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## **Influence of operating conditions on cermet inert anode corrosion in cryolite for aluminum production.**

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### **Abstract:**

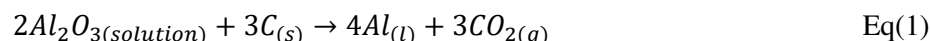
A  $(\text{Ni}_x\text{Fe}_y\text{O}_4 - \text{Ni}_{1-x}\text{Fe}_x\text{O}) / (\text{Cu}_x\text{Ni}_{1-x})$  cermet candidate as inert anode was investigated in cryolite at 960°C. Immersion tests were performed and different conditions tested: cryolite ratio, alumina content, electrolyte quality, metallic aluminium content and atmosphere. Then, electrolysis was realised at 0.8 A.cm<sup>-2</sup> for 4h in industrial conditions: industrial grade electrolyte, CR 2.2, saturated Al<sub>2</sub>O<sub>3</sub>, 960°C and presence of metallic Al. The initial material composition was still present in the bulk and the phases compositions in the oxidised zone are Ni<sub>0.90</sub>Fe<sub>2.10</sub>O<sub>4</sub> and Ni<sub>0.90</sub>Fe<sub>0.10</sub>O, as observed during immersion tests. The metallic phase is partly oxidised, leading to porosity in the cermet.

### **Keywords:**

Inert anode, cermet, spinel, high temperature

## **1. Introduction**

Aluminum metal is produced by Al<sub>2</sub>O<sub>3</sub> electrolysis in molten cryolite at high temperature (960°C) [1] by the Hall-Héroult process:



Liquid Al metal is obtained by reduction and oxygen ions react with a reactive carbon anode to produce carbon dioxide. The electrolyte is composed of  $\text{Na}_3\text{AlF}_6$  -  $\text{AlF}_3$  -  $\text{CaF}_2$  -  $\text{Al}_2\text{O}_3$  according to a  $\text{NaF}/\text{AlF}_3$  molar ratio of 2.2, called cryolitic ratio CR.

One of the key challenges in the aluminum industry is to replace  $\text{CO}_2$  by  $\text{O}_2$  release on an inert anode with the following requirements: a high electrical conductivity ( $> 200 \text{ S.cm}^{-1}$ ), a high stability to oxidation at high temperature and a consumption rate lower than  $1\text{cm/year}$  for  $0.8 \text{ A.cm}^{-2}$  [2].

To fulfil these conditions, three types of inert anodes for aluminium electrolysis were examined: metals or alloys [3-4], oxides [5-6], or cermets (oxide and metallic phases) which are the most promising materials. [7-8]. The first patents were published by Aluminum Company of America (ALCOA) on cermet anodes in the 80's [9-10] and many authors studied their stability and performance in the Hall-Heroult process [11-12].

Lai *et al.* [13] studied the effect of bath composition on the degradation of a cermet anode, composed of a  $\text{NiFe}_2\text{O}_4$  nickel ferrite, a  $\text{NiO}$  monoxide and a nickel metal phase. CR variation (2.3, 1.8 and 1.38),  $\text{Al}_2\text{O}_3$  content (7.5 wt% and 6.5 wt%) and working temperature ( $800^\circ\text{C}$ ,  $900^\circ\text{C}$  and  $960^\circ\text{C}$ ) were investigated. Electrolyses were performed at  $0.8 \text{ A.cm}^{-2}$  and results showed that the cermet was less degraded with a CR of 1.8 and an  $\text{Al}_2\text{O}_3$  content of 6.5 wt% at  $900^\circ\text{C}$ . Moreover, a low CR strongly increased the cermet degradation: a preferential oxidation of the metallic phase was observed. Porosity is created, leading to electrolyte infiltration and therefore oxide phase dissolution by reaction with metallic aluminum.

Then, Xiao *et al.* [14] studied the corrosion behaviour of a  $\text{NiFe}_2\text{O}_4$  cermet using a stirring system for 24 hours at  $980^\circ\text{C}$ . The experimental conditions were a CR of 1.38 and 1.43, 0 and 5 wt% of  $\text{CaF}_2$ , 5, 10 and 15 wt% of  $\text{Al}_2\text{O}_3$  and argon,  $\text{CO}_2$  and air atmosphere. Tests revealed a bath penetration along  $\text{NiFe}_2\text{O}_4$  grain boundaries, causing porosity by Fe and Ni dissolution but no metal phases were detected in the molten salt. Authors demonstrated that  $\text{CaF}_2$  content has no effect on the ceramic corrosion and that  $\text{Al}_2\text{O}_3$  content, close to saturation, limits  $\text{NiFe}_2\text{O}_4$  solubility. Finally, the lowest  $\text{NiFe}_2\text{O}_4$  solubility was obtained at CR 1.38 and air atmosphere, assuming that oxygen from the atmosphere would played an important role on the ceramic stability.

The same material was investigated at 980°C for 2, 4 and 24h under argon atmosphere with different Al<sub>2</sub>O<sub>3</sub> contents (10 wt% and 6 wt%) by Nightingale *et al.* [15]. The authors confirmed that the material is attacked at the grain boundaries leading to its dissolution. A Ni-Fe alloy was detected and no influence of the Al<sub>2</sub>O<sub>3</sub> content on the nickel ferrite stability is noticed, contrary to Xiao *et al.* A different degradation mechanism of NiFe<sub>2</sub>O<sub>4</sub> was also suggested: a Ni substitution in the spinel by Al from the bath, associated with a reduction of Fe<sup>3+</sup> into Fe<sup>2+</sup>.

This last work was recently confirmed and completed on Fe<sub>3</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub> degradation in cryolite (CR 2.2 saturated in Al<sub>2</sub>O<sub>3</sub>) under argon atmosphere at 960°C [16]. Results showed a spinel dissolution by Ni<sub>x</sub>Fe<sub>3-x-y</sub>Al<sub>y</sub>O<sub>4</sub> aluminate formation, due to a substitution between Fe<sup>3+</sup> and Al<sup>3+</sup> from the bath, coupled with a crystallographic site inversion between Fe<sup>2+</sup> and Fe<sup>3+</sup>.

