Preparation and electrical properties of dense micro-cermets made of nickel ferrite and metallic copper

Valérie Baco-Carles [a], Isabelle Pasquet [a], Véronique Laurent [b],
Armand Gabriel [b], Philippe Tailhades [a,*]

[a] Institut Carnot CIRIMAT, Université de Toulouse, CNRS, Université Paul Sabatier, 118 Route de Narbonne, 31 062 Toulouse Cedex 9, France
[b] Rio Tinto Alcan, Centre de Recherche de Voreppe, ZI Centr'Alp, 725 Rue Aristide Berges, 38341 Voreppe Cedex, France

ABSTRACT

Dense micro-cermets made of nickel ferrites and copper micrometric particles were obtained from partial reduction under hydrogenated atmosphere at 350 °C of mixed copper nickel ferrites, and sintering in nitrogen at 980 °C. The small copper particles are homogeneous in size and well dispersed in the spinel oxide matrix. No exudation of copper metal was observed after sintering. The micro-cermets prepared are semi-conducting materials with electrical conductivity lying from 44 to 130 S/cm at 980 °C. Their overall characteristics make them interesting for inert anodes dedicated to aluminium electrolysis in melted cryolite.

1. Introduction

Aluminium metal is industrially produced by the so-called Hall–Heroult electrolytic process. Liquid aluminium is then obtained at about 960 °C at $E = 1.2V$, by the reduction of alumina dissolved in a bath of melted cryolite. The bath/metal interface acts as a cathode and the oxygen coming from the alumina is combined with the carbon anode, in such a manner the overall reaction of the process is:

$$2Al_2O_3 + 3C \rightarrow Al + 3CO_{2(g)}$$
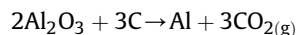
The carbon anode is thus consumed along the electrolytic process making its monthly replacement necessary, for industrial fittings. The resulting shortcomings of the conventional Hall–Heroult process are:

- the frequent anode adjustment needed during electrolysis in order to maintain inter-electrode gap,
- the cost due to the anode change, which tends to increase according to the petroleum products price,
- the emission of carbon dioxide (1.5 kg per 1 kg of Al) which is a greenhouse gas.

Corresponding author. Tel.: +33 5 61 55 61 74; fax: +33 5 61 55 61 63.
E-mail address: tailhade@chimie.ups-tlse.fr (P. Tailhades).

Extensive researches (see for instance Refs. [1] and [2]) are then carried out to find alternatives to Hall–Heroult process or to find new materials that are stable enough at about 1.2 V anodic potential in melted cryolite, to make inert anodes. For this last purpose, cermets, made of metal dispersions inside an oxide ceramic matrix, were proposed [3–6]. Pure copper or copper–nickel alloys are generally chosen for the metallic part of the cermet and a $Ni_xFe_{3-x}O_4$ spinel ferrite, combined or not with $Ni_{1-x}Fe_xO$ monoxide phase, makes the matrix. Such cermets are mainly prepared from a mixture of metallic and oxide powders with an organic binder. This mixture is pressed, to get a green compact with the required shape, and then heat-treated at a temperature higher than 1300 °C under argon atmosphere containing less than 100 ppm of oxygen. The decomposition of the organic binder when heat-treated, leads to the formation of reducing species which can act upon the metal/oxide ratio and the microstructure of the sintered material. The mean grain size of the metal particles in such cermets is generally bigger than 10 μm. The high sintering temperature involves also bumps at the surface of the cermets due to exuded copper droplets of millimetre size.

For this study, an original preparation route is followed to improve the homogeneity of the cermets, reduce the mean size of metallic particles and avoid exudation. Such cermets, which will be called "micro-cermets", are prepared from pure $Ni_{1-x}Cu_xFe_2O_4$ ferrite green compacts previously heat-treated at low temperature to remove the organic binder used for shaping. Dense cermets,
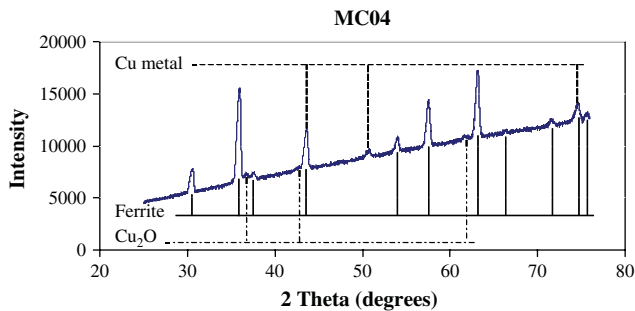
Fig. 1. Typical X-ray diffraction pattern of a cermet reduced at 350 °C for 2 h and sintered at 980 °C for 30 min.

made of metallic copper and nickel ferrites, are thus obtained by partial reduction of the ferrite in a mixture of argon and hydrogen and subsequent sintering below 1000 °C in a nitrogen atmosphere. The experimental conditions leading to the formation of such original cermets are described and the samples microstructures are investigated in relation with the nature and the chemical composition of the phases formed.

