



Consolidation of mechanically alloyed Cu–Ni–Fe material by spark plasma sintering and evaluation as inert anode for aluminum electrolysis



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ABSTRACT

A Cu₆₅Ni₂₀Fe₁₅ powder was prepared by mechanical alloying at semi-pilot scale to form a face-centered-cubic (fcc) phase (γ -phase). This powder was then consolidated by spark plasma sintering (SPS) to form a pellet. The crystallographic structure of the material is not affected by the consolidation process, although there is a slight increase of the crystallite size from 20 to 32 nm, and a slight decrease of the lattice strain from 0.5% to 0.2%. The relative density of the SPS consolidated sample is 95%. Thermogravimetric analysis confirms the good oxidation resistance of the SPS sample with a mass gain of only 0.4% after 20 h of oxidation at 700 °C, which is attributed to the rapid formation of a protective NiFe₂O₄ layer. The SPS sample was then evaluated as inert anode for Al electrolysis in low-temperature (700 °C) KF–AlF₃ electrolyte. After 20 h of electrolysis at an anode current density of 0.5 A cm⁻², the cell voltage reaches an unstable value of 5.0 V. The purity of the produced aluminum is 99.4% and the wear rate of the electrode is estimated at 1.8 cm year⁻¹.

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1. Introduction

The substitution of the consumable carbon anodes by inert anodes (also called O₂-evolving anodes) in the Hall–Héroult electrolysis process is a long-standing goal of the primary aluminum industry [1,2]. The search for a suitable non-carbon anode has gained impetus in the last decade with increasing pressure on the Al industry to reduce their greenhouse gas emissions. The development of new Al electrolysis cells with inert anodes and wetted cathodes promises not only significant environmental benefits but also energy savings and reduction in capital and operating costs [3].

Metallic O₂-evolving anodes have received widespread attention, largely owing to their good electrical conductivity, excellent thermo-mechanical robustness, ease of fabrication and simplicity of electrical connections in comparison to ceramic and cermet anodes [4]. Unfortunately, metallic anodes are not inert under the highly corrosive Hall–Héroult cell conditions and thus, it is necessary to control the surface oxidation of the metal to generate a protective layer during Al electrolysis. This layer should have a low solubility in the electrolyte, a low and stable thickness, a relatively high electrical conductivity, a minimal porosity, a good adherence to the metal and ability for self-repairing during Al electrolysis.

Cu–Ni–Fe based alloys have shown promising properties as inert anodes for Al production in low-temperature electrolyte due to

their ability to form a protective, adherent and electronically conducting NiFe₂O₄-rich scale on their surface during Al electrolysis [5]. However, Cu–Ni–Fe alloys present a two-phase microstructure (a Cu-rich phase and a Fe–Ni-rich phase), which decreases their corrosion resistance because the iron-rich phase is preferentially dissolved during Al electrolysis, inducing the formation of iron fluoride corrosion tunnels in the anode scale [6].

We have recently shown that monophasic Cu–Ni–Fe alloys can be obtained by mechanical alloying over a large composition range [7,8]. Best results were obtained with the Cu₆₅Ni₂₀Fe₁₅ (wt.%) anode, which presents good corrosion resistance in low temperature KF–AlF₃-based electrolyte, resulting in the production of Al with a purity of 99.3%. Further improvement in the anode corrosion resistance was obtained by milling the Cu₆₅Ni₂₀Fe₁₅ alloy powder under an oxygen atmosphere during an appropriate time [9]. For the Cu–Ni–Fe–O anode containing 1.4 wt.% O, the produced Al had a purity of 99.8% and the anode dissolution rate was estimated at 0.8 cm year⁻¹. Such promising results were obtained at laboratory scale (2 A, 20 h) and they must be validated with prolonged electrolysis tests at pilot scale. However, the fabrication of large area electrodes, as required for pilot-scale electrolyses, is challenging because the high chemical homogeneity of the mechanically alloyed Cu–Ni–Fe powders must be conserved during the powder consolidation procedure.