As authors not agree on the dissolution mechanism, this work aims at determining the impact of operating conditions on a (Ni<sub>x</sub>Fe<sub>y</sub>O<sub>4</sub> – Ni<sub>1-x</sub>Fe<sub>x</sub>O) / (Cu<sub>x''</sub>Ni<sub>y''</sub>) cermet material used as inert anode for aluminum production, where:

- $0.70 \leq x \leq 0.85$  and  $2 \leq y \leq 2.20$  wt%
- $0.75 \leq x' \leq 0.85$  wt%
- $7 \leq x'' \leq 20$ ,  $40 \leq y'' \leq 70$  and  $20 \leq z'' \leq 45$  wt% [17]

Cermets were first investigated by immersion tests and then galvanostatic electrolyses at 0.8 A.cm<sup>-2</sup> in Na<sub>3</sub>AlF<sub>6</sub> – AlF<sub>3</sub> – CaF<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> at 960°C for 7 different operating conditions, gathered in Table 1: CR; CaF<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and metallic aluminum content; electrolyte purity and atmosphere.

Operating conditions	Cryolitic ratio	CaF <sub>2</sub> content (wt %)	Al <sub>2</sub> O <sub>3</sub> content (wt %)	Electrolyte purity (%)	Al(0) content (wt %)	Atmosphere
1	2.2	5	8	99.99	Residual	Argon
2	1.2	5	8	99.99	Residual	Argon
3	2.2	5	0	99.99	Residual	Argon
4	2.2	5	8	97	Residual	Argon
5	2.2	5	8	99.99	2	Argon
6	2.2	5	8	97	2	Argon
7	2.2	5	8	97	2	Air

*Table 1. Summary of operating conditions*

Cermets were analyzed by Scanning Electron Microscopy (SEM), coupled with the energy-dispersive X-ray spectroscopy (EDX), and by optical microscopy to determine the microstructure and the phases composition. Observations were validated by thermodynamic calculations using Factsage 7.1 software.

## **2. Material and methods**

### **a) The cell**

- Under argon atmosphere, a vitreous carbon crucible was placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled by circulating water. The inside part of the walls was protected against fluoride vapours by a graphite liner. The argon gas (4.5 grade) was previously dehydrated. The cell was heated using a programmable furnace and the temperatures were measured using a chromel–alumel thermocouple.
- Under air atmosphere, the same set-up was used by replacing the carbon parts (crucible, liner) and the refractory steel set-up by alumina.

### **a) The electrolyte**

- Synthetic cryolite melt is composed of pure compounds:  $\text{Na}_3\text{AlF}_6$  (Carlo Erba, purity 99.99%), with additions of  $\text{AlF}_3$  (ProChem Inc, purity 99.99%) and 5wt% of  $\text{CaF}_2$  (Apollo Scientific, purity 99.99%). Alumina saturation was achieved by addition of 8wt% of alumina (Alfa Aesar, purity 99%). The salt mixture was heated until 960°C and the electrolyte purity is higher than 99%.
- Industrial grade cryolite was provided by RTA and the major impurities are oxides (1-2 wt% O) and sulphur (450±150 ppm).

### **b) Electrodes**

A parallelepiped shaped cermet (1.25cm<sup>2</sup> surface area) was used as working electrode. The auxiliary electrode was the vitreous carbon crucible (Mersen V25 quality) with a surface area of 38 cm<sup>2</sup>. The reference electrode is a molybdenum wire (Goodfellow 99.99%, 0.5 mm diameter) enclosed in a boron

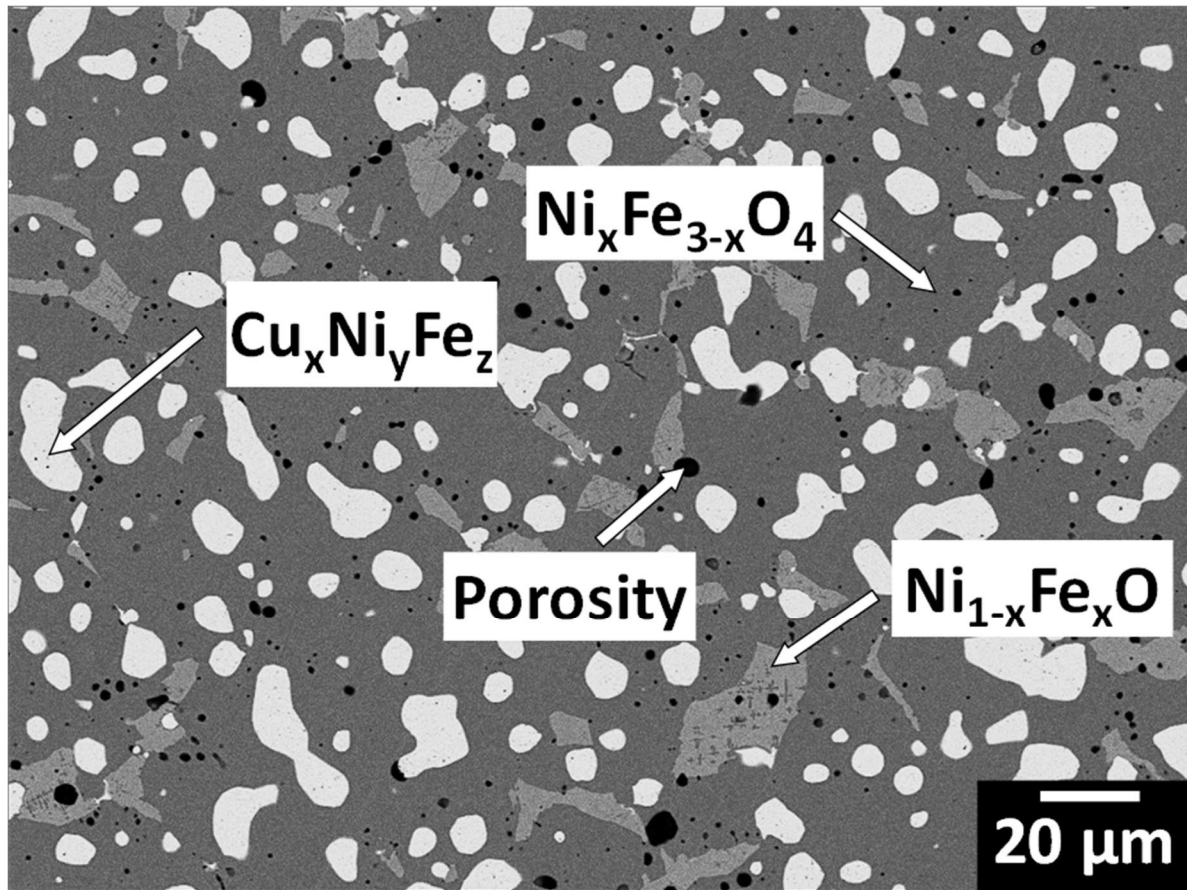
nitride crucible (BN, AX05 grade) containing a cryolite- $\text{AlF}_3$  mixture, immersed into the bath, in contact with the solution through a 0.3 mm diameter hole.

