERRITE – DOES IT HAVE POTENTIAL AS A SIDEWALL MATERIAL?

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Abstract

A great deal of work has been done on evaluation of nickel ferrite as a material for fabrication of inert anodes, usually as a component in a metal-ceramic composite. Its relatively good resistance to corrosion by cryolite rich baths has led to the suggestion that it might be feasible to use nickel ferrite as a sidewall material. This is a very attractive option, as elimination of the frozen ledge has significant benefits in terms of energy savings and increased productivity. However, very little work has been done to assess its suitability as a refractory material

Benchmark testing of the properties of nickel ferrite as a refractory have been conducted as part of a project funded by the CSIRO Flagship Cluster “Breakthrough Technology for Primary Aluminium”. Results of initial work confirm that the nickel ferrite spinel does have a relatively high resistance to attack by cryolite based baths, but the corrosion mechanism is complex, and is not yet understood. However, design of a corrosion resistant grain boundary phase may be the key to development of a successful spinel based refractory.

Keywords

nickel ferrite, sidewall refractory, Hall-Héroult cell, aluminium production

1.0 Introduction

In recent years there has been renewed interest in the sidewall materials used in the Hall-Héroult cell. Currently used carbonaceous or silicon carbide based sidewall refractories rely on the formation of a solid ledge of cryolite to help prevent attack. For this ledge to form and be stable, a large energy flux through the sidewalls is needed. This flux needs to be balanced such that the ledge is neither too thin, leading to attack of the sidewall; nor too thick, leading to unstable cell operation. However, in the context of improving productivity and reducing the environmental impact of the Hall-Héroult cell, this flux represents a large energy cost[1].

The high energy loss required to maintain the frozen ledge is one of several key issues identified as driving research related to the improvement of Hall-Héroult cells. Others include high maintenance and capital costs and the reduction of greenhouse gas emissions. However, the heat flux through the sidewall to maintain the frozen ledge is around 35% of the total input power [2], and therefore reducing this is a high priority. Eliminating the side ledge of

frozen electrolyte may also allow the use of larger anodes, which would increase the capacity and productivity of a cell of the same dimensions.

The properties that would be desirable in a new sidewall material for a “ledge free” cell can be divided into physical and chemical characteristics. Physical properties include low electrical and thermal conductivity, low porosity, resistance to thermal shock, mechanical strength, and abrasion resistance [4,5]. Chemical properties include low reactivity with cryolite and molten aluminium, very low solubility in cryolite and liquid aluminium, low wettability by cryolite and liquid aluminium, and high oxidation resistance.

Nickel ferrite spinel, NiFe_2O_4 , has been identified as a possible material that could be used as a sidewall refractory, either as a bulk refractory or as part of a multi-refractory system [3,5,6,7,8]. The main property that nickel ferrite features is a resistance to corrosion by the cryolite based electrolyte used in the Hall-Héroult cell. The main weakness of nickel ferrite is a high likelihood to contaminate molten aluminium

Most of the literature involving nickel ferrite in respect to the Hall-Héroult cell involves its use as an inert anode. Inert anodes require many of the same properties as sidewall materials, except that anodes require high electrical conductivity. For this reason, cermets, mixtures of metals and ceramics, have been extensively investigated for use as inert anodes. This research provides a good starting point for development of sidewall materials.

2.0 Previous Assessment of Nickel Ferrite for Sidewall Refractories

From the work involving inert anodes, it is known that nickel ferrite is relatively stable against attack by cryolite-based baths. However, there have been very few laboratory scale studies into nickel ferrite as a refractory material for the sidewalls of a Hall-Héroult cell.

Yan *et al.* [6] studied the effect of apparent porosity (2.5 to 7%), atmosphere and bath chemistry on the corrosion behaviour of nickel ferrite in cryolite-based baths. After 24 hours immersion in a synthetic cryolite containing 10% Al_2O_3 with a sample rotation speed of 25rpm, it was found that there was no significant attack of the nickel ferrite samples. A surface layer with higher porosity was found which was associated with infiltration of the bath. Analysis of the bath after reaction gave an iron content of 0.62-0.75 wt% and 0.01-0.22 wt % nickel, with no relationship between these levels and the porosity of the samples. A cross section of a reacted sample is shown in Figure 1.

