ELECTRODEPOSITION OF NICKEL FROM ALL-CHLORIDE ELECTROLYTE①

Gong, Qian Liao, Hong Yang, Tao Hu, Jiexue Fang, Zhaoheng
Institute of Chemical Metallurgy, Academia Sinica, Beijing 100080, China

ABSTRACT

The optimum operating conditions for the electrodeposition of nickel from all-nickel chloride electrolytes were studied, based on measurements of conductivity, surface tension, viscosity of nickel chloride electrolytes at different temperatures and concentrations of nickel chloride as well as the experiments of electrodeposition arranged using experimental design in the normal table. Through studying cathode polarization and examination of physical features of cathodic nickel, the effects of trace Fe, Co, Pb, TBP and N−235 in all-nickel chloride electrolyte on cathode potentials, cell voltages, current efficiency and energy consumption as well as the morphology and the internal stress of cathodic nickel in electrodeposition of nickel were examined.

Key words: electrodeposition nickel chloride

1 INTRODUCTION

It is one of the important units in the hydrometallurgical process of chlorination to electrodeposit nickel from all-chloride electrolyte. Aqueous chlorination has significant advantages such as high reaction rate, high solubilities of metal chlorides in water, easy separation of metal from impurities. Moreover the leaching agent, chlorine, can be regenerated in situ on anode while nickel is electrodeposited in cathode. Therefore chlorination is considered as a very interesting process in potentialities.

It is reported[1] that there are three companies to recovery nickel from nickel chloride electrolyte[2−4]. Compared to sulfate or sulfate-chloride electrolytes, in dessolved anode electrodeposition in an all-chloride electrolyte has the lowest cell voltage, but the stress of the electrodeposited metal from chloride increases. In order to eliminate the stress, the temperature and pH of the electrolyte must be controlled[2].

This paper is going to describe, at first, the correlation between physical characters (conductivity, surface tension, viscosity) of the electrolyte and the composition at various temperatures. The relations of physical quality of cathodic nickel with electrolytic conditions are then explained. On the basis of these results, the technical conditions of the electrodeposition of nickel from all-nickel chloride electrolyte are investigated. Then under conditions for industrial electrodeposition, the effects of trace Pb, Fe, Co, TBP and N−235 in electrolytes on electrodeposition of nickel and physical natures of the cathodic nickel are

---

①Manuscript received February 16, 1992

discussed in detail.

2 MEASUREMENTS OF THE PHYSICAL FEATURES OF NICKEL CHLORIDE ELECTROLYTES

It is known that any additive to the all-chloride solutions in electrodeposition of nickel is unnecessary. Electrolytes therefore consists of nickel chloride alone. It is only needed to determine the effects of the concentration of $NiCl_2$ and the temperature on conductivity, surface tension, viscosity of electrolyte for technical exploration. The conductivity, surface tension, viscosity of electrolyte for technical exploration. The conductivity was measured with a DDS−11 type conductivity meter. The surface tension was obtained using the maximum pressure of bubble. The viscosity was determined with a Ostwald Viscosimeter. The temperature error of the electrolyte was controlled within ± 1 ℃ by a thermostat. The electrolytes were prepared by dissolving nickel chloride of reagent grade in deionized water. The results in an average of several experiments are given in Table 1. From this table it can be seen that at a fixed concentration of nickel, the conductivity increased with the temperature. At a fixed temperature, it increased with the concentration of $NiCl_2$ in its low range, and then almost kept at a constant maximum value in a certain range, for example from 100 and 180, and reduced in the range of higher. At a fixed concentration of $NiCl_2$, the surface tension reduced with the temperature, at a fixed temperature it increased with the concentration of $NiCl_2$. The viscosity reduced with temperature and increased with the concentration of $NiCl_2$. According to the requirements of the technology of the nickel electrodeposition, an electrolyte with high conductivity and low viscosity should be expected. Hence the concentration of Ni^{2+} is from 115 to 150 g / L, and the temperature is normally between 60～70 ℃.