### **c) Analytical techniques**

Galvanostatic electrolyses were performed with an Autolab PGSTAT302N potentiostat/galvanostat controlled with the NOVA 2.1 software. Cermets were embedded in a conductive resin and polished for cross-sections analysis. Scanning electron microscopy (SEM) with field emission gun (MEB-FEG) and Backscattered Electron (BSE) detector coupled with EDX analysis, was performed on a JEOL JSM 7100F. EDX analysis parameters were: 15kV of Electron beam voltage, 9.7mm of working distance and 77 $\mu\text{A}$  of emission current. For dimensional measurements, an optical metallographic microscope ZEISS AXIO Imager.M2m was used.

### **d) The cermet**

Cermet was obtained by powder metallurgy process [17] and its microstructure is shown in Fig. 1, where monoxide and metal phases are included in a continuous spinel matrix. A residual porosity (in black) is observed (around 2% $_{\text{vol}}$ ).



*Fig.1. SEM micrograph of the initial cermet material.*

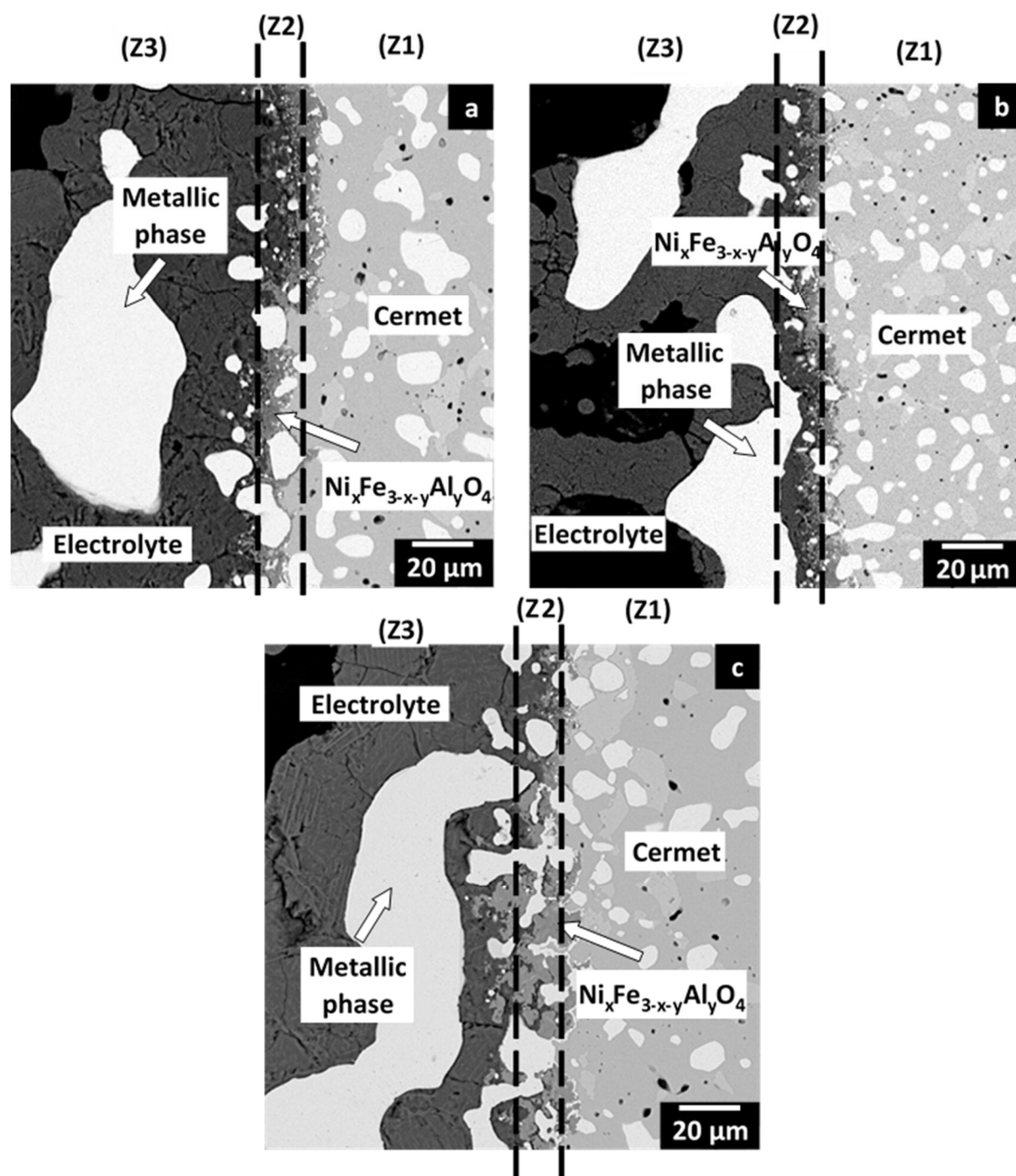
### 3. Results and discussions

Immersion tests were at first performed under argon atmosphere, with different electrolyte compositions (CR,  $\text{Al}_2\text{O}_3$ , Al metal) and purities. The detailed experimental conditions are gathered in table 1 (conditions 1 to 7).