2. Analytical methods

Phase characterisation and lattice constants measurements were performed on a Siemens D5000 X-ray diffractometer. The wavelength of the radiation used was 0.15406 nm, corresponding to the $K_{\alpha 1}$ copper emission line. The surface area measurements were done on ferrite powders with a Micromeritics FlowSorb II 2300, operating with nitrogen at liquid nitrogen temperature. Microscopic studies were carried out with a Veeco Dimension 3000 Magnetic Force Microscope (MFM), a Jeol JSM 6700F field emission guna Jeol JSM 6400 scanning electron microscope (SEM), and a Jeol transmission electron microscope (TEM). Netszch 402 E apparatus was used for dilatometry analyses. Electrical conductivity (σ) at room temperature was measured according the four probes Van der Pauw method

on sintered discs of about 20 mm in diameter and less than 1 mm high. The values obtained by this method were used as reference to calibrate measurements performed from room temperature to 1000 °C, by a simple two points method on $1 \times 5 \times 20$ mm^3 parallelepipedic samples.

3. Ferrite powders preparation

In spite of slightly different crystalline structures between $CuC_2O_4 \cdot nH_2O$ ($n \leq 1$) and $MC_2O_4 \cdot 2H_2O$ with M = Ni or Fe, mixed di-hydrated $(Ni_{1-x}Cu_xFe_2)_{1/3}C_2O_4 \cdot 2H_2O$ oxalates were obtained using the precipitation method in hydro–alcoholic medium, proposed by Villette et al. [7,8]. Two samples, with x equal to 0.4 and 0.6, respectively, were precipitated. These mixed oxalates were then decomposed at 700 °C under airflow. The resulting oxide powders, which display solely the X-ray diffraction lines of the cubic spinel structure, can be assumed to be pure $Ni_{1-x}Cu_xFe_2O_4$ ferrites. According to their copper content, the ferrite samples will be called F04 and F06 in what follows. The specific surface area of these powders was close to 10 m^2/g. The measured ferrite lattice constants for F04 and F06 were 0.8355 and 0.8362 nm, respectively.

4. Micro-cermets reduction and sintering

The previously prepared ferrite powders were mixed with 0.34 mass percent polyvinylic alcohol, then pressed into discs under an uniaxial pressure of 200 MPa. The organic binder was removed by heat treatment at 450 °C under air atmosphere. The resulting compact made of pure ferrite, was first reduced in a mixture of hydrogen (4 vol. %) and argon (96 vol. %). Several experiments were performed to find the required reduction temperature. It was shown that 350 °C allows to form metallic copper and a new spinel phase. The reduction was then carried out at 350 °C for 2 h, for both F04 and F06 samples. The corresponding reaction can be described, in a first approximation, by the following chemical equation:
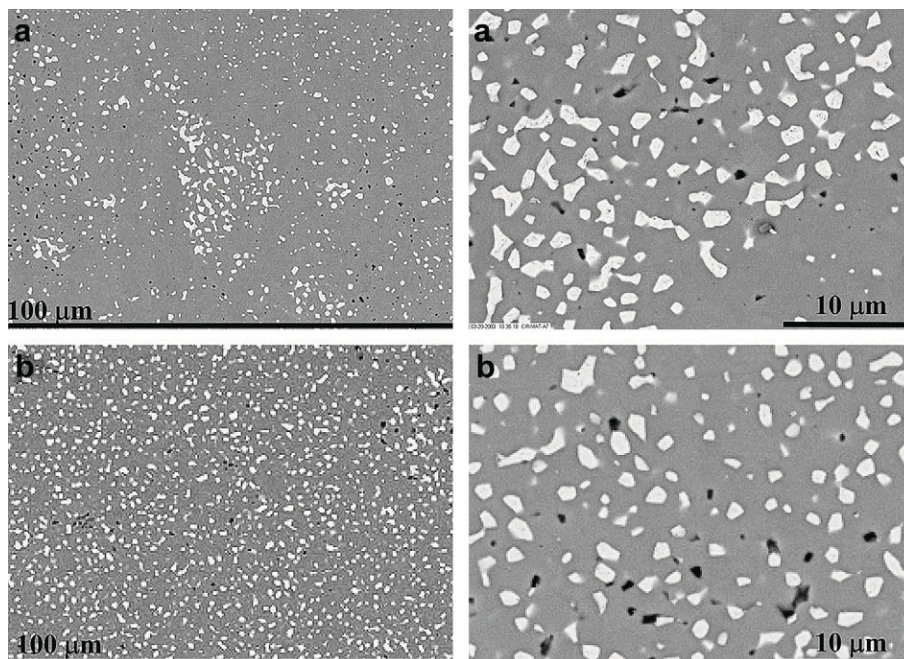