Spark plasma sintering (SPS) is an emerging powder consolidation process, which has been successfully applied for sintering various materials (metals, ceramics, composites) to their full density

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in a much shorter time and at a lower temperature than usually achieved through conventional sintering methods [10,11]. In the SPS process, a powder is uniaxially compressed between two electrodes through which a high pulsed DC current is simultaneously applied. During the procedure, the powder is internally heated by spark discharges between the particles and also by heat transfer from the container. This favors a very high heating rate (up to 1000 K min^{-1}) and the total sintering time can be shortened to a few minutes. The SPS method is thus suitable for the consolidation to near their theoretical density of nanocrystalline and metastable powders with retention of their nanostructure and metastability [10,11]. SPS has been successfully used for sintering various nanostructured materials produced by ball-milling such as Fe–Al alloy [12], Nb/Nb₅Si₃ composite [13], oxide dispersed strengthened steel [14] and Mg–Al–Zn alloy [15]. Recently, SPS have been used to fabricate Fe–30Ni–5NiO anodes for low-temperature Al electrolysis [16].

The objective of the present study is to show that the SPS method is an efficient way for the consolidation of mechanically alloyed Cu₆₅Ni₂₀Fe₁₅ material used as inert anode for aluminum electrolysis.

2. Experimental

2.1. Powder synthesis

Cu₆₅Ni₂₀Fe₁₅ (in wt.%) powder was prepared by ball milling at semi-pilot scale using a Union Process 10SD attritor. Typically, 16 kg of elemental Cu, Ni, Fe powders (Cu purity $\geq 99.5\%$, Ni and Fe purity ≥ 99.9 , -325 mesh) in appropriate proportion were introduced in a stainless steel tank (capacity of 61 L) containing 160 kg of 1/4 in. stainless steel balls, corresponding to a ball-to-powder mass ratio (BPR) of 10:1. The milling was performed for 50 h at 200 rpm under Ar flow ($50 \text{ cm}^3 \text{ min}^{-1}$). Also, 1.5 wt.% stearic acid was added to the initial mixture as process control agent. The milling yield, defined as the ratio of the powder masses after and before milling, was around 98%. The composition of the as-milled powder, checked by energy dispersive X ray (EDX) analysis, was in accordance (within 1–2 wt.%) with its nominal composition. The oxygen content in the as-milled powder measured with a LECO oxygen analyzer was 1.1 wt.%. The crystalline structure of the as-milled powder was determined by X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu K α radiation.

2.2. Powder consolidation

SPS was carried out on a HPD25 SPS machine manufactured by FCT (Germany). The as-milled powder was first sieved to select only the powder fraction with a particle size between 20 and 75 μm (corresponding to about 85 wt.% of the as-milled powder). Typically, 27 g of the sieved powder was then introduced into a graphite die with an inside diameter of 2 cm. The SPS chamber was evacuated and back-filled with argon. An uniaxial pressure of 72 MPa (23 kN) was applied during sintering and progressively decreased during cooling. A high dc current was applied, increasing from 0 to 1020 A in 5 min and then stabilized at 710 A for 30 min to reach a sintering temperature of 600 °C. The pulse cycle was 10 ms on and 10 ms off. The temperature, current, load and displacement (shrinkage) profiles during the SPS are shown in Fig. 1. The obtained pellet had a diameter of ~ 20 mm and a thickness of ~ 10 mm. The structure of the consolidated sample was determined by XRD. Its morphology was characterized by scanning electron microscopy (SEM) in backscattered electron (BSE) mode using a JEOL JSM-6300F scanning electron microscope. Its porosity was calculated according to the equation:

$$\text{porosity (\%)} = \left(\frac{d_t - d_{\text{exp}}}{d_t} \right) \times 100 \quad (1)$$

where d_t is the theoretical density calculated from the alloy lattice parameter determined from XRD measurement, and d_{exp} is the experimentally measured density obtained by weighing and measuring the thickness of the pellet.

2.3. Oxidation test

Thermogravimetric analysis (TGA) was performed on the consolidated sample using a Thermo 500 equipment. The sample was first heated up from room temperature to 700 °C at 10 °C min^{-1} under an Ar atmosphere. The oxidation experiment was then conducted at 700 °C under Ar–20%O₂ with a flow rate of $240 \text{ cm}^3 \text{ min}^{-1}$. The mass variation of the samples was recorded for 20 h. The oxides formed during the TGA experiment were characterized by XRD and by SEM coupled to energy dispersive X-ray spectroscopy (EDX) mapping.