#### 3.1 Cermet immersion tests under argon atmosphere

##### 3.1.1 Influence of CR and $\text{Al}_2\text{O}_3$ content (conditions 1, 2 and 3)

Immersion tests were realised under argon atmosphere for 4 hours in condition 1 (CR 2.2 saturated in alumina), 2 (CR 1.2 saturated in alumina) and 3 (CR 2.2 without alumina); their SEM micrographs are presented in Figures 2 a) b) and c) respectively.



*Fig.2. SEM micrograph of cermet in: a) condition 1, b) condition 2, c) condition 3*

In these 3 conditions, the same structure was observed: the cermet was not degraded in the bulk (Z1) but only at the interface where two zones (Z2 and Z3) can be identified:



- A thin layer (10  $\mu\text{m}$ ) is observed (Z2) and EDX analysis revealed Ni, Fe, Al and O elements. This phase, already detected in [16], is a  $\text{Ni}_x\text{Fe}_{3-x-y}\text{Al}_y\text{O}_4$  aluminate, spontaneously formed by reaction between the spinel and the electrolyte ( $\text{Fe}^{3+}/\text{Al}^{3+}$  substitution and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  site inversion).

- In the zone (Z3), a metallic phase surrounded by electrolyte is observed. The spinel phase is absent, confirming nickel/iron aluminate solubility into the electrolyte. The monoxide disappeared as well and a Ni enrichment in the metallic phase up to 90% is noticed. Ni(II) from  $\text{Ni}_x\text{Fe}_{1-x}\text{O}$  monoxide is then assumed to be reduced into metallic nickel, thereafter transferred into the metallic phase. This assumption is confirmed in figure 2 where the metallic phase after immersion in Z3 is much bigger than the initial one in Z1.

Thus, by changing the CR (conditions 1 and 2) or the alumina content (conditions 1 and 3), the same degradation process is obtained: a spinel dissolution, a monoxide reduction and a metallic phase enriched in Ni. CR and alumina content have then no influence under Ar on the cermet degradation, in agreement with Nightingale *et al.* [15].

### 3.1.2 Influence of electrolyte quality (condition 4)

The industrial grade electrolyte was then studied, where pollutants were mainly sulphur and oxygen, and compared to synthetic electrolyte (condition 1). The electrolyte composition was a CR of 2.2 saturated in alumina, with 5 wt% of  $\text{CaF}_2$  (condition 4). After immersion under Ar atmosphere for 4h, the cermet SEM micrograph of the interface is presented in figure 3.

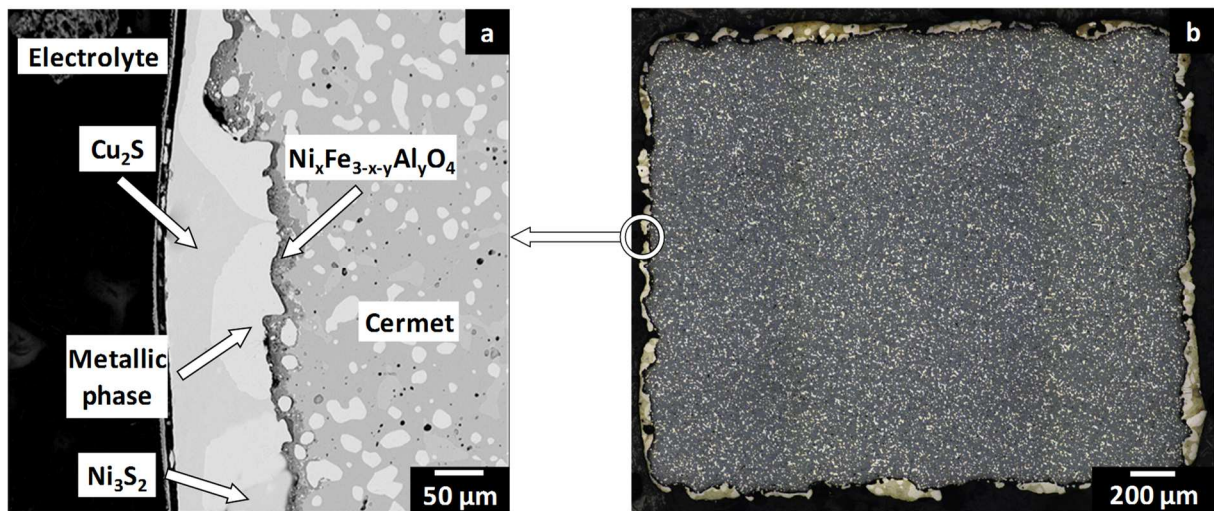


Fig.3. SEM micrograph of cermet in condition 4

This figure shows the formation of a  $\text{Ni}_x\text{Fe}_{3-x-y}\text{Al}_y\text{O}_4$  aluminate at the interface and reveals once again the spinel phase dissolution, as observed with the high purity electrolyte (§ 3.1.1).

A new phase, in light grey, is observed close to the metallic phase and corresponds to  $\text{Cu}_2\text{S}$  and  $\text{Ni}_3\text{S}_2$  phases (EDX analysis). These compounds formation can be explained thanks to Ni - S and Cu - S phase diagrams, in figure 4 a) and b) respectively.