The effect of atmosphere on the corrosion of nickel ferrite was investigated by using argon, carbon dioxide and air [6]. The results are shown in Figure 2. The lowest bath content of nickel and iron occurred under the most oxidising atmosphere. This led to the proposal that the oxidation state of the iron in the nickel ferrite may play an important role in the corrosion.

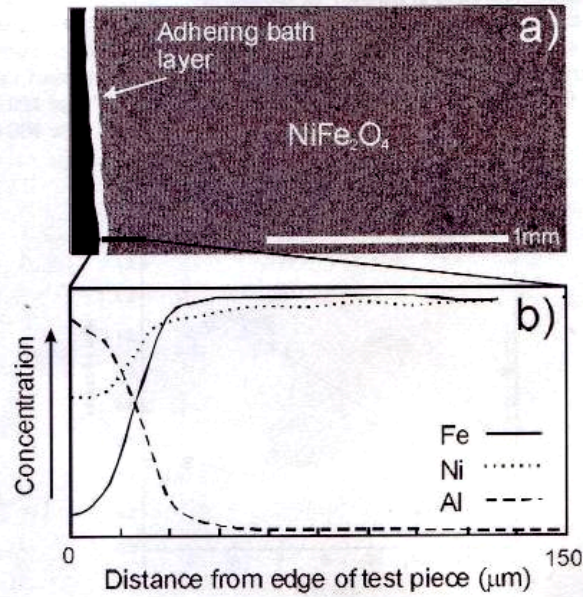


Figure 1 SEM and EPMA results from a cross section of a reacted nickel ferrite test piece with 2% porosity [6]. (a) Back-scattered electron image; (b) Elemental concentration profile across the interface.

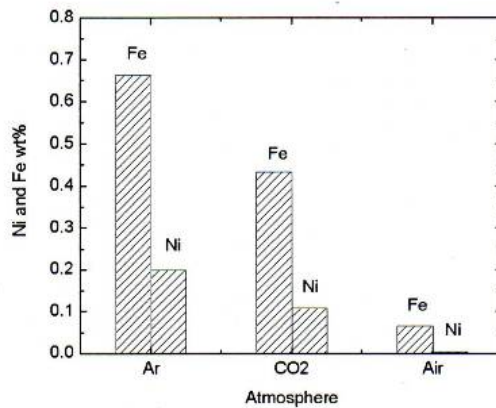


Figure 2 Effect of atmosphere on bath content of Ni and Fe [6].

The effect of the alumina content of the bath was also investigated. With 5% alumina in the bath, the test piece was significantly corroded after 24 hours. At 10 and 15% alumina, the measurable corrosion was much lower. Decreasing the bath ratio (mass ratio NaF:AlF₃) from 1.43 to 1.38 by addition of AlF₃ was also found to decrease the corrosion of nickel ferrite test pieces. It was proposed that the mechanism of corrosion involved the bath attacking the nickel ferrite along the grain boundaries and therefore selection of a larger grain size distribution may play an important role in reducing the corrosion of nickel ferrite in the bath.

Downie [7] also studied the corrosion of nickel ferrite in cryolite-based baths. In this case the samples had properties more typical of commercial refractories (apparent porosity approx. 25%, and larger grains). It was found that the corrosion resistance after long testing periods was less than that reported by Yan et al, probably due to the much higher porosity. The cryolite-based bath penetrated the pore networks, increasing corrosion. After 120 hours of exposure under static conditions at 980°C, an aluminium-rich oxide phase was formed inside the sample, while an Fe-Ni metal alloy was formed at the surface of the test piece. The differences in terms of the reaction products compared to the other study may be due to the differences in test conditions, particularly the rotation of the samples in the study by Yan et al., which would tend to cause any reaction products not strongly bonded to the refractory to be stirred into the bath. However, it was also observed that material with a larger average grain size (approx 120µm) performed better than one with smaller grains (approx 90µm), which is consistent with a grain boundary attack corrosion mechanism.

