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Nickel electrodeposition from leaching solution containing ammonia and chloride①

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Abstract: The effects of temperature, nickel concentration and current density on the current efficiency and the electrolyzer voltage were investigated in the process of electrowinning nickel. The results show that the current efficiency is above 90% under the various experimental conditions, and the electrolyzer voltage is less than that of traditional electrolyzer system. Therefore, the optimized parameters, i. e. temperature of 50 ℃, current density of 400 A/m^2, are determined. It is also elucidated that anodic product is high valent nickel compound in the process of electrodeposition in terms of X-ray diffraction and chemical analysis. The amount of solid product formed on the electrode surface decreases with an increase in ammonium chloride concentration by cyclic voltammetry analysis. It is also indicated that the anodic gas species are mainly composed of nitrogen by vapor phase chromatograph.

Key words: nickel; electrodeposition; ammonia coordinate
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1 INTRODUCTION

The fundamental aspects of nickel electrodeposition were studied by various approaches in view of its industrial interest[1-6]. Generally, these studies were performed in modified industrial baths of nickel chloride or sulfate, usually in the presence of boric acid acting as buffer to keep the electrolyte near neutral, and thus to prevent hydrogen from evolution. Therefore, the operation procedure is complicated relatively. Moreover, the yielding ratio of nickel electrodeposited from the electrolyzer is rather low in the process of electrowinning. The electrolyte demanded for electrowinning nickel is massive, which increases the production cost.

The electrodeposition of other metals in a leaching solution containing ammonia and chloride have also been studied in recent years[7, 8]. But nickel electrodeposition in its bath has not been reported. Compared with the regular nickel electrodeposition techniques, nickel electrodeposition carried out in leaching solution containing ammonia and chloride has several advantages:

1) It is dispensable to add boric acid as a buffer agent. Buffering properties of the ammonia-ammonium couple limit the local change of pH in the vicinity of the electrode surface caused by simultaneous hydrogen evolution. Meanwhile, it is unnecessary to use membrane to segregate anode electrode and cathode electrode.

2) The yielding ratio of nickel electrodeposited from the electrolyte is so high that the electrolyte demanded for nickel electrodeposition is decreased, and finally the production cost is reduced.

3) Under the various conditions, current efficiency is high. The solution resistance in this electrolyte system and the consumption of electric energy are less than those of traditional system mentioned before. 30% of electric energy is economized in comparison with the traditional electrowinning methods.

4) The serious corrosive gas such as Cl_2 would not be escaped from the anode surface owing to the utilization of RuO_2-TiO_2 material, which contributes to environmental protection.

In this paper, the process of nickel electrodeposition from leaching solution containing ammonia and chloride is investigated. In addition, the mechanism of anodic reaction is demonstrated initially in terms of cyclic voltammetry, vapor phase chromatograph and X-ray diffraction analysis.

2 EXPERIMENTAL

All the solutions were prepared with commercial chemicals (Merk, G. R) and distilled water, unless otherwise mentioned. Ammonium chloride was added into the nickel chloride solutions as a supporting electrolyte. In addition, for the nickel chloride solutions the pH was adjusted to 7-8 by addition of ammonium chloride and

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strong ammonia solution. The alkaline solution, with a pH of 7－8, was stored in a closed vessel to prevent from loss of ammonia vapor.

Preparation of RuO_2-TiO_2 was similar to that described in previous work. The substrate was polished with silicon carbide paper, washed with ethanol in an ultrasonic cleaner, etched for 20 min in 3 mol/L HCl solution at 80－90 ℃, and finally washed and stored in ultrapure water. Afterward, the substrates were dipped in coating solution consisting of $RuCl_3 \cdot xH_2O$ (42.25% metal), with total concentration of 0.25 mol/L by adding 10% HCl (volume fraction) in isopropanol. After dipping and drying, the substrates were heated under air flow at 450 ℃ for 10 min. The entire procedure was repeated five times, then the substrate was heated at the annealing temperature for 1 h.