Fig. 2. Scanning electron micrographs (backscattered electron mode by chemical contrast) of the upper surface of the cermets reduced at 350 °C for 2 h and sintered at 980 °C: (a) cermet obtained from $Ni_{0.6}Cu_{0.4}Fe_2O_4$ (MC04); (b) cermet obtained from $Ni_{0.4}Cu_{0.6}Fe_2O_4$ (MC06).

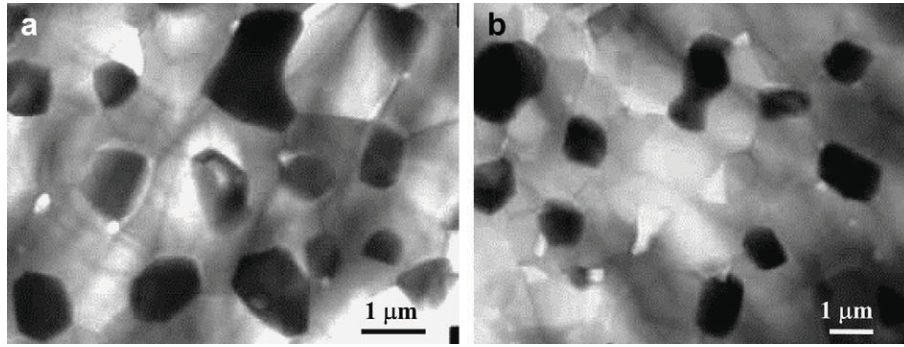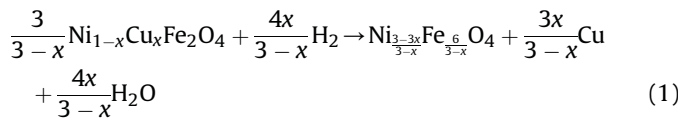**Fig. 3.** Transmission electron micrographs of micro-cermets: (a) cermet obtained from $Ni_{0.6}Cu_{0.4}Fe_2O_4$ (MC04), (b) cermet obtained from $Ni_{0.4}Cu_{0.6}Fe_2O_4$ (MC06).

$$\frac{3}{3-x}Ni_{1-x}Cu_xFe_2O_4 + \frac{4x}{3-x}H_2 \rightarrow Ni_{\frac{3-3x}{3-x}}Fe_{\frac{6}{3-x}}O_4 + \frac{3x}{3-x}Cu$$

$$+ \frac{4x}{3-x}H_2O \qquad (1)$$

Just after the reduction step, the mixture of hydrogen and argon was replaced by a nitrogen atmosphere (purity 99.995 vol. %) and the furnace temperature was risen up to 980 °C for half an hour, to sinter the samples. The sintering was carried out at the maximal temperature used in conventional electrolytic cells for aluminium production. The micro-cermets obtained after this two steps treatment will be called MC04 and MC06 according to the copper content of the starting ferrite from which they come from. They are mainly made of spinel ferrite and metallic copper as revealed by X-ray diffraction patterns (Fig. 1). Because the sintering temperature is lower than the copper melting point, no exudation is observed at the sample surface. Cuprous oxide can however be detected on the X-ray diffraction patterns, mainly on the side of the sample placed in contact with the holder. For samples reduced in "more severe" conditions (i.e., at 350 °C for a longer time or at a temperature higher than 350 °C for 2 h) Cu_2O phase is not detected, but the sintering at 980 °C gives rise to a lower relative density. It is the reason why the reduction conditions were fixed at 350 °C–2 h for the samples studied in detail in the following part of this work.

For such samples, the SEM (Fig. 2) and TEM (Fig. 3) micrographs reveal a good dispersion of copper particles inside the ferrite matrix. The better homogeneity is however observed for the sample obtained from the F06 ferrite. When x is close to 0.4 in the starting ferrite, the cermet is divided into several zones, differing from each other by the copper particles number per unit surface. A high copper concentration in the starting material seems to promote a better dispersion of the metallic particles in the remaining ferrite matrix. For both samples, the copper grains are closely embedded in the spinel oxide. The mean size of the metal particles is close to 0.7 μm for MC04 and 1 μm for MC06. A very small proportion of copper metal particles, between 150 and 350 nm in size, is also observed by field emission gun SEM (Fig. 4). The mean size of the ferrite grains, determined by MFM observations (Fig. 5), is about 1.8 and 1.2 μm for MC04 and MC06, respectively.