These studies into the corrosion of nickel ferrite as a sidewall demonstrated that the material could have potential as a sidewall refractory, but that the effects of the microstructure needed to be further assessed, and a better understanding of the corrosion mechanism obtained. It was therefore decided to undertake a more extensive study of the properties and corrosion resistance of nickel ferrite based refractories.

3.0 Experimental Work

3.1 Properties of Nickel Ferrite

As nickel ferrite has not been assessed as a refractory material, there was found to be a lack of data in the literature on basic properties such as apparent porosity, bulk density and strength. It was therefore necessary to begin by making and testing samples to provide a benchmark.

Samples of stoichiometric nickel ferrite were prepared from both laboratory grade powders of NiO and Fe₂O₃, and from pre-sintered nickel ferrite grain to give a range of microstructures. Three different sintering temperatures (1350, 1400, 1450°C) were used.

X-ray diffraction showed that all samples had successfully formed the NiO·Fe₂O₃ spinel phase during sintering. Optical and electron microscopy confirm XRD results. The stoichiometric samples have a uniform microstructure, comprised mainly of the spinel phase. There is a very small amount of retained nickel oxide present, which is shown in Figure 3. However, observations at higher magnifications show that even these remnant NiO grains contain some dendritic nickel ferrite.

Table 1 lists properties of the test specimens.

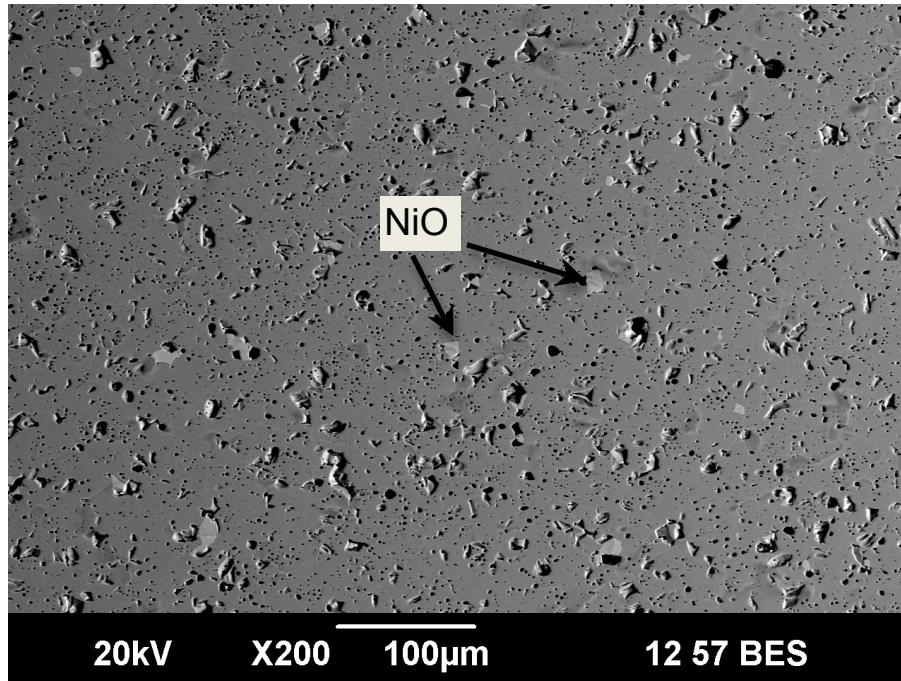


Figure 3: SEM image of stoichiometric nickel ferrite sintered at 1450°C. The small, light grey grains are nickel oxide.

Table 1: Apparent Porosity (AP), Bulk Density (BD) and Modulus of Rupture (MoR) of test specimens. Each result is the average of 9 to 16 tests.

