Investigating the Corrosion Behaviors of Fe-Ni-Cr Anode Material for Aluminum Electrolysis

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Keywords: Anode materials, Aluminum electrolysis, Corrosion

Abstract

Corrosion resistance in cryolitic melts is the most important property for inert anode used in aluminum electrolysis. Ni-Fe-Cr alloy anodes were prepared with a protective layer on their surface through a pre-oxidation procedure, and corrosion tests were carried out in a laboratory aluminum electrolysis cell at 950 ºC. The microstructures of the anodes before and after the electrolysis were inspected using XRD and SEM techniques. It is found that a starting protective layer formed after 10 - 20 hour pre-oxidation could be sufficient to make the anode maintaining function during the corrosion tests. A corrosion layer with varying thickness on the metal anodes at a current density of 0.75 A/cm^2 was formed in aluminum electrolysis in the cryolitic melts, where various metal fluorides were involved in the surface reactions. Detailed analysis revealed that the chemical compositions of the corrosion-oxide protective layers on the metal anodes varied due to selective corrosion and migration of Fe, Ni, Cr, and O crossing the interface. The results may provide useful technical data for materials design and process development for metal inert anode that can maintain the function through a dynamic oxide protective layer during aluminum electrolysis.

Introduction

The primary aluminum production for today involves the reduction of alumina with carbon anodes, forming carbon dioxide:

$$2Al_2O_3 + 3C = 4Al + CO_2 \tag{1}$$
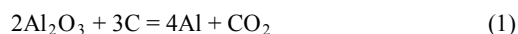
Using an inert anode to replace the consumable carbon anodes, the primary anodic product will be oxygen:

$$2Al_2O_3 = 4Al + 3O_2 \tag{2}$$

This can significantly reduce greenhouse emissions and production costs associated with the carbon anode consumption. To withstand the highly corrosive conditions in aluminum electrolysis cell, the inert anode materials must have excellent high-temperature oxidation and corrosion resistance to oxygen and cryolite melts.

Among the materials under consideration, Ni-Fe-based alloys and their composite materials have shown a promise for practical application that has received great attention [1-5]. However, Ni-Fe alloys under the oxidizing conditions in the reduction cells may develop corrosion layers containing Fe$_x$O and/or other metal oxides, which may either provide protection to the metal anode or result in more corrosion on the anodes during aluminum electrolysis [6, 7].

Cu-Ni-Fe ternary alloys have been studied as the inert anodes where Cu-Ni-Fe alloy had a two- phase microstructure of Cu-rich phase and Fe-Ni-rich phase [8, 9]. The Fe-rich phase can be preferentially corroded during aluminum electrolysis, thus providing iron-fluoride corrosion tunnels within the anode corrosion layers [9]. The additions of 10 - 30 wt.% Co to Ni-Fe alloy system were found to significantly improve the anodic wear and oxidation resistance due to the suppression of Fe$_x$O formation. However, the reaction scales had excessive porosity, non-homogeneity and poor surface adherence, so that it could not provide sufficient protection to the anodes [10, 11].

In a previous work [12], a relative short time experiments on Fe-Ni-Cr alloys were carried out to check the influence of pre-oxidation with various temperatures on the corrosion resistance of the metal anodes. In this work, the corrosion behaviors of ternary Ni-Fe-Cr alloy as inert anode material in aluminum electrolysis were investigated mainly at high-temperatures. In particular, the protective function of the pre-oxidation layer and its corrosion scale were experimentally studied in laboratory aluminum electrolysis. The aim is to have better understanding of the property of the complex oxides scale on the metal anode and its *in-situ* protective function that could be maintained during electrolysis. The addition of Cr into the Fe-Ni alloy is considered with the low solubility of its oxide and possible formation of a stable, dense oxide scale. The information obtained can be used in materials design and process development for the metal inert anodes and their long term performance in aluminum electrolysis.