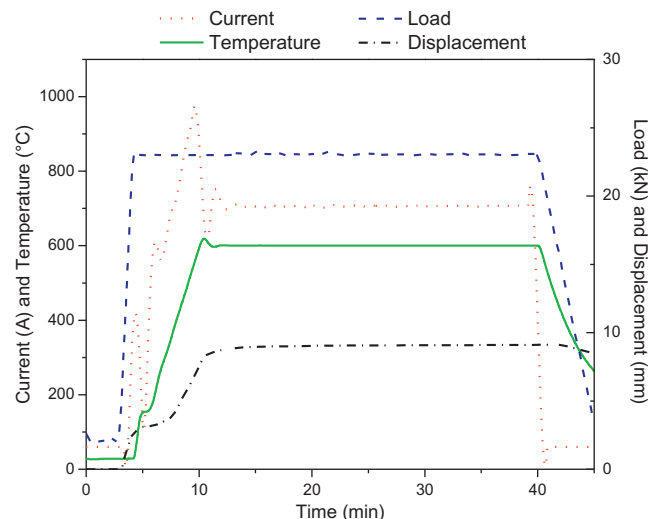


Fig. 1. Evolution of the temperature, current, load and displacement (shrinkage) during the SPS procedure.

2.4. Electrolysis test

For the electrolysis test, an Inconel 718 rod protected by an alumina-based cement coating was screwed in the consolidated sample to serve as current lead. Electrolysis was performed at 700 °C under argon atmosphere using a two-electrode configuration cell controlled by a VMP3 Multichannel potentiostat/galvanostat (BioLogic Instruments). More details on the cell geometry are presented elsewhere [17]. The geometric surface area of the anode was 12 cm^2 and only a part of the electrode ($\sim 4 \text{ cm}^2$) was immersed in the electrolyte. The counter electrode was a graphite rod ($\sim 13 \text{ cm}^2$ immersed in the electrolyte). The anode–cathode distance was 2.3 cm. The crucible containing the electrolyte was made of sintered alumina. The electrolyte composition was 50 wt.% AlF₃–45 wt.% KF–5 wt.% Al₂O₃. No alumina was added during the electrolysis since its consumption is compensated by the dissolution of the alumina crucible, as confirmed by LECO oxygen analyzes of the electrolyte (not shown here). Electrolysis was performed at an anode current density of 0.5 A cm^{-2} for 20 h. Current interruption measurements were performed periodically during the 20 h of electrolysis to determine the evolution of ohmic drop. The ohmic drop was defined as the difference between the operating voltage measured before the current interruption and the voltage taken a few ms after the current interruption. The oxide scale formed on the electrode after 20 h of electrolysis was characterized by SEM–EDX and XRD analyzes. The amounts of Cu, Ni and Fe dissolved in the produced aluminum and in the electrolyte were quantified by neutron activation. The annual wear rate of the anode was calculated according to the equation:

$$\text{Wear rate (cm year}^{-1}\text{)} = \frac{(m_b w_b + m_{\text{Al}} w_{\text{Al}}) \times 365 \times 24}{100 \times \rho_a \times S_a \times t} \quad (2)$$

where m_b is the mass of electrolyte (g); w_b is the mass fraction of contaminants (Cu + Ni + Fe) in the electrolyte (wt.%); m_{Al} is the mass of produced Al (g); w_{Al} is the mass fraction of contaminants (Cu + Ni + Fe) in the produced Al (wt.%); ρ_a is the anode density (g cm^{-3}); S_a is the geometric surface area of the anode immersed in the electrolyte (cm^2); and t is the electrolysis time (h).

3. Results and discussion

Fig. 2 shows the XRD patterns of the as-milled and sintered Cu₆₅Ni₂₀Fe₁₅ samples. Both XRD patterns exhibit only one series of peaks corresponding to a face-centered-cubic (fcc) phase (γ -phase) attributed to a Cu(Ni, Fe) solid solution. The SPS treatment induces a decrease of the full width at half maximum (FWHM) of the diffraction peaks. The lattice parameter of the γ -phase was calculated from the peak positions, while the crystallite size and the lattice strain were determined from the FWHM of the diffraction peaks by using Williamson–Hall plot (not shown). The results are summarized in Table 1. The lattice parameter of the γ -phase decreases slightly (from 3.608 Å to 3.605 Å) with the consolidation treatment. The crystallite size increases from 20 to 32 nm and the lattice strain decreases from 0.5% to 0.2% with the consolida-

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