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Effect of thermal treatment of copper anodes on electrorefining process

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ABSTRACT

The aim of this paper is to study the effect of thermal treatment of the conventional copper anodes on the dissolution behavior and passivation of anodes during electrorefining process. Four similar impure copper anode samples were heated to 800 °C with holding time of 1800 s followed by quenching in different media to achieve different cooling rates such as brine 10%, water, machine oil and/or still air. Each anode sample was centered in an electrolytic cell together with two stainless steel permanent cathode sheets and all was immersed in an acidified electrolyte containing 0.040 kg/l of Cu^{2+} and 0.170 kg/l of H_2SO_4 with some bath organic additives like bone glue and thiourea. The process was carried out at a constant electrolyte temperature of 65 °C, an electrolyte stirring rate of 350 rpm and a constant cathodic current density of 350 A/m^2. Polarization curves for the different copper anodes using a potentiodynamic technique with a scanning rate of 0.5 mV/s were conducted to examine the dissolution rate and passivation of different anodes. The obtained results indicated that, the best anodic dissolution rate and anodic passivation time are obtained with anodes quenched in water ($2.685 * 10^{-6}$ kg/s & 450 s), while that of untreated anode is only $2.023 * 10^{-6}$ kg/s and 348 s. Thermal treatment of copper anodes has a good effect on the specific energy required for the electrorefining process where it is about 0.329 kWh/kg when quenched anode in water is electrolyzed, while it is about 0.491 kWh/kg when untreated anode was electrorefined.

1. Introduction

Copper refining is a very necessary step for impurity removal in order to achieve the desired properties for specific application. For this, Cu electrorefining has been given much attention and has advanced recently (Filzwieser et al., 2012). Increasing the current density in the electrolytic refining of copper anodes has resulted in an increased copper production rate and hence a cost reduction (Arentzen, 1984; Imamura and Katoh, 1984). To improve the efficiency of electrorefining process, the electrolyte characteristics (such as: temperature, circulation rate, copper and acid concentrations, residence time in the cell, and addition of organic compounds) have been extensively studied by many researchers (Gladysz et al., 2007; Moats et al., 2000; Owais, 2003, 2009). On the other hand, the anode casting process is of special importance as the quality of the anode is one of the main factors affecting the efficiency of the electrorefining process (Antrekowitsch et al., 1999). During solidification of the anodes from fire refined melt, some elements are enriched in the solid phase (e.g. Ni) and others in the melt (e.g. O, Pb, Sn, As, Sb, Se, Bi). This leads to either solid solutions or separate phases of various compositions in the solidified anode and hence affects the properties and therefore the subsequent electrorefining steps (Dimitrijević et al., 2009; Filzwieser et al., 2012; Wenzl et al., 2007). Many works have been done to improve the quality of the anode through optimization of the casting process (Ahan et al., 2005; Antrekowitsch et al., 1999; Imamura and Katoh, 1984; Wenzl et al., 2007, 2008).

The effect of different cooling rates of the copper electrode during its solidification from fire refined melt on its microstructure and the electrolysis process was studied previously (Ahan et al., 2005; Antrekowitsch et al., 1999; Arentzen, 1984; Imamura and Katoh, 1984; Wenzl et al., 2007, 2008). It is known that the cooling rate determines the structure: high cooling rates lead to fine grains and suppress segregation of impurities, whereas slow cooling results in coarse microstructure and micro- and/or macro-segregation (Antrekowitsch et al., 1999; Arentzen, 1984). Since fine structure is reported to result in better dissolution behavior, rapid cooling seems to be preferable (Imamura and Katoh, 1984; Wenzl et al., 2008). Indeed, those works considered the effect of mold cooling rate from the mold materials which affects the solidification process and hence the grain size and grain distribution as well as the impurity segregation.

However, the effect of cooling rate of the already solidified anode has not been studied yet. The thermal treatment can be applied on copper anode during the cooling step after its partial cooling to about 800 °C by picking up the electrode from the mold and exposing it to a suitable cooling media like water or by reheating the completely cooled anode to room temperature to about 800 °C followed by its cooling in a suitable media.

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Table 1
Cooling rates of different quenching media compared to water.

Quenching medium	Cooling rate compared to water
Brine 10% at 20 °C	1.96
Water at 20 °C	**1.00**
Machine oil	0.22
Still air	0.032

In the present work, the effect of thermal treatment of copper anodes in different media on both anodic passivity and anodic dissolution rate is studied. Different media such as brine 10%, water, machine oil and/or in a still air were chosen to give different cooling rates as illustrated in Table 1 (NavaChing (2008)).

To accomplish the objective, four impure copper anodes with the same chemical composition and dimensions were heated in a muffle furnace for 30 min at 800 °C and quenched in the different media. Another untreated sample was subjected to the electrorefining experiment with the same conditions as the other treated samples. The same experimental conditions like that used in industry were applied. Two stainless steel sheets used as starting cathodes together with the impure copper anode were put in the electrolytic cell containing an acidic solution composed of 40 g/l Cu^{2+}, 170 g/l H_2SO_4 and some organic additives "bone glue and thiourea". The cathodic current density, electrolyte temperature and electrolyte stirring rate were set at 350 A/m^2, 65 °C and 350 rpm, respectively. Cubic samples taken from different treated and untreated anodes were subjected to current density-potential tests with a scanning rate of 0.5 mV/s, to examine the passivation time and dissolution rate of different anodes. The electrodeposited copper cathodes were analyzed using Atomic Emission Spectroscopy.