Experimental

Anode Material and Pre-Oxidation Treatment
Ni-Fe-Cr alloy (about 11 wt. % Ni, 66 wt. % Fe and 23 wt. % Cr) was obtained from commercial metal supplier. All samples were machined to a cylindrical form (Φ20×30 mm) for oxidation and corrosion tests. Their surfaces were cleaned in ultrasound cleaner before a test.

Figure 1 shows the set-up used for pre-oxidation of the metals anode samples at high-temperature, which was built up based on thermo-gravimetric analysis method (TGA). The sample was suspended by Pt wire inside a vertical alumina tube furnace. The variation of the mass of a sample vs. the time in heat treatment was recorded every 5 s by continuous weight measurements. The measured data were stored in a PC connecting to an electronic balance (Sartorius, BS124S, Max: 120 g, resolution: 0.0001 g). Isothermal oxidations of alloy anodes were measured at various temperatures and duration in air under heat treatments.
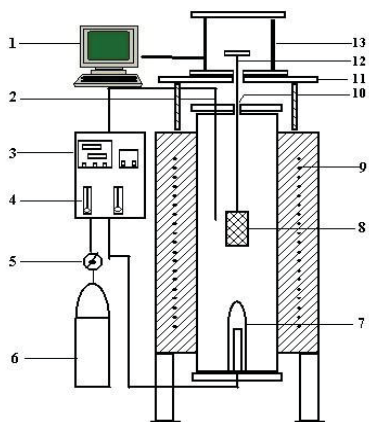
Figure 1. Set-up for high-temperature oxidation tests: 1- PC; 2- Thermocouple; 3- Temperature controller; 4- Flowing meter; 5- Pressure reducing valve; 6-Gas flask; 7- Preheat tube; 8- Testing specimen; 9- Heating element; 10- Gas outlet; 11- Supporting plate; 12- Connecting wire; 13-Electronic balance

Laboratory Aluminum Electrolysis
The laboratory aluminum electrolysis cell system has been described in the previous work [12]. The electrolysis experiments were performed under argon atmosphere at anode current density of 0.75 A/cm^2 for 2 h, where the anode–cathode distance was kept about 33 mm during the tests.

Characterization and Analysis
After oxidation or electrolysis corrosion tests, the working surface of the alloy samples was inspected by X-ray diffraction (XRD) using a M21X diffractometer with Cu Ka radiation. The cross-section of the anode samples were examined using a JSM-6480LV scanning electron microscope (SEM). The compositions of the oxide scales and corrosion layers on the anode samples after polishing were also determined by energy dispersive X-ray spectroscopy (EDS).

Results and Discussion

Protective Scale Formed by Pre-Oxidation of Alloy Anodes

In early stage of this work, lower temperatures (700 – 800 ºC) and shorter processing time (less than 2 hours) have been tried in heat treatment, but the oxidation scales obtained could not satisfy the quality standard for use as anode in aluminum electrolysis.

Figure 2 shows an oxidation scale formed on the alloy anode after 10 hours heat treatment in air at 950 ºC. XRD spectrum revealed that complex oxides of $NiFe_2O_4$ and $(Fe_{0.4}Cr_{0.4})_2O_4$, and metal phase of (Fe, Ni) and $(Fe_{0.4}Cr_{0.4})_2$ co-existed on the scale surface. Post-inspection found that the adherence of the oxidation scale to the metal substrate was not strong enough to maintain the anode function in a high temperature, corrosive environment.