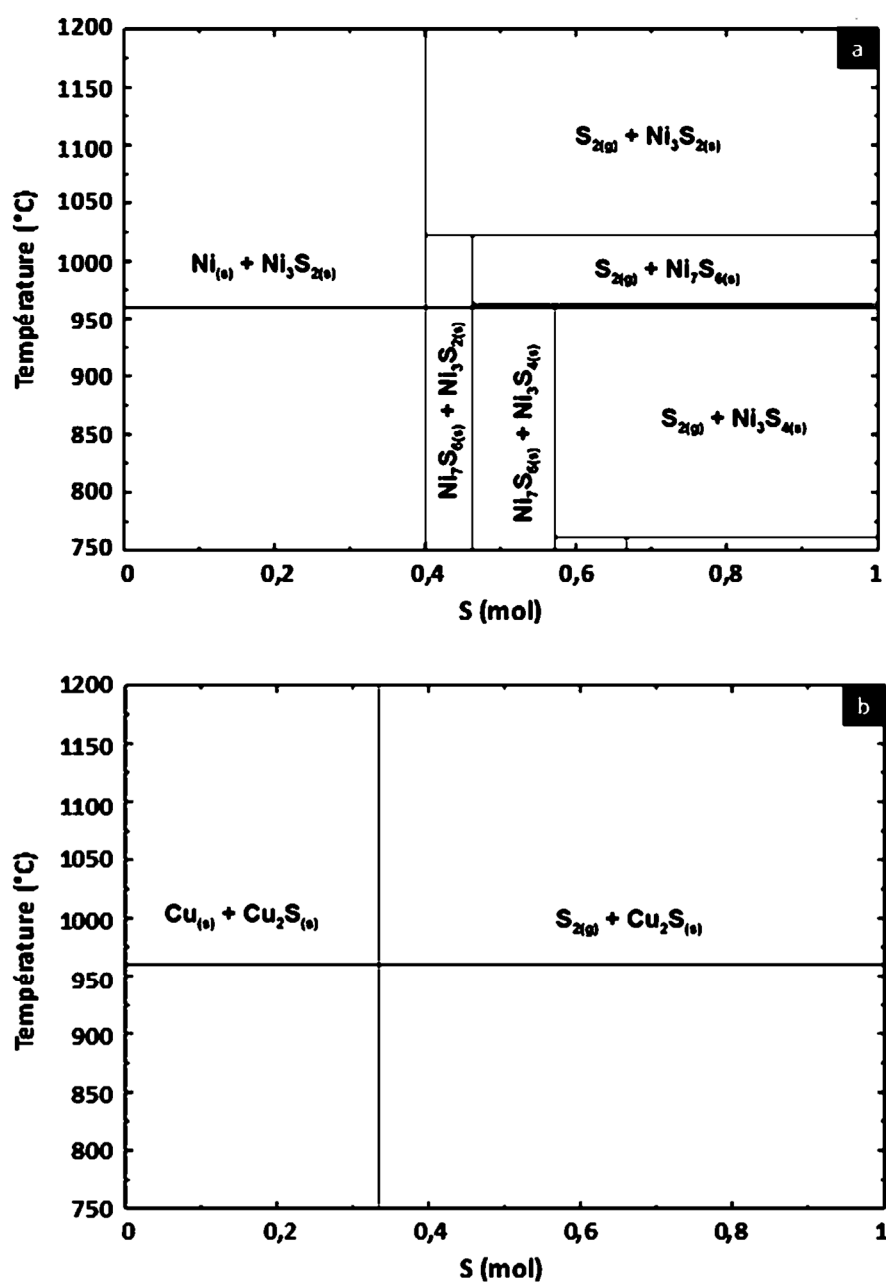


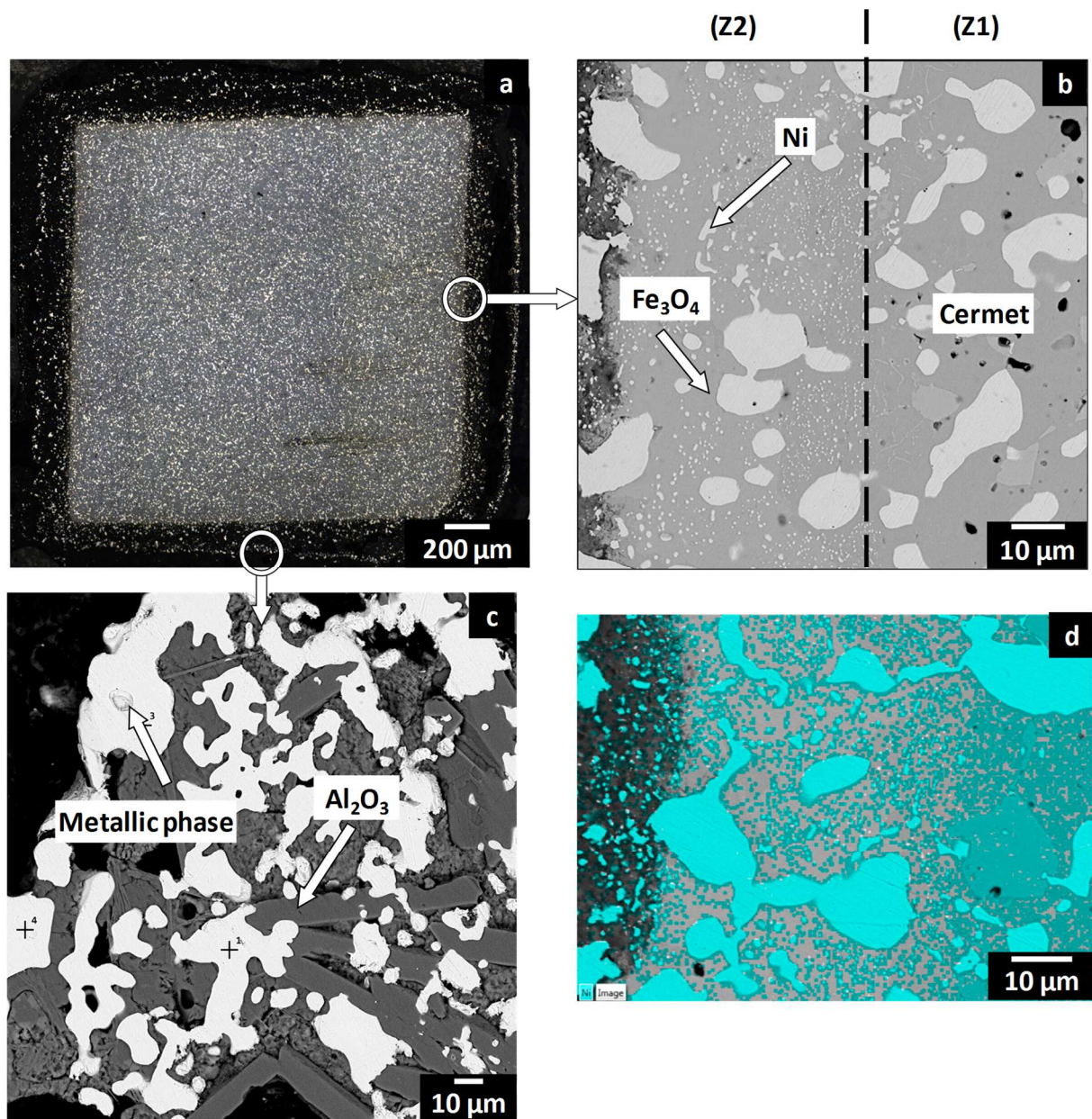
Fig.4. Phase diagrams of Ni – S a) and Cu – S b) systems.