Energy dispersive X-ray measurements (EDX) show that metallic particles contain a small rate (less than 2 mass %) of nickel, but less than 1% of copper remains in the spinel ferrite grains after sintering. The measured oxide matrix lattice constants for MC04 and MC06 are close to 0.8360 and 0.8374 nm, respectively.

Eq. (1) gives then a quite satisfactory description of the whole chemical process leading to the formation of the cermets.

Only few pores can be observed in the samples which then display a very good densification, in spite they were sintered at only 980 °C. The relative densities, estimated from the ratio of the real density of the sample to the theoretical density, calculated for cermets having the compositions given by Eq. (1), are at least 95%. These values confirm the high densification of the micro-cermets.
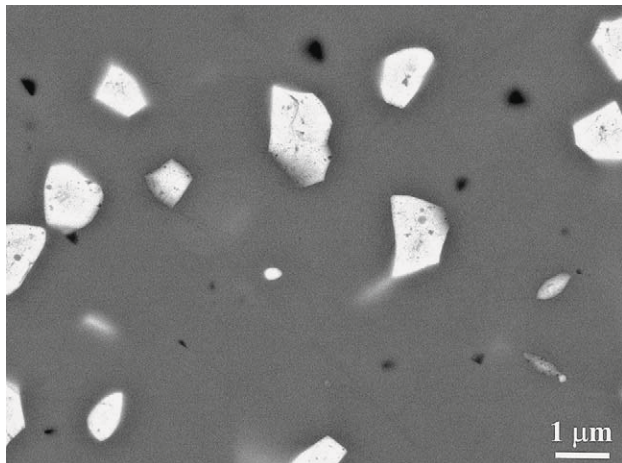

Fig. 4. Evidence by field emission gun SEM observations of nanometric copper metal particles in the micro-cermet MC06.
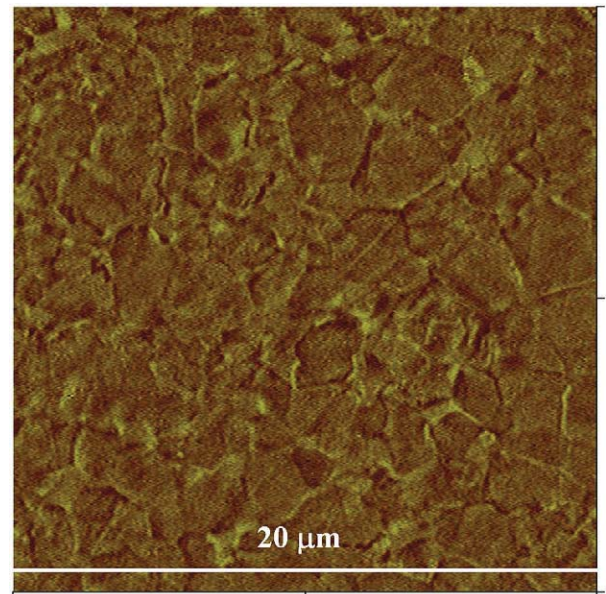

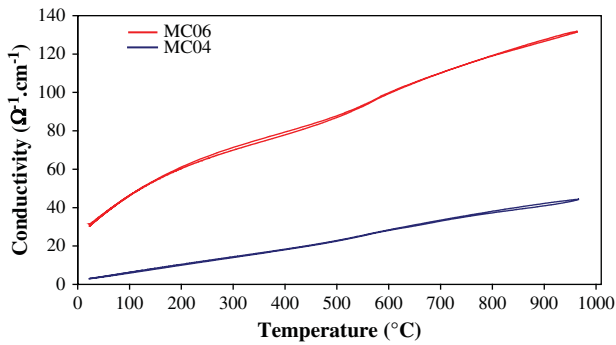**Fig. 5.** MFM micrograph of the cermet obtained from $Ni_{0.6}Cu_{0.4}Fe_2O_4$ (MC04).

Fig. 6. Electrical conductivity versus temperature for (a) MC04 and (b) MC06.