In Figure 3, the heat treatment time for the alloy sample has been prolonged to 20 hours at 950 ºC, resulting further chemical change in composition of the scale. XRD analysis indicated that there were $FeCr_2O_4$, $Cr_{1.3}Fe_{0.7}O_3$, and (Fe, Cr) on the oxidation scale. Both the density of the oxidation scale and the adherence of the scale to the metal matrix were improved, so that it could be used further in aluminum electrolysis tests.
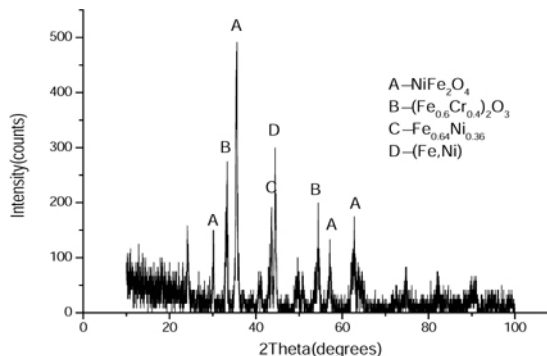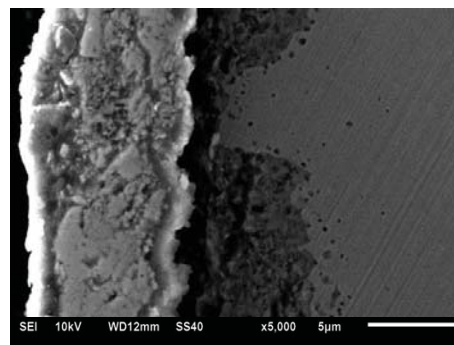

Figure 2. SEM microphotograph (up) on the cross-section and XRD spectrum (down) on the surface of the oxidation scale of Fe–Ni–Cr alloy sample heat treated in air at 950 ºC for 10 h
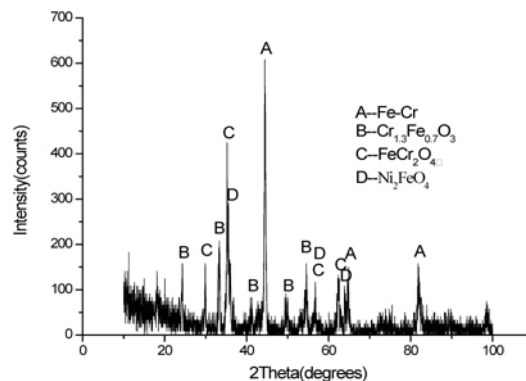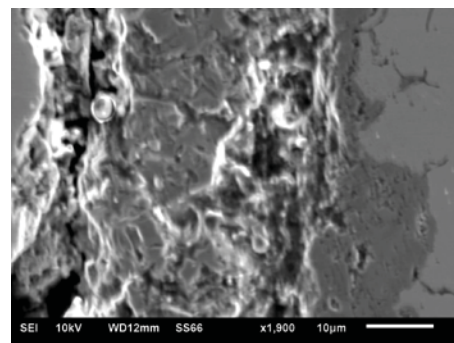

Figure 3. SEM microphotograph (up) on the cross-section and XRD spectrum (down) on the surface of the oxidation scale of Fe–Ni–Cr alloy sample heat treated in air at 950 ºC for 20 h

It is noted that more $FeCr_2O_4$ is presented in the scales with longer time of pre-oxidation that may contribute the growth in

thickness of the oxidation scales. The thickness of the oxidation scales increased with prolonged time in pre-oxidation treatment, as shown in Table I. For the purpose of comparison, the oxidation scales with a range of lower temperature are also listed, indicating a strong influence of the raised temperatures on the scale thickness. However, the mechanism on variation in chemical composition of the oxidation layers still needs further investigation.

Table I Thickness of Oxidation Scales with Various Temperatures and Time in Heat Treatment

Temperature (ºC)	Treating Time (Hours)	Thickness (μm)
700	10	1.79
800	10	1.30
950	10	9.35
950	20	34.55

Corrosion Layer on the Alloy Anodes after Electrolysis

Figure 4 is the photograph of the alloy anodes after aluminum electrolysis. The oxide scale on the anodes can provide a protective function to the chemical attack of the cryolite melts. The extra frozen electrolyte was cleaned from the surface of the alloy anode, and then XRD inspection was applied on the surface of the anodes.