Table 1 The conductivity, surface tension, viscosity of chloride electrolytes with different nickel concentrations at various temperatures

	C / g · L^{-1}	29.500	59.000	88.500	115.000	150.700	176.600	191.500
25 / ℃	*v*	1.008	1.290	1.560	1.870	2.430	3.080	3.620
	L	0.072	0.111	0.140	0.151	0.145	0.140	0.128
	ST	73.600	74.600	76.900	79.400	81.800	84.500	85.800
50 / ℃	*v*	0.707	0.828	0.982	1.163	1.480	1.830	2.060
	L	0.102	0.176	0.207	0.232	0.220	0.216	0.212
	ST	70.700	71.700	74.100	75.800	79.300	80.900	82.000
60 / ℃	*v*	0.615	0.735	0.867	1.019	1.260	1.530	1.740
	L	0.141	0.200	0.234	0.264	0.249	0.249	0.234
	ST	68.500	70.200	71.100	73.600	77.700	79.300	80.600
70 / ℃	*v*	0.566	0.652	0.771	0.902	1.133	1.340	1.510
	L	0.187	0.225	0.263	0.275	0.277	0.278	0.262
	ST	67.100	68.500	70.100	72.100	74.800	78.000	79.600
80 / ℃	*v*	0.519	0.595	0.685	0.804	0.982	1.183	1.330
	L	0.219	0.252	0.291	0.300	0.308	0.306	0.290
	ST	65.400	66.800	68.800	71.300	73.600	76.600	78.800

c—concentration of Ni^{2+}, g / L; *v*—viscosity, Mpa · s; *L*—conductivity, $\Omega^{-1} \cdot cm^{-1}$; *ST*—surface tension, MN / m

3 THE EFFECTS OF THE TECHNOLOGICAL CONDITIONS ON ELECTRODEPOSITION OF NICKEL

The experiments were carried out with a glass vessel merged in a thermostat. The anode was a platinum foil of 2.5 cm^2 and the cathode a pure nickel sheet of 4 cm^2. The saturated calomel electrode with the Luggin capillary was used as reference electrode. The space between the anode and cathode was about 6 cm. The experimental duration was generally 3 h. The cathodic or anodic potentials was measured with a digital voltmeter. The current was measured with a milliammeter. During experiment, $NiCl_2$ electrolyte was not supplemented because of high concentration of Ni^{2+}, large volume of solution, small cathode and low current. The concentration of Ni^{2+} and pH of solution had no significant variation after experiments . The current efficiency was determined by measurement of the electricity and the weight of the cathode increased after the experiments. The crystal orientation of cathodic nickel obtained under different conditions were detected with a Y−2 type X−ray diffractometer, and morphology of cathodic nickel was observed with a S−530 type scanning electromicroscope.

The effects of four factors (concentration of $NiCl_2$, temperature, pH of electrolytes, cathodic current density) on electrodeposition of nickel were examined. The preliminary experiments were designed according to L_9 (3^4) Normal Table. the electrolyte was prepared with $NiCl_2 \cdot 6H_2O$ of reagent grade, hydro- chloric acid and deionized water. The concentration of nickel was determined with EDTA titration. The experimental results were plotted in Fig. 1 and 2.

From Fig. 1 and 2, it was seen that the cathodic super-potential reduced, and the surface state was getting better as temperature raised. As pH raised, the cathodic super-potential increased, the surface state was getting worse. When the current density increased, cathodic super potentials increased, the surface state was obviously getting worse. As the concentrations of Ni^{2+} increased, the cathodic super-potentials reduced, the surface state of cathodic nickel were reduced for the first time, the surface state of cathodic nickel were getting better, then worse again. The change of the concentration of Ni^{2+} had no effect on the surface state of nickel and had considerable effect on the cathodic super-potential.

