

Evaluation of a Pre-Oxidation Treatment for Limiting Electrolyte Penetration in Cu-Ni-Fe Anode during Al Electrolysis

G. Goupil¹, E. Gavrilova¹, B. Davis², D. Guay¹ and L. Roué¹

¹ INRS-Énergie, Matériaux et Télécommunication, 1650 Blvd Lionel-Boulet, Varennes (QC) J3X 1S2 Canada

² Kingston Process Metallurgy Inc.; 759 Progress Avenue, Kingston, Ontario, K7M 6N6, Canada

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Abstract

A comparative study on untreated and pre-oxidized Cu₆₅Ni₂₀Fe₁₅ inert anodes for aluminium electrolysis in low temperature (700°C) KF-AlF₃ electrolyte was conducted. The pre-oxidation treatment was performed at 700°C under Ar-20%O₂ for 3 h, leading to the formation of a CuO-NiFe₂O₄ layer on the anode. This preformed oxide layer has a positive impact on the anode corrosion resistance by favoring the formation of a denser oxide scale with limited electrolyte infiltration during Al electrolysis.

Introduction

Cu-Ni-Fe and Cu-Ni-Fe-O based materials produced by mechanical alloying have shown promising properties as inert anodes for Al production in low-temperature electrolyte due to their ability to form a protective NiFe₂O₄-rich scale on their surface during Al electrolysis [1,2]. However, the outward diffusion of Cu in Cu oxides is not fully impeded, inducing the formation of a porous Cu-depleted region at the oxide/alloy interface. As a result, electrolyte penetration occurs in the scale, which favors the progressive formation of an iron fluoride-rich layer at the oxide/alloy interface and FeF₂ tunnels in the bulk anode [3]. This corrosion region could be problematic for the long-term viability of the anode and thus, further work must be performed to overcome this issue.

In this context, the objective of the present study is to evaluate the influence of a pre-oxidation treatment for limiting the electrolyte penetration in Cu-Ni-Fe anode during Al electrolysis.

Experimental

Cu₆₅Ni₂₀Fe₁₅ (in wt%) alloy was prepared by ball milling using a Union Process SD01 attritor. 16 kg of elemental Cu, Ni, Fe powders (Cu purity ≥ 99.5%, Ni and Fe purity ≥ 99.9, -325 mesh) in appropriate proportion were introduced in a stainless steel vial (capacity of 61 L) containing 160 kg of 1/4 inch stainless steel balls, corresponding to a ball-to-powder mass ratio (BPR) of 10:1. 1.5 wt.% of stearic acid was added to the initial mixture as process control agent. The milling was performed for 40 h at 200 rpm under Ar flow (50 cm³ min⁻¹). The composition of the as-milled powder determined by energy dispersive X-ray (EDX) analysis was in accordance (within 1-2 wt%) with their nominal composition. The oxygen content in the as-milled powder measured with a LECO analyzer was 0.55 wt%.

The milled powder was consolidated according to the procedure described in [2] to form disc samples (11.5 mm diam., 5 mm

thickness, ~7% porosity) for the electrolysis tests. The crystalline structure of the as-milled and consolidated powders was determined by X-ray diffraction (XRD) using a Bruker D8 diffractometer with Cu K_α radiation. Their morphology was characterized using a JEOL JSM-6300F scanning electron microscope (SEM) in backscattered electron (BSE) mode.

The pre-oxidation treatment of the anode was performed at 700°C under Ar-20%O₂ with a flow rate of 240 cm³ min⁻¹ for 3 h. The oxide scale formed on the anode was characterized by XRD and SEM-EDX analyzes.

Electrolysis tests were performed on untreated and pre-oxidized anodes at I_{anode} = 0.5 A cm⁻² for 20 h at 700°C under argon atmosphere using a two-electrode configuration cell as described in [4]. The geometric surface area of the anode immersed in the electrolyte was ~4 cm². The counter electrode was a graphite rod (~13 cm² immersed in the electrolyte). The crucible containing the electrolyte was made of sintered alumina. The electrolyte composition was 50 wt% AlF₃-45 wt% KF-5 wt% Al₂O₃. The oxide scale formed on the anodes after 20 h of electrolysis was characterized by XRD and SEM-EDX analyzes.