Figure 4. Photographs of the alloy anodes after aluminum electrolysis at 950 ºC

Figure 5 shows the presence of various oxides ($NiCrO_4$, CrO_2, Al_2O_3, Fe_2O_3, and $NiAl_2O_4$), fluoride (AlF_2), Fe-Cr and Fe-Ni in the corrosion layer on the alloy anode surface after aluminum electrolysis.

In Figure 6, more complex oxides ($FeCr_2O_4$, $NiCr_2O_4$, $NiFe_2O_4$, $FeAl_2O_4$) generate on the surface of the corrosion layer after aluminum electrolysis, while no base metal phase shows on the corrosion layer on the anode with a prolonged time of pre-oxidation. Under these conditions, the alloy anode demonstrated a better protective function with a thick scale prepared through a prolonged time in pre-oxidation treatment. This suggests that the pre-oxidation should produce a thick scale that is dense, adhesive to the alloy anode.
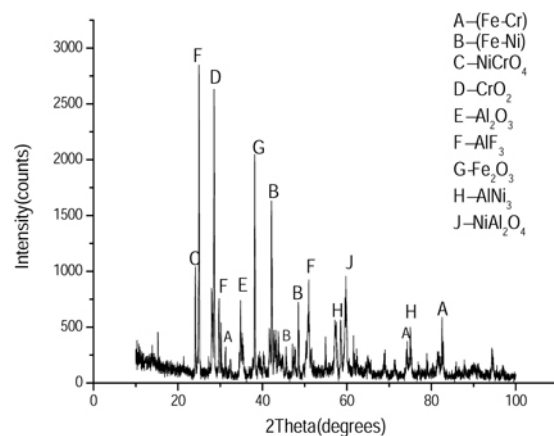

Figure 5. XRD spectrum on the surface of the electrolysis corrosion layer of Fe–Ni–Cr alloy anode (pre-oxidation at 950 ºC for 10 h)
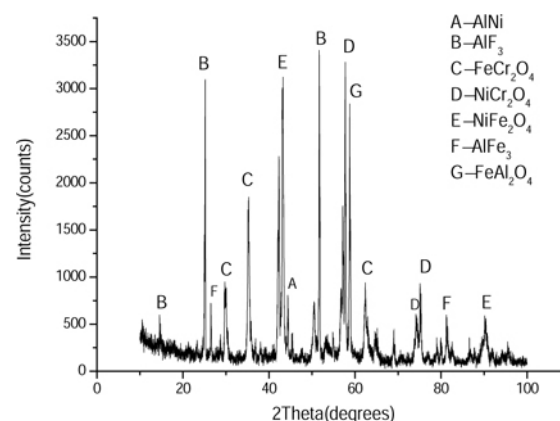

Figure 6 XRD spectrum on the surface of the electrolysis corrosion layer of Fe–Ni–Cr alloy anode (pre-oxidation at 950 ºC for 20 h)

Composition Change Crossing Corrosion-Oxidation Layers on the Alloy Anodes after Eletrolysis

The alloy anodes after electrolysis were sectioned for SEM examination, where scanning lines of Fe, Ni, and Cr were performed on the surface of the cross-section. The quantity of these elements is summarized relative to each other.

Figure 7 and figure 8 show the change of Fe, Ni and Cr against the distance crossing the section surface of the alloy anodes. Both Fe and Cr contents decreased from inside to out-side, while Ni increased from inside to out-side. This fact suggests that Ni-rich layer may be formed due to the decrease in Fe and Cr contents.