Commercial instrumentation (Parc, 273 mode) was used for all cyclic voltammetry experiments. A conventional three-electrode configuration with an aqueous saturated calomel electrode (SCE) was used. A Luggin probe was used to minimize the resistance effects. The counter electrode was a graphite rod. All the experiments were carried out at room temperature and under nitrogen atmosphere. The potentiodynamic tests were conducted at potential scan rate of 50 mV/s. In this study all potentials are referred to the saturated calomel electrode (SCE) and corrected for ohmic drop.

The species of the solid product formed on the anode surface was investigated by X-ray diffractometry, and the content of this production was calculated by volumetric analysis.

The gas from anode was analysed by a chromatographer (GC1102), with a column packed with molecular sieve 13X ranging 120－180 μm, a TCD detector, and H_2 as carrier, working under the condition of 8 mV/m in detection scope and 100 mA in bridge current.

3 RESULTS AND DISCUSSION

3.1 Cathode current efficiency

Figs. 1, 2 and 3 show the effects of temperature, current density and nickel concentration on the current efficiency, respectively. It can be seen that cathode current efficiency is above 90% under the various experimental conditions. The cathode current efficiency increases first, and then decreases with the increase in temperature. While the cathode current efficiency decreases gradually with the increase in current density. The current efficiency is still above 90% when the nickel concentration is reduced from 100 g/L to 40 g/L. This desired consequence meets appropriately the demands of industrial production, in which there is a major difference in nickel concentration between the initial and the waste electrolyte.

Fig. 4 shows the temperature effect of current density on voltage. It is admitted that the voltage increases sligh-

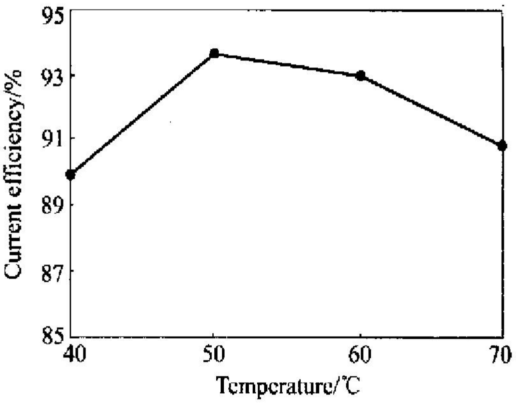

Fig. 1 Plot of current efficiency against temperature

($\rho(Ni^{2+})$ = 60 g/L; $[NH_4^+]$ = 3 mol/L; $[NH_3 \cdot H_2O]$ = 3 mol/L; J = 400 A/m^2)

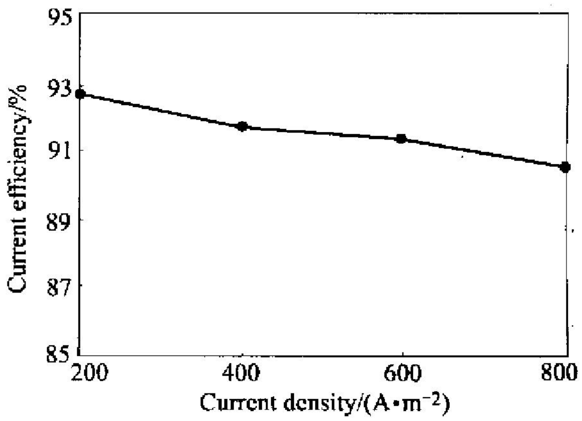

Fig. 2 Plot of current efficiency against current density

($\rho(Ni^{2+})$ = 60 g/L; $[NH_4^+]$ = 3 mol/L; $[NH_3 \cdot H_2O]$ = 3 mol/L; t = 50 ℃)

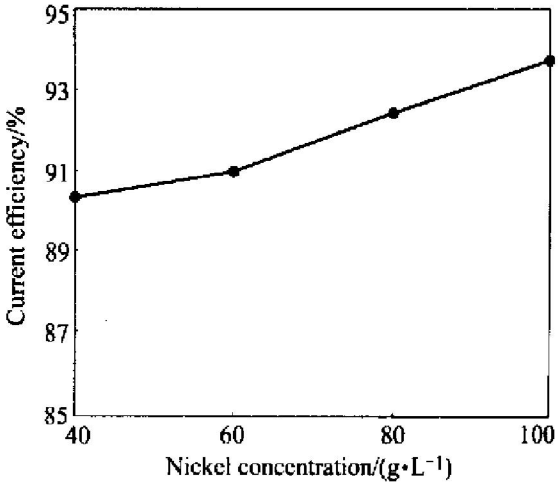

Fig. 3 Plot of current efficiency against nickel concentration

($[NH_4^+]$ = 3 mol/L; $[NH_3 \cdot H_2O]$ = 3 mol/L; J = 400 A/m^2; t = 50 ℃)