Results and discussion

The XRD patterns of the as-milled and consolidated Cu₆₅Ni₂₀Fe₁₅ samples (Fig. 1a) show only one series of peaks characteristic of the fcc Cu(Ni,Fe) phase. Structural refinement using Fullprof software indicates an increase of the crystallite size (from 20 to 30 nm) and a decrease of the lattice strain (from 0.5 to 0.3%) with the consolidation procedure. A slight decrease of the lattice parameter of the Cu(Ni,Fe) phase (from 3.608 to 3.603 Å) is also observed, which may reflect the slight decrease of the Fe content in Cu(Ni,Fe) phase due to the formation of Fe₂O₃ precipitates during the consolidation procedure [2]. These precipitates are not detected on the XRD pattern due to their small size and low amount (1.83 wt% assuming that all the 0.55 wt% oxygen in the as-milled sample reacts with Fe to form Fe₂O₃).

Fig. 1b shows SEM images of the as-milled and consolidated Cu₆₅Ni₂₀Fe₁₅ samples. The as-milled powder (left image) consists of micron-sized particles with irregular shape. Their median diameter (determined by laser scattering method) is 20 μm. The consolidated sample appears dense (Fig 1b, right image). A few well-dispersed submicrometric dark spots are observed, which are identified as Fe₂O₃ precipitates, supporting the previous assumption.

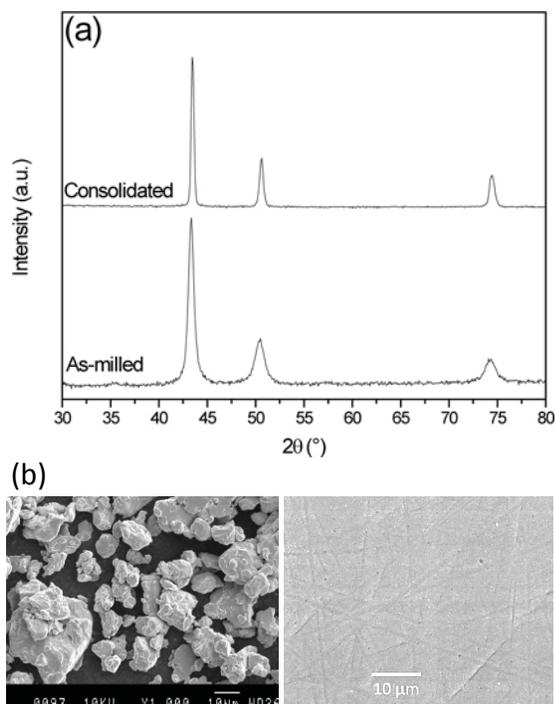


Fig. 1. (a) XRD patterns and (b) SEM micrographs of the as-milled and consolidated $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ samples.

The oxide scale formed on the consolidated $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ sample during the pre-oxidation procedure was characterized by SEM and EDX mapping (Fig. 2) and XRD (not shown). The oxide scale presents a bilayered structure. The outermost layer (20-25 μm thick) is mainly CuO whereas NiFe_2O_4 is the main constituent of the inner layer (10-15 μm thick). This structure results from the outward diffusion of Cu to form Cu oxides and the internal oxidation of Fe and Ni to form NiFe_2O_4 [1,5].

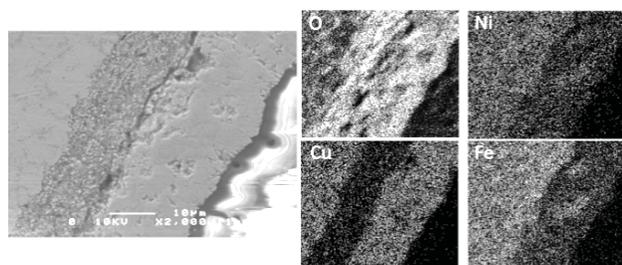


Fig. 2. SEM cross-section image and corresponding EDX-mapping images of the O, Ni, Fe and Cu elements of the $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ material after 3 h of oxidation at 700°C under $\text{Ar}:\text{O}_2$ (80:20).

Fig. 3 shows the evolution of the cell voltage during Al electrolysis with untreated and pre-oxidized $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ anodes. In both cases, the cell voltage slowly increases with the electrolysis time to reach a nearly stable value of 4.3 V after 20 h of electrolysis.