It should be pointed out that thin (<10 μm) scales are likely to offer limited protection due to bath penetration, while the thick (>60 μm) scales may significantly increase the anode resistivity and are prone to spalling. A scale thickness on the alloy anode in the range of 30–40 μm is therefore recommended, although the optimum thickness is likely to depend on the oxide constituents and the application conditions as well.
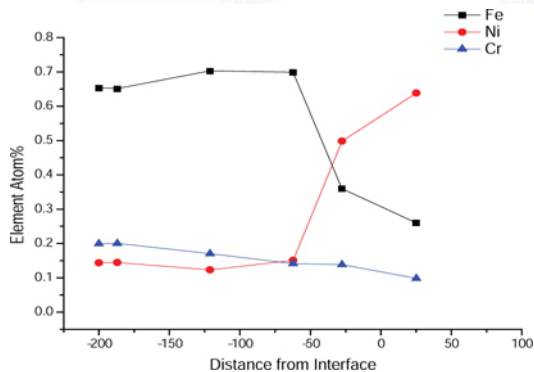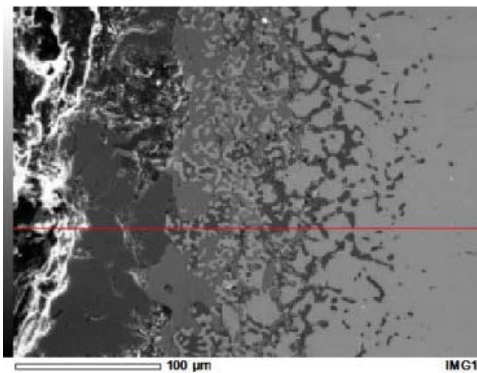
Figure 7. SEM cross-section image and composition change vs. of Fe-Ni-Cr anodes after electrolysis at 950ºC (pre-oxidized at 950 ℃ in air for 10h)
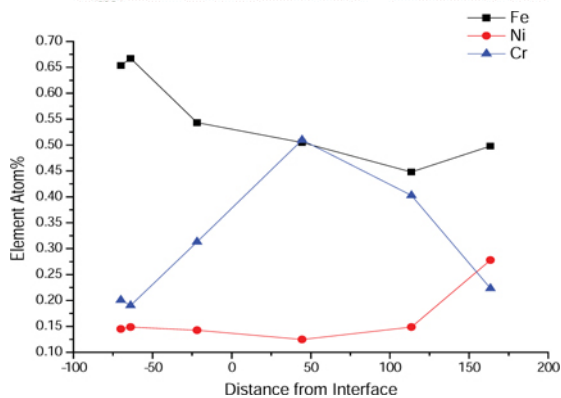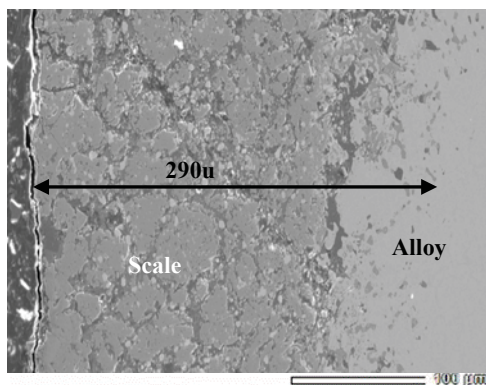

Figure 8. SEM cross-section images of Ni-Fe-Cr anodes after electrolysis at 950ºC (pre-oxidized at 950 ℃ in air for 20h : the numbered points showing the locations for EDS analysis

Here is the pre-oxidation scale of the alloy anodes provides the protective function. It is unclear how the *in situ* formed oxide scales can offer some protection to the anodes. This implies the theoretical expectation for such oxide scales to make a self-protection to the alloy anode by oxygen generated during aluminum electrolysis might be difficult to realize in practical operation.

Conclusions

1. A pre-oxidation scale on the Fe-Ni-Cr alloy anode can provide a protective function to the chemical attack and the oxidizing atmosphere in aluminum electrolysis.

2. The protective scale formed through pre-oxidation should make a starting thickness (30–40 µm recommended) to maintain its function during aluminum electrolysis,

3. The contents of Ni, Fe and Cr change along with varying distance from inside to outside of the alloy anode, crossing the metal base, scale and corrosion layers on the alloy anodes after electrolysis.

Acknowledgement

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