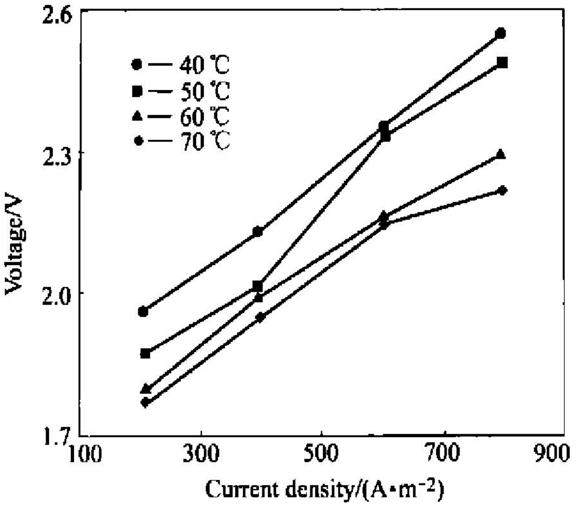

Fig. 4 Plot of voltage against current density under the various temperatures
([Ni^{2+}] = 60 g/L; [NH$_4^+$] = 3 mol/L; [NH$_3$•H$_2$O] = 3 mol/L)

tly with an increase in current density, and decreases with an increase in temperature. From this results, it can be drawn a conclusion that the voltage of nickel electrowinning from leaching solutions containing ammonium chloride is less than that of traditional nickel deposition system[9]. Based on the principle of high current efficiency and the low consumption of electric energy, the optimum process parameters, i. e. temperature of 50 ℃, current density of 400 A/m^2, can be chosen.

3.2 Solid formed on anode surface

Fig. 5 shows the X-ray diffraction pattern of solid product formed on anode surface. It can be seen that solid product is Ni(OH)$_2$, which results from the reduction of high valent nickel compound during the process of electrodeposition or during the washing using dilute ammonia and distilled water. It seems that high valent nickel compounds are formed on the anode surface in the leaching solution containing ammonia and chloride. The solid product washed by distilled water is immediately added into the chlorhydric acid solution, but no reaction is found. However, as soon as the sodium sulfite was added into the solution, the solid product was reduced and dissolved into the solution. Fig. 6 shows the mass change of anodic solid product during the nickel electrodeposition in the leaching solution containing ammonium chloride at various concentrations. It is admitted that the amount of anodic product formed on the anode surface decreases with the increase in ammonium chloride concentration. Owing to the decrease of relative content of Ni(OH)$_2$(aq) in the solution, which is ascribed to a concentration increase of ammonium chloride, the formation rate of nickel solid product is reduced greatly. The formation of high valent nickel compound is probably similar to the electrolyzing preparation of black nickel in alkaline solution[10].