Material	Sintering Temperature (C)	AP (%)	BD (kg/m ³)	MoR (MPa)
stoichiometric nickel ferrite	1350	1.61	4897	37
	1400	<1%	5023	40
	1450	1.37	4985	40

3.2 Corrosion Testing

Corrosion tests were conducted in a vertical tube furnace with controlled atmosphere, as shown in Figure 4. Details of the testing conditions are listed in Table 2. These tests were designed to provide a benchmark against which candidate materials and effects of changing bath composition can later be assessed. Therefore, an alumina saturated bath was used.

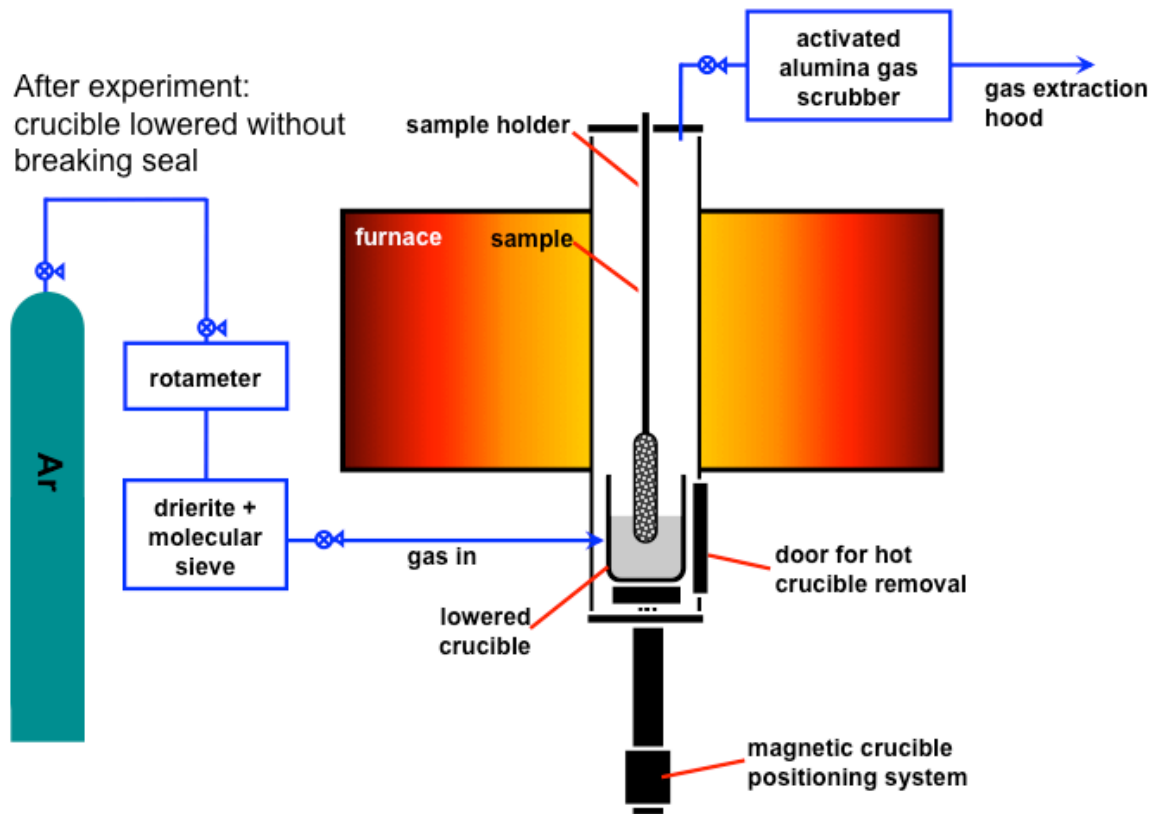


Figure 4: Schematic diagram of the corrosion test apparatus.