Preliminary experiments showed that the optimum conditions can be considered as: 150 A / m^2 cathoic current density, 120 g / L Ni^{2+}. In order to further verify these results, some supplemental experiments were carried out. The results showed that the cathodic current efficiency were all higher than 96 %. Addition of boric acid in electrolytes was unnecessary while the electrolyte was kept at pH = 1. When the nickel was electrodeposited with low current density, under other same conditions the cathodic super-potential was lower, and the surface appearance of nickel looked nice. On the other hand, with the elevation of the concentration of nickel, the cathodic super-potential reduced, but the surface appearance and the current efficiency did not change markedly. These results are consistent with the preliminary experiments.

The electrolytical experiments mentioned above were carried out in a cell with nickel cathode of 4 cm^2 and platinum anode. Following conditions were recommended: 120 g / L Ni^{2+}, pH = 1, 65 ℃ , cathodic current density

250 A / m^2 in order to approach industrial practices. The experiments of electrodeposition were performed again in a cell with 31 cm^2 cathode of nickel sheets, and two Ti-supported manganese oxide electrode as anode at cathode- anode spacing 6 cm, in 1 L glass beaker. One experiment lasted four hours, another eight hours. The average results of the two experiments were shown in Table 2.

4 THE EFFECTS OF IRON, COBOLT AND LEAD ON CURRENT EFFICIENCY AND ENERGY CONSUMPTION DURING THE ELECTRODEPOSITION OF NICKEL[5]

In experiments, 120 g / L nickel solutions containing various impurities were used as electrolytes, pure nickel sheet as cathode, platinum sheet as anode. The temperature of the solutions was controlled at 65 ℃, cathodic current density was constantly 25 mA / cm^2, and electrodeposition duration was normally 2 h. The results showed that the effects of impurities Fe, Co on current density and energy consumption were not remarkble. However, when lead presented in the solution, the energy consumption increased, and the cathodic current efficiency reduced.

When electrodeposition were carried out in nickel chloride solution containing Co, Fe and Pb at a higher level respectively, the cathodic nickel obtained showed rough appearance with a lot of cracks; and this appearance was getting worse with the increase of the content of impurity. When Co, Fe, Pb were lower than 0.051, 0.013, 0.000,15 g / L respectively, the appearance of the cathodic nickel obtained from nickel chloride solutions containing impurities were similar to that of nickel obtained from pure nickel chloride solution.

The results from X−ray diffraction analysis of these samples showed that the growth of (220) surface of nickel became fast and growth

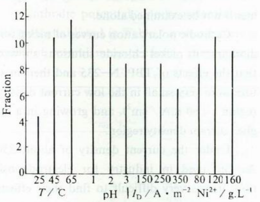

Fig. 1 Effects of experimental parameters on the surface state of cathodic nickel

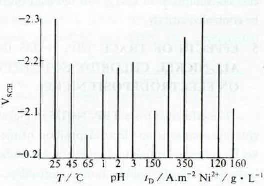

Fig. 2 Effects of experimental parameters on cathodic potential

Table 2 Results of the experiments with 31 cm^2 nickel cathode

cathodic potential / $V_{S.C.E}$	anodic potential / $V_{S.C.E}$	cell voltage / V	current efficiency / %	energy consumption / kWh · t^{-1}	appearence of cathodic nickel
−0.708	1.31	2.05	96.5	1,940	grey and smooth

of (111) surface was controlled because of adding Pb, Fe and Co into electrolyte

The above results were obtained from the nickel chloride solutions only containing one impurity. As various impurity elements in an amount allowed above were simultaneously put in nickel chloride solutions, the quality of electrodeposited nickel was very poor. As Co, Fe were kept at the amounts allowed in single impurity, the amount of lead decreased to half amount allowed, or as Pb was kept at the amount allowed in single impurity, Fe, Co amount decreased to half the amount allowed, the same cathodic nickel with cathodic nickel obtained from pure nickel electrolytes can be obtained.

