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Morphology, roughness and microhardness of nickel electrodeposits produced in sulfate media on 316 L SS or Ti cathodes

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ABSTRACT

The current paper describes the effect of key operating variables (i.e. pH, presence of sodium sulfate, boric acid and sodium lauryl sulfate – SLS) on important features of nickel deposits by means of morphologic and surface roughness analyses and indentation hardness tests. Two substrates (cathodes) were used: 316 L stainless steel (SS) or titanium (grade 2). Only changes of pH and additions of Na_2SO_4 and SLS to the electrolyte largely affected the morphology of the deposits, regardless of substrate type. At pH 3, a condition in which relatively high values of current efficiencies were obtained, the addition of 155.9 g L^{-1} of Na_2SO_4 or 10 mg L^{-1} of SLS to the electrolyte lead to the production of Ni deposits with few hydrogen pits on the surface and regular edges. However, the presence of 155.9 g L^{-1} of Na_2SO_4 in the electrolyte caused an increase of the average roughness of the deposits in the order of 27 and 54% when 316 L SS or Ti cathodes were used, respectively. By adding 10 mg L^{-1} of SLS to electrolyte containing 155.9 g·L^{-1} of Na_2SO_4 and 8 g L^{-1} of H_3BO_3, the surface roughness decreased about 24 and 17% when 316 L SS or Ti cathodes were used, respectively, without any effect on the materials' microhardness. The results of this work suggest that only the replacement of 316 L SS blank cathodes by Ti may not represent significant benefits in terms of product quality.

1. Introduction

Nickel cathode is priced according to its purity and also surface quality. It is well-known that the deposit's surface quality is affected by many variables, such as applied current density, temperature, pH and concentration of nickel in the sulfate electrolyte (Kittelty and Nicol, 2000, 2001; Holm and O'Keefe, 2000a), presence of metallic (Gogia and Das, 1988, 1991; Holm and O'Keefe, 2000b; Mohanty et al., 2002a, 2002b, 2005; Kittelty and Nicol, 2003; Samal et al., 2013; Tripathy et al., 2001a) and organic (Kuzeci et al., 1994; Tripathy et al., 2001b; Kittelty and Nicol, 2003; Freire et al., 2017) impurities. In terms of product's characterization, most of these previous studies have described the effect of such variables on the morphology and crystal structure of nickel deposits only.

It is important to recognize that in order to produce nickel cathodes with the desired characteristics a detailed assessment of roughness and hardness is extremely important, which are key properties to distinguish the product value and its performance during the stripping and cutting stages. As the deposits are bent during stripping and cut to produce small sheets, coins or loops for nickel starter sheets, measurements of hardness are relevant. Kittelty and Nicol (2001) investigated the microhardness of nickel deposits produced on titanium blank cathodes under practical conditions. It was found that the product's microhardness increases with increases of temperature and concentration of nickel in the electrolyte, but decreases with the increase of pH and concentration of sodium sulfate and boric acid.

What has not been reported yet is how these operating variables may affect the morphology, roughness and mechanical property of the metal deposit by using not only the conventional stainless steel blank cathodes but also titanium cathodes. In the industrial practice, 316 L stainless steel is commonly used to produce nickel cathodes or nickel starter sheets, but permanent Ti cathodes have also been employed mainly due to the longer service life of this material in comparison to 316 L SS and also due to simplification of the operating sequence in the tankhouse. As a result of the reduction in operational steps, worker exposure to solutions and aerosols containing nickel sulfate is reduced, which is a very important implication in terms of occupational safety. Permanent Ti cathodes are used with success at the Rustenburg plant, South Africa (Crundwell et al., 2011).

In this context, the current paper describes the effect of some operating variables, such as pH, presence of sodium sulfate (Na_2SO_4), boric acid (H_3BO_3) and also sodium lauryl sulfate (SLS), on important

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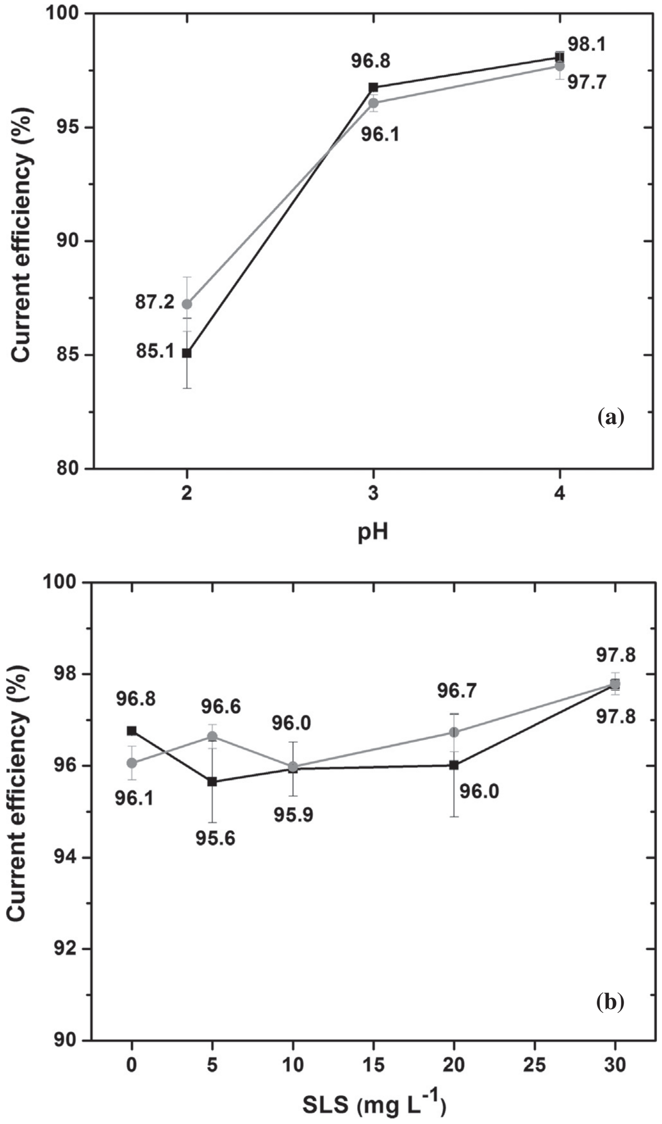