Table 2: Corrosion testing conditions

Parameter	Details
Atmosphere	Ar, 1000ml/min
Bath Composition	82.1wt% cryolite (Na_3AlF_6) 2.9wt% AlF_3 5.0wt% CaF_2 10.0wt% Al_2O_3
Bath Mass	100g
Sample Dimensions	Approx 5x6x30mm
Temperature	980°C
Time at temperature	2 hours , or 4 hours

4.0 Results

Following corrosion testing, macroscopic examination of the samples showed no significant dissolution of the nickel ferrite. Figure 5 shows a micrograph of the interface between the bath and a stoichiometric nickel ferrite sample after two hours immersion in the bath. There is

a distinct two layer reaction zone. The layer adjacent to the bath (hot face) has a fairly uniform width of approx. 150 μ m, and has a more open texture than the bulk material. Behind that is a layer approx 100 μ m wide that contains small metallic particles. Some larger metallic particles are contained in the residual bath.

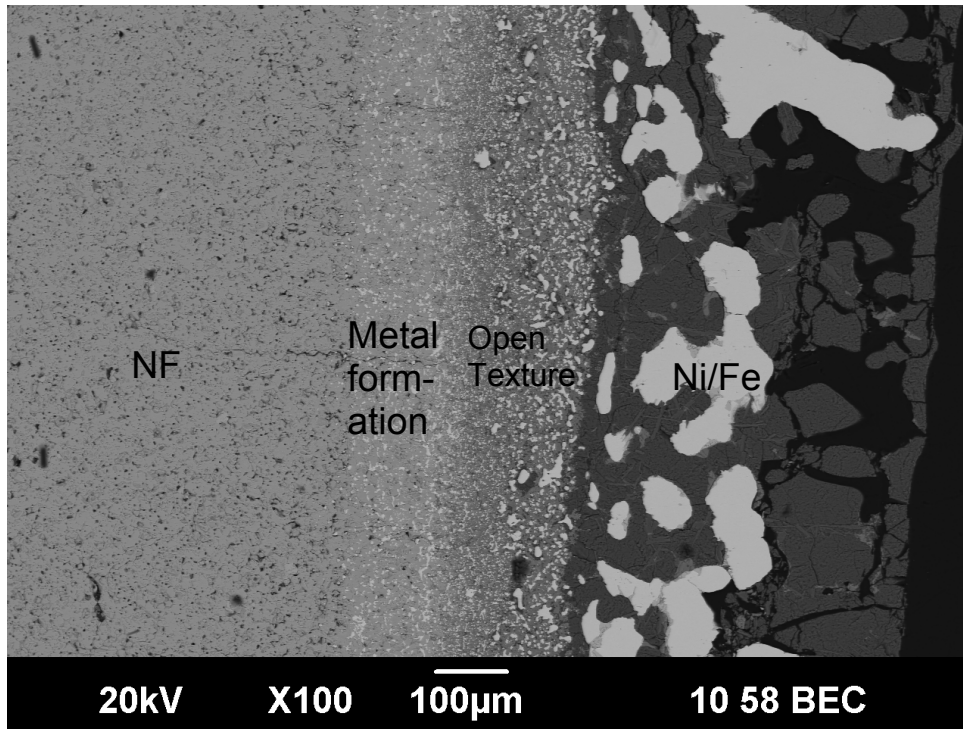


Figure 5: Stoichiometric nickel ferrite (NF) sintered at 1450°C after immersion in cryolite based bath for 2 hours at 980°C. The dark material on the right is residual bath, including some needles of Al₂O₃.

Energy dispersive spectroscopy (EDS) revealed that the metallic phase contains Ni and Fe, with the tiny droplets further from the hot face being predominantly Ni, while the larger globules in the bath contained approximately equal amounts of Ni and Fe.