They represent the stable phases as function of temperature and sulphur content. They confirm, at 960°C and in presence of S, that both metals react to form  $\text{Ni}_3\text{S}$  et  $\text{Cu}_2\text{S}$ .

The use of an industrial grade electrolyte containing sulphur generates other reactions with new corrosion products during immersion under argon atmosphere. The metallic phase is then degraded without polarization by sulphides formation.

### *3.1.3 Influence of metallic aluminum*

The influence of metallic aluminium was then explored. A first immersion experiment with high purity, CR 2.2, saturated in alumina, containing 5 wt% of  $\text{CaF}_2$  and 2 wt% of metallic aluminium was realised during 4 hours under argon (condition 5). Figure 5 a) is the entire image, b) and c) the SEM micrographs of cermet/electrolyte interfaces and d) an EDX mapping of the cermet/electrolyte interface showing Ni element.



*Fig.5. SEM micrograph of cermet in condition 5 a) entire image, b) and c) cermet/electrolyte interfaces and d) Ni EDX mapping of cermet/electrolyte interface*

The global image of the cermet (figure a) shows that the cermet degradation is homogeneous with a non-degraded material in the bulk. The electrolyte-cermet interface is divided into two distinct zones (fig 5 b and 5c):

- The first zone (Z1) corresponds to the genuine material.

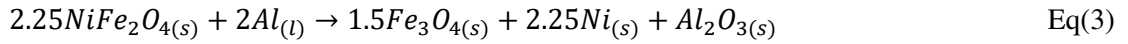
- The zone (Z2), with a thickness of 50  $\mu\text{m}$ , is composed of two phases. A  $\text{Fe}_3\text{O}_4$  spinel and a micrometric Ni metal phase, in addition to the initial Ni metal, were detected by EDX mapping analysis (5d). Moreover, the monoxide phase is no longer present at the interface and the metallic phase composition remains constant.

The outer interface presented in figure 5 c) revealed an  $\text{Al}_2\text{O}_3$  phase with its typical needle-like shape and a metallic phase of Ni-Fe-Cu with variable composition.

From these observations, spontaneous reductions of both oxide phases by metallic aluminium can be proposed as follows:



$\Delta G$  (2) = - 612 kJ per mole of aluminum

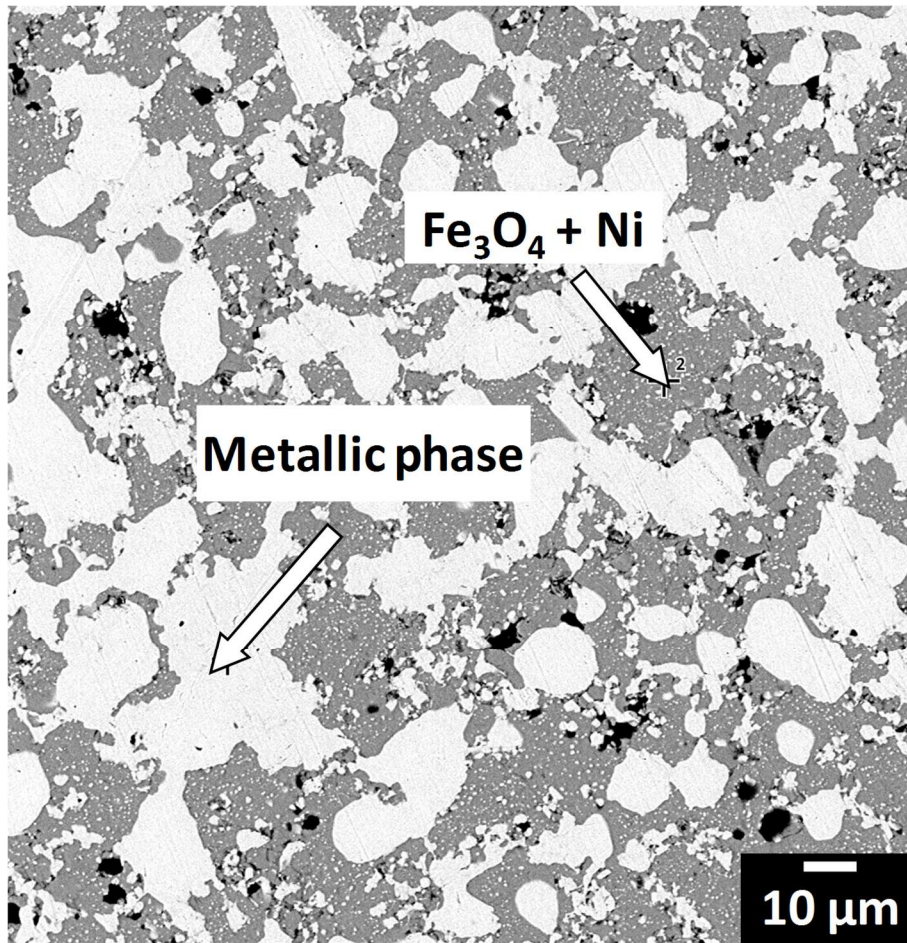


$\Delta G$  (3) = - 449.2 kJ per mole of aluminium.

Thermodynamic calculations confirm the spontaneous reactions involving Al metal with highly negative values of Gibbs enthalpies.

The same experience was performed by only changing the electrolyte purity to industrial grade (condition 6). The SEM micrograph of the cermet/electrolyte interface is presented in figure 6.





*Fig.6. SEM micrograph of cermet in condition 6*

No metallic sulphides were detected and the same structure as in the synthetic electrolyte is observed.

By comparing immersion tests in industrial grade purity electrolyte with and without metallic Al in the solution (conditions 4 and 6), it seems that Al avoids nickel and copper sulphides formation under Ar atmosphere.