Fig. 1. Effect of pH and SLS addition to electrolyte at pH 3 on the average values of CE by using 316 L SS (black line) or Ti (grey line) cathodes. Fixed operating conditions: 85 g L^{-1} Ni^{2+}; 300 A m^{-2}; 60 °C; 6 h.

features of Ni deposits (*i.e.* morphology, roughness, crystal structure and hardness), which were produced on 316 L stainless steel or Ti cathodes. The combined effect of Na_2SO_4, H_3BO_3 and SLS was described as well due to the possible, simultaneous presence of these species in the industrial electrolytes. The findings obtained here may be helpful assisting industry to identify opportunities for producing a material with better surface quality and higher commercial value.

2. Experimental

2.1. Electrolyte

Synthetic electrolytes (1 L) containing 85 g L^{-1} of nickel ions (Ni^{2+}) were prepared by adding 99% nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$, Sigma-Aldrich®) in deionized water (Millipore® Milli-Q). The pH of the electrolytes was adjusted to 2, 3 and 4 using 96% sulfuric acid (H_2SO_4, Química Moderna Gold®). The electrolytes containing 155.9 g L^{-1} of Na_2SO_4, 8 g L^{-1} of H_3BO_3 and 5–30 mg L^{-1} of SLS were prepared by adding 99% sodium sulfate (Na_2SO_4, Sigma-Aldrich®), ≥ 99.8% boric acid (H_3BO_3, Sigma-Aldrich®) and ≥ 99.0% sodium lauryl sulfate ($C_{12}H_{25}NaSO_4$, Sigma-Aldrich®) to the electrolyte, respectively. The concentrations of nickel, sodium sulfate and boric acid in the synthetic electrolyte were fixed according to the operating conditions at the São Miguel Paulista plant (Brazil), which are 80–85 g L^{-1} Ni^{2+}, 45–50 g L^{-1} Na^{+}, and 6–10 g L^{-1} H_3BO_3, respectively. The concentration levels selected for SLS were defined according to the literature (Mohanty et al., 2009).

2.2. Electrowinning

The electrowinning experiments were conducted in duplicate using electrochemical cell consisting of three cathodes (316 L stainless steel or titanium grade 2) in the form of vertically aligned disks with a 10 mm diameter (surface area of 78 mm^2 each) and a central platinum anode (99.99% pure) in the form of a vertical rod (surface area of 250 mm^2). Cathodes and anode were located at a constant distance (15 mm). Prior to each experiment, fresh cathode surfaces were prepared by wet-polishing using silicon carbide (*SiC*) paper (grit size 1200), and were then thoroughly rinsed with deionized water (Millipore® Milli-Q). All of the experiments were conducted in a 2 L Pyrex® reactor with a Teflon lid. The cell operated for 6 h at constant current density (300 A m^{-2}) under stirring (350 rpm). The temperature of the electrolyte was maintained at a constant level (60 ± 1 °C) using a temperature-controlled hot plate (IKA® RET basic). The current density and temperature were fixed according to the operating conditions at the São Miguel Paulista plant (Brazil).

In this experimental set up, it is expected that cathode bags are not required, since a small total deposition area was used within a large volume of electrolyte under stirring. In industrial operations, the competing hydrogen evolution is minimized by controlling the interfacial cathode pH using bags that restrict the diffusion of the protons (H^{+}) formed on the anode to the cathode. In the experimental set up, the acidity of this electrolyte and also concentration of Ni^{2+} remained at nearly constant level. For instance, for electrolytes with nominal pH equal to 3, condition used in most of the experiments, the average pH decreased from 3.03 to 2.76 after 6 h.

After electrowinning, the nickel deposits were manually stripped from the cathodes, thoroughly rinsed with deionized water and dried in a furnace at 100 °C for 30 min. The average mass of the three deposits produced in each experiment was measured by using an analytical balance with a high degree of precision and readability of up to 0.1 mg (Mettler AE200). The CE, in %, was determined according to:

$$CE = \left(\frac{nFm}{ItM}\right) \times 100\% \tag{1}$$

where m represents the mass of the Ni deposit after 6 h (g), n the number of electrons in the overall deposition reaction (1), F the Faraday constant (96,485C mol^{-1}), M the atomic weight of nickel (56.69 g mol^{-1}), I the total applied current (A), and t the deposition time (s).

2.3. Electrochemical measurements

Electrochemical measurements by cyclic voltammetry were conducted for better understanding specific trends observed during the electrowinning. The measurements were carried out in a conventional three-electrode cell using an Autolab® (PGSTAT 20) potentiostat controlled by NOVA software (version 1.5). The working electrode and counter-electrode consisted of the same 316 L SS or Ti grade 2 cathodes and Pt electrode used for electrowinning, respectively. The reference electrode was an Ag/AgCl/KCl (3 mol L^{-1}) (+ 0.179 V vs. SHE – Standard Hydrogen Electrode, at 60 °C). Prior to each measurement, the working electrode surface was wet-polished using *SiC* paper (grit 1200) and thoroughly rinsed with deionized water. The voltammetric sweeps, which were conducted in triplicate, started in the negative direction from − 0.18 up to − 0.8 V. Afterward, the potential sweep was reversed toward positive potentials up to 0.1 V and reversed again down to