Elemental mapping (see Figure 6) showed that in the area where the structure was more open, there were significant compositional changes occurring. The Ni content of oxide grains decreased greatly (from approx. 40 to <5wt%) as the hot face was approached, and the F content increased (from <1 to approx 10%). There was also an increase in the Al content of oxide grains, which rose to levels of nearly over 25wt% near the hot face. Al was present in an oxide form in grain boundaries of the nickel ferrite up to about 200 μ m from the hot face.

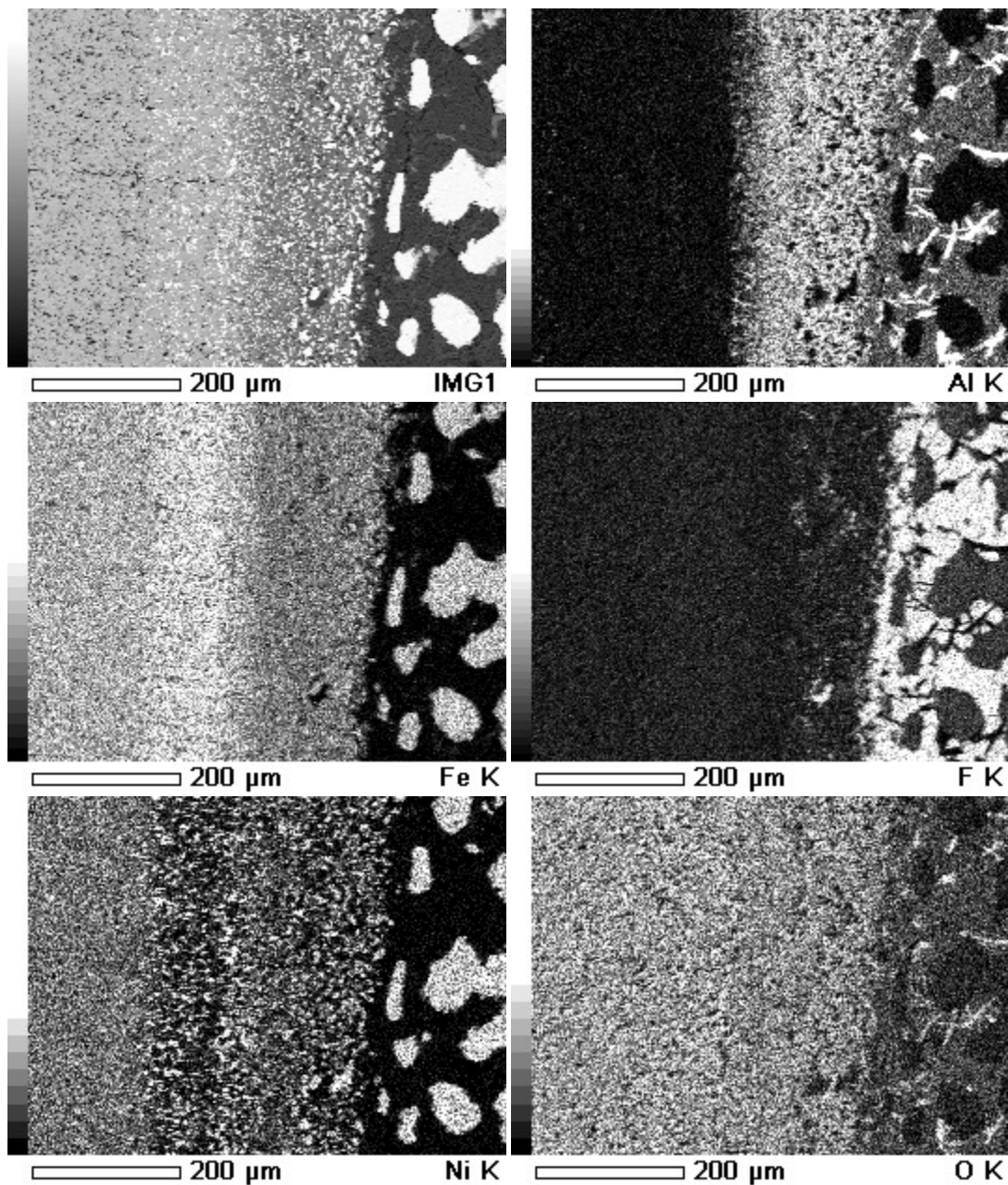


Figure 6: Elemental maps of stoichiometric nickel ferrite (sintered at 1450°C) after 2hrs in the bath.