Moreover, whatever the electrolyte purity and in presence of metallic aluminium, two additional reactions take place:

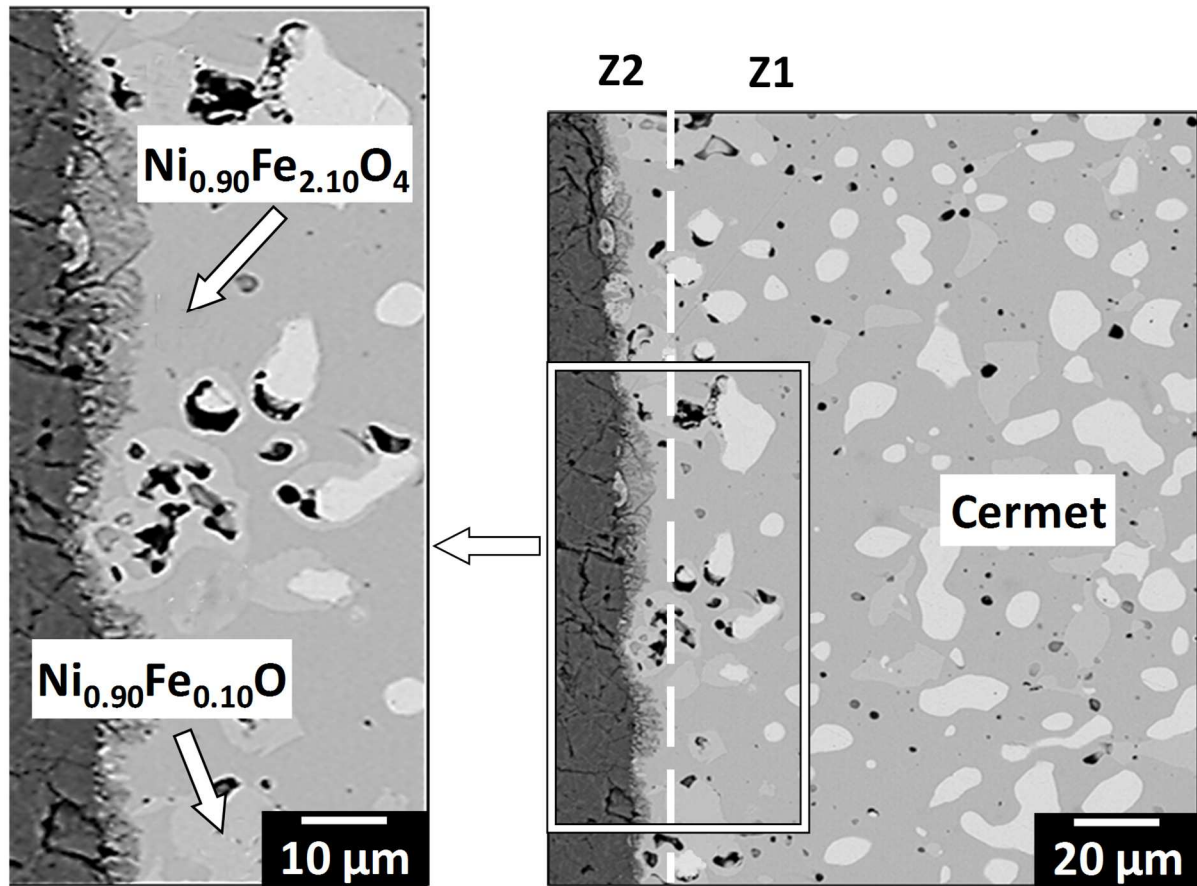
- monoxide reduction into metallic nickel and alumina formation
- spinel reduction into metallic nickel,  $\text{Fe}_3\text{O}_4$  formation and alumina as well.

From the experiments performed under argon atmosphere, here are the main conclusions on the electrolyte composition influence:

- Whatever the CR and the  $\text{Al}_2\text{O}_3$  content, the same degradation features were observed: the spinel phase is dissolved as a  $\text{Ni}_x\text{Fe}_{3-x-y}\text{Al}_y\text{O}_4$  aluminate, the monoxide is spontaneously reduced and the metallic phase is enriched in Ni
- The sulphur in the low purity electrolyte reacts with the cermet metallic phase to form  $\text{Ni}_3\text{S}$  and  $\text{Cu}_2\text{S}$
- The presence of metallic aluminum leads to the spinel and monoxide reduction into metal,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_3\text{O}$ , and avoids the metallic sulphides formation.

### 3.2 *Cermet immersion tests under air atmosphere (condition 7)*

The influence of the atmosphere was then considered, by immersion in an electrolyte composed of CR 2.2, 5 wt% of  $\text{CaF}_2$  saturated in alumina, purity of 97%, and 2 wt% of metallic aluminum. Figure 7 shows a SEM micrograph of the cermet cross-section after 4 hours of immersion under air atmosphere.



*Fig.7. SEM micrograph of cermet in condition 7*

The figure can be divided into 2 zones:

- Z1 corresponds to the original material, meaning that no degradation took place in the bulk
- Z2 is a narrow degradation zone (10µm) at the cermet/electrolyte interface, where spinel and monoxide phases are enriched in Ni up to  $\text{Ni}_{0.90}\text{Fe}_{2.10}\text{O}_4$  and  $\text{Ni}_{0.90}\text{Fe}_{0.10}\text{O}$ .

Moreover, metallic sulphides and metallic clusters were not detected.

Thus, comparison with previous experiments under Ar atmosphere demonstrates that the Al, as well as electrolyte purity, has no longer influence under air atmosphere; one explanation could be a  $\text{SO}_2$  gaseous formation, by reaction between sulphur and oxygen as proposed in [18]. In addition, under air atmosphere, a Ni enrichment of both oxide phases limits the spinel and the monoxide dissolution, as suggested in [16] and by De Young [19]: a Ni rich composition in the oxide phases leads to a better resistance to degradation. Thus, the cermet under air is protected against spinel dissolution and monoxide and spinel reduction, and is less degraded.