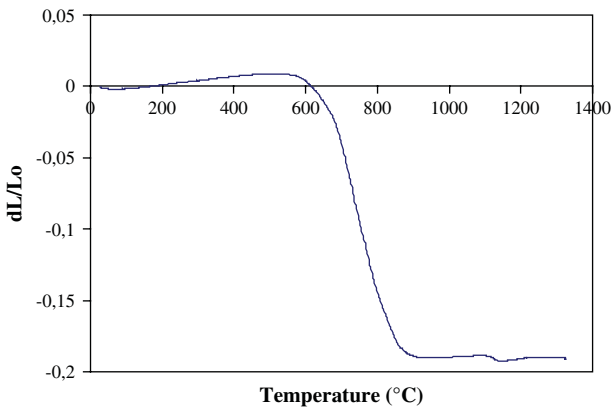**Fig. 7.** Dilatometric curves corresponding to $Ni_{0.6}Cu_{0.4}Fe_2O_4$ when sintered under argon atmosphere.

In spite of a quite high metallic rate in the samples (about 11 and 17 mass %, respectively), the micro-cermets display semi-conducting properties, as revealed by the increase in electrical conductivity with temperature (Fig. 6). The electrical properties are thus mainly governed by the spinel phase in such samples. In ferrites like magnetite, the electronic hopping between Fe^{2+} and Fe^{3+} ions located on octahedral sites, is the mechanism which allows electrical transport. On the other hand, it was demonstrated [9] the nickel ferrites are described by the structural formula $Fe^{3+}[Fe^{3+}Fe^{2+}_{1-x}Ni^{2+}_x]O_4$, in which the ions located in octahedral sites are written inside square brackets. After reduction, the spinel phases in MC04 and MC06 are then close to $Fe^{3+}[Fe^{3+}Fe^{2+}_{0.3}Ni^{2+}_{0.7}]O_4$ and $Fe^{3+}[Fe^{3+}Fe^{2+}_{0.5}Ni^{2+}_{0.5}]O_4$, respectively, and due to a biggest number of octahedral Fe^{2+}/Fe^{3+} pairs, MC06 has a higher electrical conductivity than MC04. Because of the positive $d\sigma/dT$, the electrical conductivities at 980 °C reach quite high values in both cases ($\sigma = 130$ S/cm for MC06 and $\sigma = 44$ S/cm for MC04). That makes the micro-cermets interesting as new cermets for inert anodes devoted to aluminium electrolysis.

5. Comparison with conventional copper/nickel ferrite cermets

Temperatures close to 1300 °C are required to get dense copper/ferrite, or copper/monoxide/ferrite, conventional cermets prepared by reacting metallic copper with nickel and iron oxides. Dense micro-cermets are however sintered 300 °C below. The differences between the sintering temperatures are obviously the cause of dramatic dissimilarities between their respective microstructures, especially the ten times bigger size of the grains in the conventional cermets. But the reasons why the process leading to the micro-cermets allows lower sintering temperature are not so obvious.

Bibliographical data about ferrites for microwave technologies show however that copper ions are used in nickel ferrites [10,11] or in garnets [12] to lower the sintering temperature. Additional experiments carried out for this study also reveal the sintering of $Ni_{0.6}Cu_{0.4}Fe_2O_4$ under argon atmosphere, ends at about 900 °C only (Fig. 7), to give dense ceramics containing a spinel ferrite and a delafossite phase. On the other hand, the sintering of similar $Ni_xFe_{3-x}O_4$ $(0 < x < 1)$ ferrites, coming from oxalic precursors heat-treated at 700 °C, requires temperature as high as 1350 °C [9]. A mixture of 0.87 $Ni_{0.7}Fe_{2.3}O_4$ and $0.2Cu_2O$ was also reduced and sintered for this work, in the same conditions than those used for the micro-cermets. In spite of the same global chemical composition of F04 ferrite, the resulting copper/spinel ferrite cermet has a relative density lower than 65%. From these data and experiments, it is then clear that copper ions inside the spinel structure play a decisive and positive role in the sintering mechanism of spinel ferrites.

6. Conclusion

The partial reduction of green compacts made of mixed copper–nickel ferrites coming from oxalate precursors, allows to obtain materials which can be sintered at only 980 °C in inert atmosphere. The resulting micro-cermets obtained display a high relative density, a very good dispersion of homogeneous metallic particles in the oxide matrix and no exudation of copper. For these materials, the outstanding proclivity towards sintering seems due to the copper ions as it was already observed for pure spinel ferrites or garnets. The micro-cermets prepared are semi-conducting materials with electrical conductivity lying from 44 to 130 S/cm at 980 °C. Their overall physico-chemical characteristics make them interesting for inert anodes dedicated to aluminium electrolysis in melted cryolite.

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