A similar pattern of chemical and microstructural changes was observed in the samples of nickel ferrite sintered at 1400°C after 2 hours exposure to the bath, and for the nickel ferrite sintered at 1400°C and tested for 4 hours. The surface of the latter sample was more irregular, and the material adjacent to the hot face was more dispersed, but compositional trends were the same, and the presence of an aluminium rich phase in the grain boundaries of the nickel ferrite is quite clear, as Figure 7 shows.

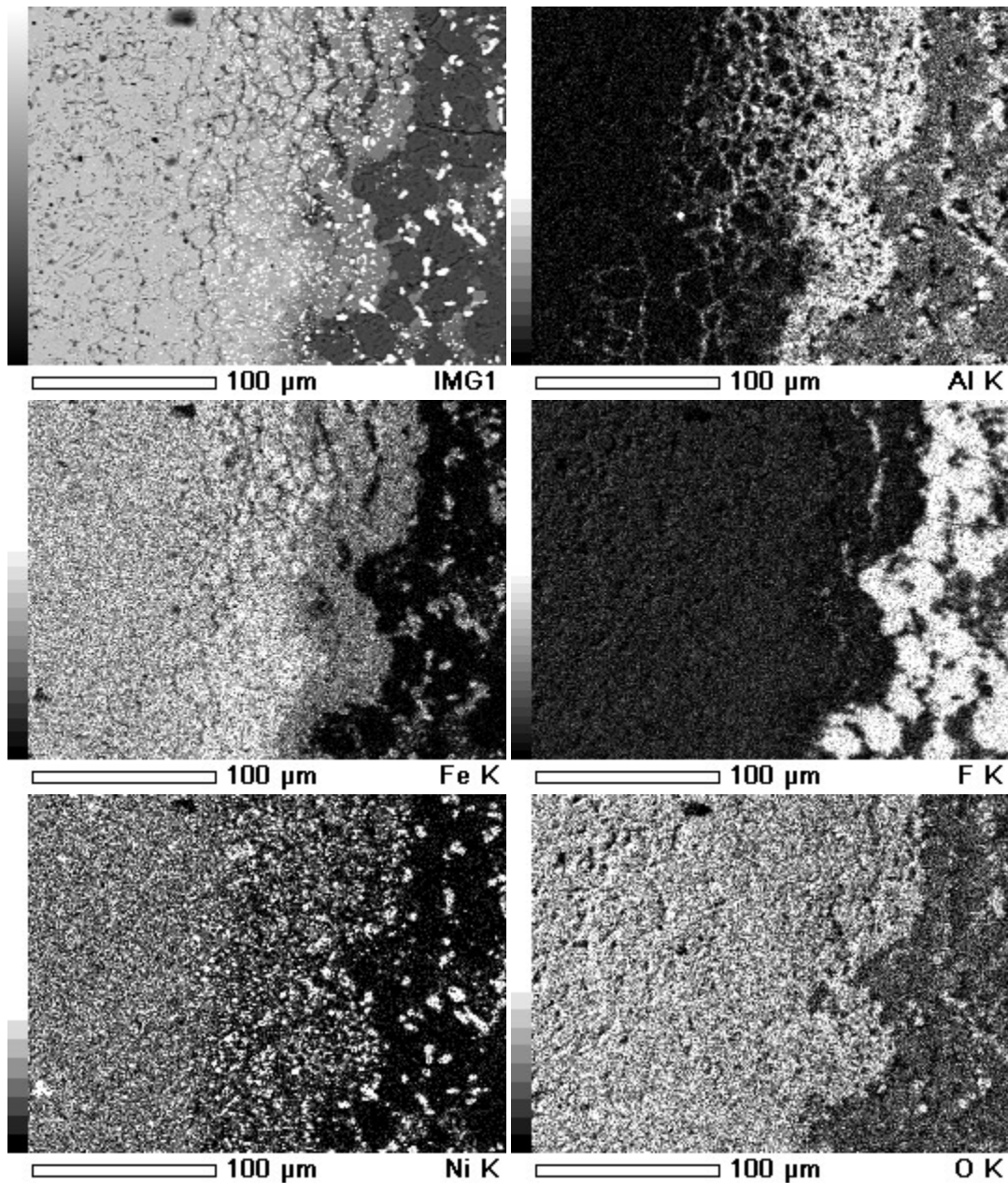


Figure 7: Elemental maps of stoichiometric nickel ferrite (sintered at 1400°C) after 4hrs in the bath. The presence of an aluminium rich phase in the grain boundaries is clearly visible.

5.0 Discussion

These observations are in good general agreement with those made by Downie [6] in the earlier study. In that investigation, samples were tested for 120hrs, and there was little of the original nickel ferrite spinel left, making any comment regarding corrosion mechanisms difficult. It was observed that a NiFe alloy was formed, and remnant oxide was depleted in Ni. However, initially this study appears to differ from the results of Yan et al [6] who did not report finding any metal formation in their experiments. As the samples in that study were

rotated at 25rpm during testing, reaction products may have been stripped away. They did not find any Fe or Ni alloys in the bath, but both elements were present in the bath.

This work does provide strong support for the proposal that the corrosion proceeds via a grain boundary attack. Aluminium is present as part of an oxide in grain boundaries well ahead of any bulk corrosion, and a metal phase is formed. Whilst it is still too early to identify the corrosion mechanism, it is clear that some of the spinel is being reduced, forming a NiFe alloy. The process appears complex, and may involve substitution of Ni in the spinel by Al from the bath, associated with a reduction of Fe^{3+} to Fe^{2+} . However, considerably more work needs to be done before a proper analysis of the mechanism can be attempted, including effects of bath composition and temperature.