2. Experimental part

2.1. Materials

Similar samples of impure copper anodes as shown in Fig. 1, with active dimensions of 150 mm height, 65 mm width and 10 mm thickness with the chemical composition given in Table 2, were heated in a muffle furnace at 800 °C for 30 min followed by quenching in different media with a different cooling rate. The highest cooling rate was obtained when the anode was quenched in water containing 10% NaCl (brine 10%), followed by fresh tape water with no additions, followed by machine oil and finally the lowest cooling rate was obtained by cooling in still air. Another copper anode sample with the same dimensions and chemical analysis was used as a reference sample without any thermal treatment to compare its dissolution behavior with the other quenched samples. Cathode sheets made from stainless steel type 316 L with active dimensions of 160 mm height, 80 mm width, and 3 mm thickness were hanged in the electrolytic cell as the negative pole. The electrolytic cell was filled with an acidic electrolyte composed of a constant concentration of 40 g/l of Cu^{2+} which was obtained from dissolving of $CuSO_4 \cdot 5H_2O$ salt in distilled water together with H_2SO_4 with a constant concentration of 170 g/l. Some organic additives such as bone glue and thiourea "0.11 g/kg of deposited cathodic copper" were added to the electrolyte to control both the smoothness of the cathode surface and the refinement of the deposited copper grains, respectively.

A view of the copper anode sample after the electrorefining process is illustrated in Fig. 2 with a slime layer formed on the anode surface and after its washing.

2.2. Experimental apparatus and procedure

The bench scale experimental setup used for the electrorefining experiments is illustrated as a sketch in Fig. 3, while the experimental devices used in this work are shown in Fig. 4. Both impure copper anode plate and stainless steel cathode sheets were inserted in a 5 liter beaker glass filled with the electrolyte. The electrodes were suspended in the cell with an anode/cathode separating distance of 25 mm. A hot plate with magnetic stirrer (K…RH basic IKA LABORTECHNIK, Germany) was used for heating up the electrolyte to a fixed temperature of 65 °C (±0.5 °C) and agitating the electrolyte to a constant stirring rate of 350 rpm. A constant DC current was supplied to the electrodes to give a cathodic current density of 350 A/m^2 by a power supplier (GW Instek, DC Power supply sps-1820, Taiwan). The output cell voltage (V) against time (h) was directly recorded to the computer using digital multimeter VA18B with PC-Link computer software.

Both samples of copper anodes and the electrodeposited copper cathodes were extensively washed in distilled water, dried, weighed and analyzed using Atomic Emission Spectroscopy (ARL 31000 RET, Switzerland).

2.3. Current density–potential curves

Semi-Cuboid anode samples of around 1 cm edge length as shown in Fig. 5, were taken from the tested copper anode plates. The samples coated on five faces with an epoxy resin. The active area of each sample (1 cm^2) was grinded up to 600 mesh using emery papers.

The polarization tests were carried out using the same electrolyte composition as that used in electrorefining experiments (40 g/l Cu^{2+} and 170 g/l H_2SO_4). A constant electrolyte temperature (65 ± 0.5 °C) was maintained during the tests with a magnetic stirring of 350 rpm. The recording process was carried out by applying a potentiodynamic

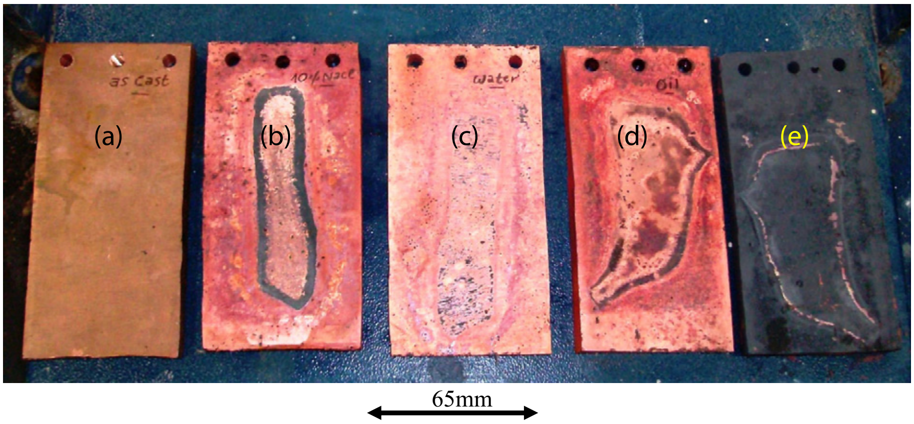

Fig. 1. A photo of copper anode samples used in the experiments (a) without thermal treatment, (b) quenched in brine 10%, (c) quenched in fresh water, (d) quenched in machine oil, (e) normal cooling in still air.