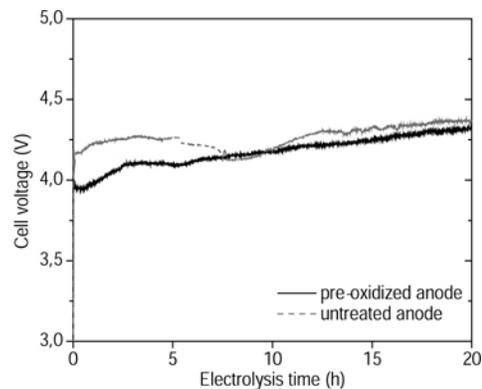


Fig. 3. Cell voltage versus electrolysis time at $I_{\text{anode}} = 0.5 \text{ A cm}^{-2}$ in KF-AlF_3 electrolyte at 700°C with untreated and pre-oxidized $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ anodes.

Fig. 4 shows cross-section SEM images and corresponding EDX mapping images (O, Al, F, K, Cu and Ni elements) of the untreated and pre-oxidized $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ anodes after 20 h of electrolysis. In both cases, the oxide scale is delaminated from the bulk alloy probably due to the thermal shock when the electrodes were removed out of the electrolyte. The thickness of the oxide scale is 550 and 450 μm for the untreated and pre-oxidized anodes, respectively. On both anodes, the surface scale is composed of three main layers: (i) an outer CuO_x rich layer, (ii) an intermediate NiFe_2O_4 rich layer and (iii) an inner F-rich layer. However, for the pre-oxidized anode, the intermediate Cu-depleted layer is less discernable and the oxide scale seems to be denser. Moreover, it clearly appears by comparing the F mapping images in Fig 4a-b that the inner F-rich layer is much thinner for the pre-oxidized anode.

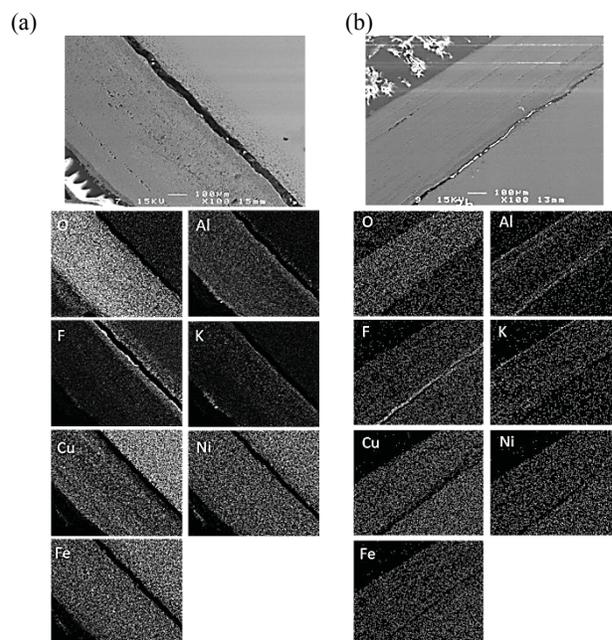


Fig. 4. SEM cross-section image and corresponding EDX images of the O, Al, F, K, Cu, Ni and Fe elements of the untreated and pre-oxidized $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ anodes after 20 h of electrolysis.

As shown in our previous study [3], the presence of a F-rich layer at the oxide-bulk interface is related to the infiltration of the

electrolyte in the oxide scale, which accumulates at the oxide-bulk alloy interface and preferentially reacts with iron of the alloy to form FeF_2 tunnels in the bulk anode. This process seems to be less marked on the pre-oxidized anode, probably because the presence of NiFe_2O_4 on the starting anode limits the outward diffusion of Cu in Cu oxides in the first stage of the electrolysis. As a result, the inner porous Cu-depleted region favoring electrolyte infiltration is less important and thus, the formation of FeF_2 in the bulk anode is less favorable.

Conclusion

This study demonstrated that the pre-oxidation of the $\text{Cu}_{65}\text{Ni}_{20}\text{Fe}_{15}$ anode has a positive impact on its corrosion resistance by inducing the formation of a denser oxide scale during Al electrolysis. This limits electrolyte penetration and prevents the formation of a thick fluoride-rich layer at the oxide-alloy interface. The duration of this effect will have to be evaluated through prolonged electrolysis tests.

References

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