What is clear is that overall, the extent of attack is quite small given the very corrosive nature of cryolite baths. Complex oxides such as nickel ferrite have been shown to have a lower solubility in cryolite than simple oxides, as noted in reviews of corrosion tests. [9, 10] However, the need to avoid contamination of the metal means that the refractory must either have extremely low solubility, or that any dissolved material is not considered a contaminant. As it appears that the corrosion mechanism involves grain boundary attack, both increasing the grain size, and the use of additives that can impart resistance to grain boundary penetration have the potential to further improve the performance nickel ferrite spinel based materials, and reduce the risk of metal contamination. One of the major advantages of a spinel, is that it can accommodate many different ions in its structure, so that a very broad range of compositions is possible. The structure of spinels is based upon a cubic framework of oxygen ions containing many interstitial sites that can be occupied by a wide variety of both 3+ and 2+ metal ions.[11] As sidewalls, unlike anodes, should not be electrically conducting, a much greater range of compositions can be considered for this application, including those that would be good electrical insulators. Future work will include such materials.

The test work done on nickel ferrites to date has not included testing under anodic conditions. As such experiments are difficult to run, and require specialized equipment, it is not practical to use them as part of the initial material development process. However, those materials that do show promise, will be subjected to testing in a laboratory scale electrolysis cell.

6.0 Conclusions

Nickel ferrite spinel does demonstrate a very good resistance to dissolution in cryolite based baths, however the risk of metal contamination means that pure nickel ferrite is unlikely to meet the requirements for sidewalls. There is some evidence that supports the proposal that degradation of the ferrite occurs via a complex mechanism that includes attack of grain boundaries and formation of a metal phase. Therefore, investigation of additives that can provide resistance to grain boundary attack without contaminating the aluminium, and the effect of materials with larger grains may provide a route to a feasible spinel based refractory.

7.0 Acknowledgements

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