The results from spectrum analysis of cathodic nickel showed the content of iron was as low as that of high-purity nickel, i. e. the trade name ″Nickel−1″. Lead was the most harmful element, for it not only damaged the quality of cathodic nickel, but also made excess consumption of energy, so the lead must be controled strictly.

5 EFFECTS OF TRACE TBP, N−235 IN ALL-NICKEL CHLORIDE SOLUTION ON ELECTRODEPOSIT NICKEL

The effects of trace TBP, N−235 in nickel chloride solutions on electrodeposition of nickel have been examined using several methods, including cathodic polarization in electrodeposition, examination of crystal orientation with Y−2 type X−ray diffractometer, morphology investigation with S−530 type scanning electromicroscope and measurement of internal stress with cathodic winding method[6].

The electrolytes of nickel chloride containing TBP, N−235 were prepared by the following procedures: a) mixing 60 g / L nickel chloride solution with 20% TBP kerosene solution and 30% N−235 kerosene solution at the ratio 5 : 1 (v / v) respectively; b) shaking the mixitures; c) seperating aqueous and organic phase. The amount of TBP, N−235 in the solutions were analysed and the aqueous liquors were stored as stock solutions.

Before experiments, according to the experimental requests, the three kinds of solutions were mixed in a certain ratio, so that electrolytes of various content of nickel, TBP and N−235 were obtained.

Because organic phase containing TBP and N−235 were prepared with kerosene, the effects of TBP and N−235 were discused later, in practice, the effect of kerosene was also included. Since solubility of kerosene in aqueous phase is lower than 10 ppm, and the kerosene molecules have stable structure and weak polarity, the directional adsorption of the molecules on deposited layer should be very weak, and the effect of kerosene during the experiments not be examined alone.

Cathodic polarization curves of nickel ion discharge in nickel chloride solutions showed that the effects of TBP, N−235 and their mixture were very small in the low current density region (<60 mA / cm^2), and growing in a higher current density region.

Under the current density of about 250 A / cm^2 used in industry for electrodeposition, it was very difficult to find their effects from polarization curves. Therefore their effects were directly examined with experiments of electrodeposition. The results were listed in Table. 3. When the concentration of TBP was less than 10 mg / L, it had very little effect on surface state of nickel. No distinction between cathodic nickel obtained from electrolytes containig TBP lower than 5 mg / L and pure nickel chloride solutions was found by scanning electromicroscope. But the surface of cathodic nickel obtained from the electrolytes containing 10 mg / L TBP were more compact and smooth. As the concentrations of N−235 were less than 10 mg / L, the appearance of nickel electrodeposited had not changed obviously, but there were several organic burn and a large number of pits on nickel obtained from electrolytes containing 50 mg / L of N−235. SEM found that the cathodic nickel obtained from electrolytes containing N−235 less than 10 mg / L were more smooth and compact than that obtained from pure nickel chloride electrolytes.

The combined effects of TBP and N−235 on electrodeposition of nickel were more remarkble than that of each single. In order to obtain cathodic nickel with good appearance, TBP and N−235 in the electrolytes must be limited in a lower level, e. g. less than 2 mg / L and 3 mg / L respectively.

Cathodic potential, anodic potential and cell potential listed in Table 3 were all average value of several measurements. The variance of experimental values were within ± 2 %. Table 3 shows that effects of trace TBP and N−235 on cathodic potential, anodic potential, energy consumption and current efficiency during the electrodeposition process of nickel were indistinctive, but the combining effects of TBP and N−235 were more serious than the effect of each single.