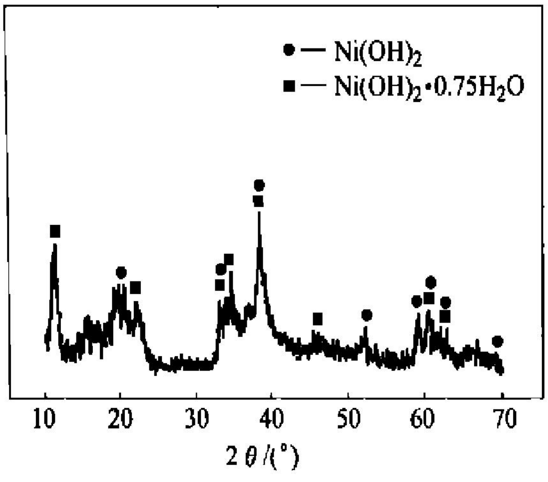

Fig. 5 XRD pattern of solid product on anode

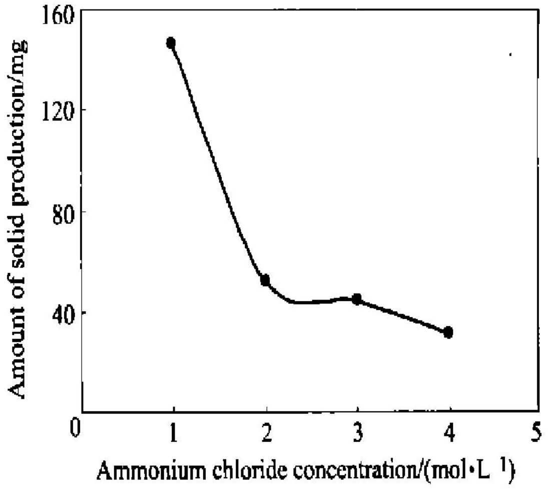

Fig. 6 Mass change of anodic solid product against ammonium chloride concentration
([NH$_3$•H$_2$O] = 3 mol/L; ρ(Ni^{2+}) = 60 g/L; J = 400 A/m^2; t = 50 ℃)

3.3 Cyclic voltammetry curve

Fig. 7 shows the cyclic voltammetry curves in the electrolyte solutions containing ammonium chloride at various concentrations. Voltammetric curves recorded with the alkaline bath containing ammonium chloride exhibited a single oxidation peak near 0.9 V (vs SCE), which can be attributed to the formation of high valent nickel solid product. It is obvious that the oxidation peak indicating the formation of nickel compound drifts from 0.9 V (vs SCE) to more positive potentials. Therefore, it is further demonstrated that the ammonium chloride concentration takes significant effect on the amount of nickel compound. The intensity of oxidation peak decreases with the increase in ammonium chloride concentration and it vanishes completely when the concentration reaches 4 mol/L.

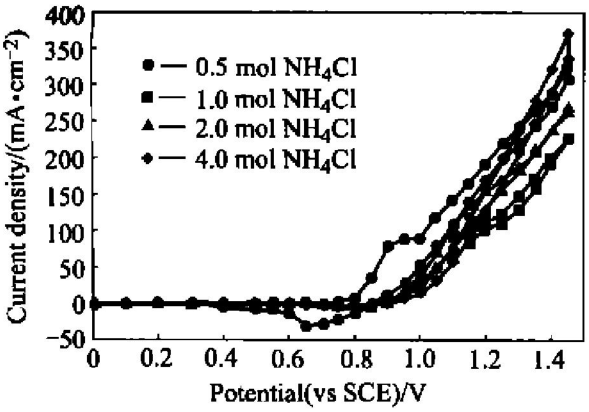

Fig. 7 Voltammetric curves dependence of ammonium chloride concentrations

(ρ(Ni^{2+}) = 60 g/L; [NH$_3$·H$_2$O] = 3 mol/L; t = 50 ℃; potential range: 0 − 1.4 V; scan rate: 50 mV/s)

3.4 Gas species

The chromatogram of gas species shows that the nitrogen evolution reaction is the main reaction accompanied with the oxygen evolution. In thermodynamic perspective, the two parallel electrochemical reaction, i.e. chlorine and oxygen evolution, can occur simultaneously at the RuO$_2$-TiO$_2$ anode in alkaline solution. However, taking dynamics into consideration, i.e. electrochemical polarization, the oxygen evolution reaction occurs slightly at the initial period, and the chlorine evolution reaction is predominant on the anode. The evolution of nitrogen is due to the oxidation of ammonia in the electrolyte by chlorine formed on the RuO$_2$-TiO$_2$ anode. The evolution of nitrogen is due to the oxidation of ammonia in the electrolyte by chlorine formed on the RuO$_2$-TiO$_2$ anode[11].

4 CONCLUSIONS

1) The optimum process parameters, i.e. temperature of 50 ℃, current density of 400 A/m^2, are chosen under the various conditions of the nickel electrodeposition from leaching solution containing ammonia and chloride. The current efficiency is above 90%, while the electrolyzer voltage is 2.00 V or so.

2) High valent nickel compound is formed on the anode surface, and its amount decreases with the increase in ammonium chloride concentration.

3) The gas species escaped from the anode are mainly composed of nitrogen, including a little portion of oxygen.

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