The atmosphere in the reactor is then a crucial parameter on the cermet corrosion during immersion: under Ar atmosphere, the cermet is more degraded than in air in agreement with Xiao *et al.*

### 3.3 Cermet electrolysis tests in industrial conditions

The cermet degradation was investigated by electrolyses in industrial conditions: industrial grade electrolyte, CR 2.2, saturated  $\text{Al}_2\text{O}_3$ ,  $960^\circ\text{C}$  and metallic Al. Electrolyses were performed at  $0.8 \text{ A.cm}^{-2}$  for 4 hours under air (condition 7).

Figure 8 presents the global image of the cermet cross-section obtained by optical microscopy under air atmosphere (a), and the SEM micrograph of the cermet/electrolyte interface (b).

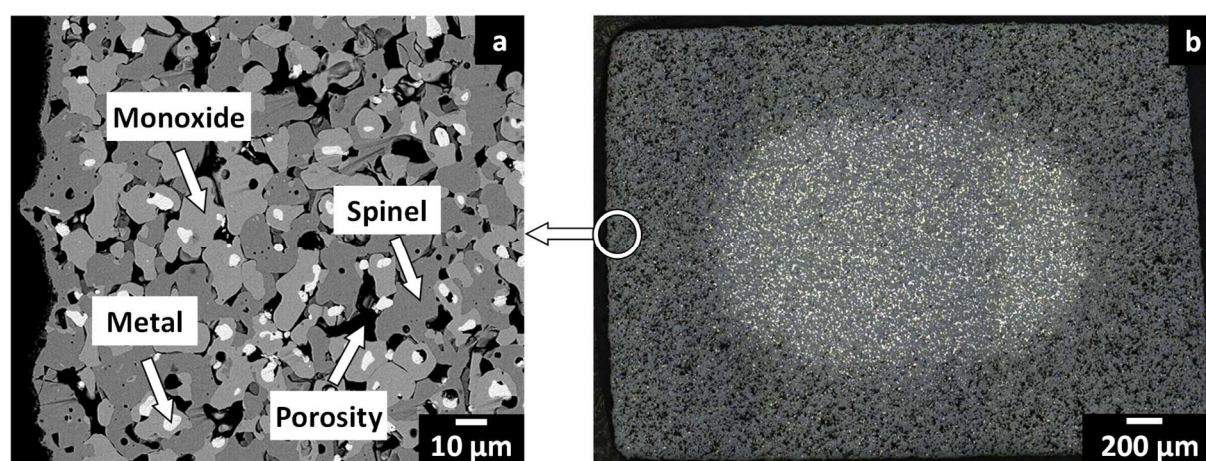


Fig.8. SEM micrograph of cermet after electrolysis in condition 7

Under air atmosphere, the cermet is partially oxidised and the initial material composition is measured in the bulk. In the modified zone, the phases compositions are  $\text{Ni}_{0.90}\text{Fe}_{2.10}\text{O}_4$  and  $\text{Ni}_{0.90}\text{Fe}_{0.10}\text{O}$  for the oxide phases as in the previous immersion tests, and close to  $\text{Cu}_{0.8}\text{Ni}_{0.2}$  in the metallic phase.

Under electrolysis, the monoxide and spinel phases are enriched in Ni up to 0.9 and the metallic phase is oxidised. The phases proportions in the cermet after electrolysis were determined by image analysis at the interfaces and results are gathered in table 2.

	Air atmosphere
Spinel	$41 \pm 1\%$
Monoxide	$22 \pm 1\%$

<b>Porosity</b>	31±1%
<b>Metal</b>	6±1%

*Table 2: Phase proportions at the cermet/electrolyte interface after electrolysis under argon and air atmosphere*

By comparing the initial and the electrolysed material, the same proportions of monoxide and spinel are observed, whereas a decrease of the metallic phase correlated with an increase of the porosity are noticed: the oxidised metallic phase disappears in favour of the porosity. Indeed, the metallic phase is oxidised into ions which are transferred into the solvent, creating porosity in the material. Thus, under electrolysis under air atmosphere, the oxide phases are enriched in Ni up to  $\text{Ni}_{0.90}\text{Fe}_{2.10}\text{O}_4$  and  $\text{Ni}_{0.90}\text{Fe}_{0.10}\text{O}$  and the metallic phase is oxidised, leading to porosity in the material.

## Conclusions

A  $(\text{Ni}_x\text{Fe}_y\text{O}_4 - \text{Ni}_{1-x}\text{Fe}_x\text{O}) / (\text{Cu}_x\text{Ni}_y)$  cermet material was examined as inert anode in  $\text{Na}_3\text{AlF}_6 - \text{AlF}_3 - \text{CaF}_2$  cryolite electrolyte at 960°C. First of all, cermet immersion tests were performed under different experimental conditions: cryolitic ratio;  $\text{Al}_2\text{O}_3$  and metallic aluminum content; electrolyte purity (synthetic or industrial grade) and atmosphere (Ar or air). Under Ar atmosphere, a global degradation mechanism was observed: a spinel dissolution via  $\text{Ni}_x\text{Fe}_{3-x-y}\text{Al}_y\text{O}_4$  aluminate formation, a monoxide reduction and a metallic phase enriched in Ni. The main conclusions on the parameters influence are: CR and  $\text{Al}_2\text{O}_3$  content have no influence on the cermet stability; in presence of metallic Al, whatever the electrolyte, spinel and monoxide phases are reduced into metal,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ ; in presence of sulphur,  $\text{Ni}_3\text{S}$  and  $\text{Cu}_2\text{S}$  phases are formed. On the contrary, under air atmosphere, no more influence of metallic Al and electrolyte quality on the cermet degradation was observed: spinel and monoxide phases are enriched in Ni up to  $\text{Ni}_{0.90}\text{Fe}_{2.10}\text{O}_4$  and  $\text{Ni}_{0.90}\text{Fe}_{0.10}\text{O}$ , limiting the cermet dissolution. Finally, cermet was electrolysed for 4h at 0.8 A.cm<sup>-2</sup> under air atmosphere in industrial conditions and, as expected,  $\text{Ni}_{0.90}\text{Fe}_{2.10}\text{O}_4$  and  $\text{Ni}_{0.90}\text{Fe}_{0.10}\text{O}$  are formed and the metallic phase is partially oxidised, creating porosity.

## **Acknowledgements**

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