The figures of X−ray diffraction of various examples indicate that the diffraction intensity of (111), (200), (220) and (311) surface of nickel deposited from the electrolytes containing TBP were all weaker than those deposited from pure nickel chloride solutions, but the crystal remained mainly preferential orientaton of (220) surface. When the electrolytes contained N−235, the diffraction intensity of the (311) surface of nickel deposited did not change, those of (111), (200), (220) surfaces got weaker, but the (220) surface was still dominant and as the preferential orientation as pure nickel was kept in the crystal. In the presence of both TBP and N−235, the cases should be more complex. Under the different concentrations of N−235 and TBP, the preferential

Table 3 Effects of TBP and N−235 on electrodeposition of nickel

TBP / mg · L^{-1}	N−235 / mg · L^{-1}	cathodic potential / $V_{S.C.E}$	anodic potential / $V_{S.C.E}$	cell voltage / V	current efficiency / %	energy consumption / kw.h · kg^{-1}	appearance of cathodic nickel
0	0	−0.627	1.113	1.740	99.1	1.59	
1	0	−0.627	1.119				
3	0	−0.625	1.120	1.745	99.9	1.60	grey and smooth
5	0	−0.624	1.113	1.737	99.4	1.60	
10	0	−0.617	1.124	1.741	99.9	1.59	
0	1						
0	5	−0.630	1.112	1.742	100	1.59	
0	10	−0.628	1.121	1.749	99.0	1.61	
0	50						organic burn and lots of pits
2	3	−0.630	1.118	1.748	99.0	1.61	grey and smooth
1	2	−0.628	1.114	1.740	99.2	1.60	
5	5	−0.626	1.121	1.747	98.8	1.62	grey and little pits

orientation of nickel deposited were different.

In order to understand the effects of orgainc impuities on mechanical properties of nickel deposited, internal stress in nickel obtained from electrolytes containing TBP and N−235 of various concentrations had been measured by cathode winding method. During the electrodeposition, because nickel layer deposited produced tensile stress, the copper cathode winded toward anode. As the concentrations of TBP and N−235 increased , internal stress in nickel layer deposition decreased and the effects of N−235 on internal stress were more remarkable than those of TBP. In the presence of both N−235 and TBP in electrolytes, the combining effects were between the effects of N−235 and TBP.

6 CONCLUSION

(1) Surface tension and viscosity of nickel chloride solutions increase with the concentrations and decrease with the temperature of the solutions. As the concentrations of nickel chloride in solutions are below 120 g / L Ni^{2+}, the conductivity of the solutions increases with the concentrations of nickel. When the concentrations of nickel are between 120～180 g / L, the conductivity of the solutions changes little; but above 180 g / L Ni^{2+}, the conductivity decreases with the concentrations of the solutions; as the temperature of the solutions rises, the conductivity of the solutions increases.

(2) In order to obtain satisfactory cathodic nickel, the following conditions should be used:

120 g / L Ni^{2+}, pH = 1; 65 ℃; cathodic current density equals to 150～250 A / m^2.

Under these conditions , current efficiency is about 96.5 %.

(3) The effects of small amounts of Fe, Co in nickel chloride solutions on current efficiency and energy consumption of electrodeposition of nickel are not remarkable, but in the presence of a small amount of lead in electrolyte the energy consumption increases.

(4) According to the comprehensive analyses of morphology of nickel electrodeposited, crystal orientation, current efficiency, energy consumption, as TBP or N−235 exists alone in electrolytes, concentration of TBP or N−235 must be limited below 10 mg / L; as TBP and N−235 coexist in electolytes, TBP must be limited below 2 mg / L and N−235 below 3 mg / L.

REFERENCES

1 Mackinnon, D. J.. In: Hydrometallurgy. New York, 1983 . 664.

2 Kohga, M. *et al.* Paper Presented at the 111th Annual Meeting, Dallas, Texas, Feb. 1982, 14−18.

3 Hougen, L. R. *et al.* CIM Bull. 1977, 70: 136−143.

4 Anonymous. Eng and Min J, 1980, 52: 35−36.

5 Gong, Qian *et al.* Eng, chem & Metall, 1990, 11(1): 40−45.

6 Gong, Qian *et al.* Nonferrous Metals, 1991, 43(4): 76−80.