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SYNTHESIS OF ELECTROLYTIC COPPER AND NICKEL POWDERS FROM THE COPPER BLEED ELECTROLYTE OF A COPPER SMELTER

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The adaptation of certain processes for utilization of secondary resources to produce valuable products is currently given due attention in the metal extraction. Copper bleed solution (CBS) obtained during electropurification of the impure copper anode to produce copper cathode for the purpose of controlling impurity, is one such secondary source which can be treated to produce valuable products. Copper bleed solution generated at Indian Copper Complex (ICC), Ghatsila contains 39.86 g/L Cu, 9.58 g/L Ni, 0.26 g/L Fe, 0.108 g/L Bi, 0.007 g/L As, 0.055 g/L Sb, 198.04 g/L H_2SO_4. The recovery of copper and nickel as high value products such as metal powders from the bleed stream of the copper smelter by pretreatment-solvent extraction (SX) separation-electrowinning (EW) has been attempted to provide an alternative to the conventional process. The purity of the eletrolytic copper and nickel powders so produced was found to be 99.93% and 99.89%, respectively. The compact density of the annealed copper powder was 8.74 g/cc whereas it was 7.72 g/cc for nickel powder. The other properties of the copper and nickel powders such as flow-ability, particle size, *etc.* were found to be suitable for the P/M applications.

Introduction

Almost total copper [1] and some 50% of nickel [2] are recoved by electrorefining and electrowinning process world over. Electrocrystallisation is one of the most widely used industrial methods for the production of high purity metal powder [3]. Properties of metal powder deposited on the cathode depend on the various parameters such as concentration of ions, pH, bath temperature, current density, presence of additives in the electrolyte *etc.* A number of studies have been reported on electrowinning of copper [4-6] and nickel [7-9] from their sulphate solutions. Pierce and Davenport [4,5] have presented an empirical relationship between copper and acid concentration during electrowinning for the production of metal powder. Pavlovic *et al.* [6] have shown that apparent density of copper powder increases with decreasing current density and with increasing copper ion concentration and temperature. The pH of the electrolyte plays an important role on crystallite size of the electrodeposited nickel powder [8]. Further, it has been established that increasing the current density results in an increase in the grain size of nickel deposit [9]. To control the quality of the electrodeposits some additives are usually added during winning [10]. The grain size of nickel can easily be reduced to nano-range by using additives such as coumarin and sachharin [11]. Wang *et al.* [12] have produced copper and nickel powder of size less than 100 nm by ultrasonic electrolysis.

Recently, the processing of secondary materials for the recovery of valuable metals in an environmentally acceptable manner with low energy, capital and operating costs has been given due attention in the metal extraction/recovery. Copper bleed solution (CBS) is one of the streams generated in copper smelters [13] during electropurification of the impure copper anode to produce copper cathode. This solution contains high concentration of copper and nickel besides several other impurities. In order to recover copper and nickel as value added product from the bleed stream generated in a copper smelter, NML has developed a process comprising of pretreatment-SX seapartion-electrowinning steps. In this paper effect of various parameters on the electrowinning of copper and nickel powder has been presented. Properties of copper and nickel powders have also been evaluated.

Experimental

The copper bleed solution obtained from ICC, Ghatsila contains 39.86 g/L Cu, 9.58 g/L Ni, 0.26 g/L Fe, 0.108 g/L Bi, 0.007 g/L As, 0.055 g/L Sb, 198.04 g/L H_2SO_4. By partial decopperisation at current density of 100 A/m^2 the copper concentration is brought down to 17-18 g/L. The crystallization of decopperised solution yields mixed sulphate crystals, which on water leaching followed by iron precipitation and solvent extraction using LIX 84 produce separate copper sulphate (37.75 g/L and nickel sulphate (11.37 g/L) solutions. Synthetic copper sulphate and nickel sulphate solutions of similar composition as obtained in the solvent extraction were prepared and electrowon to get copper and nickel powder.

In the electrowinning of copper 9.0 L of copper sulphate solution comprising of 36.07 g/L Cu and 90 g/L H_2SO_4 was used as electrolyte. The solution (9.0 L) comprising of 10 g/L Ni, 40 g/L $(NH_4)_2SO_4$, 10 g/L H_3BO_3, and 0.2 g/L thiourea was used as electrolyte for electrowinning of nickel powder. In both the cases two stainless steel cylindrical rods of dimension (cm) 29.9(l) x 2.5(d) and 29.4 (l) x 2.5(d) were used as cathode and two lead-antimony (6%) alloy plates of dimension (cm) 18(l) x 15.4(b) x 0.4(t) cm were used as anode.

The copper powder produced was washed with sodium carbonate solution to neutralise the acid and then treated with sodium potassium tartarate to avoid surface oxidation of copper powder. Both copper and nickel powders were annealed at 973 K under hydrogen atmosphere for 1 h. Various properties of metal powders were evaluated for P/M application.

Results and discussion

Copper sulphate and nickel sulphate solutions were obtained from the copper bleed solution following the scheme [14] presented in Fig. 1. These solutions were electrolysed to get the copper and nickel powder.

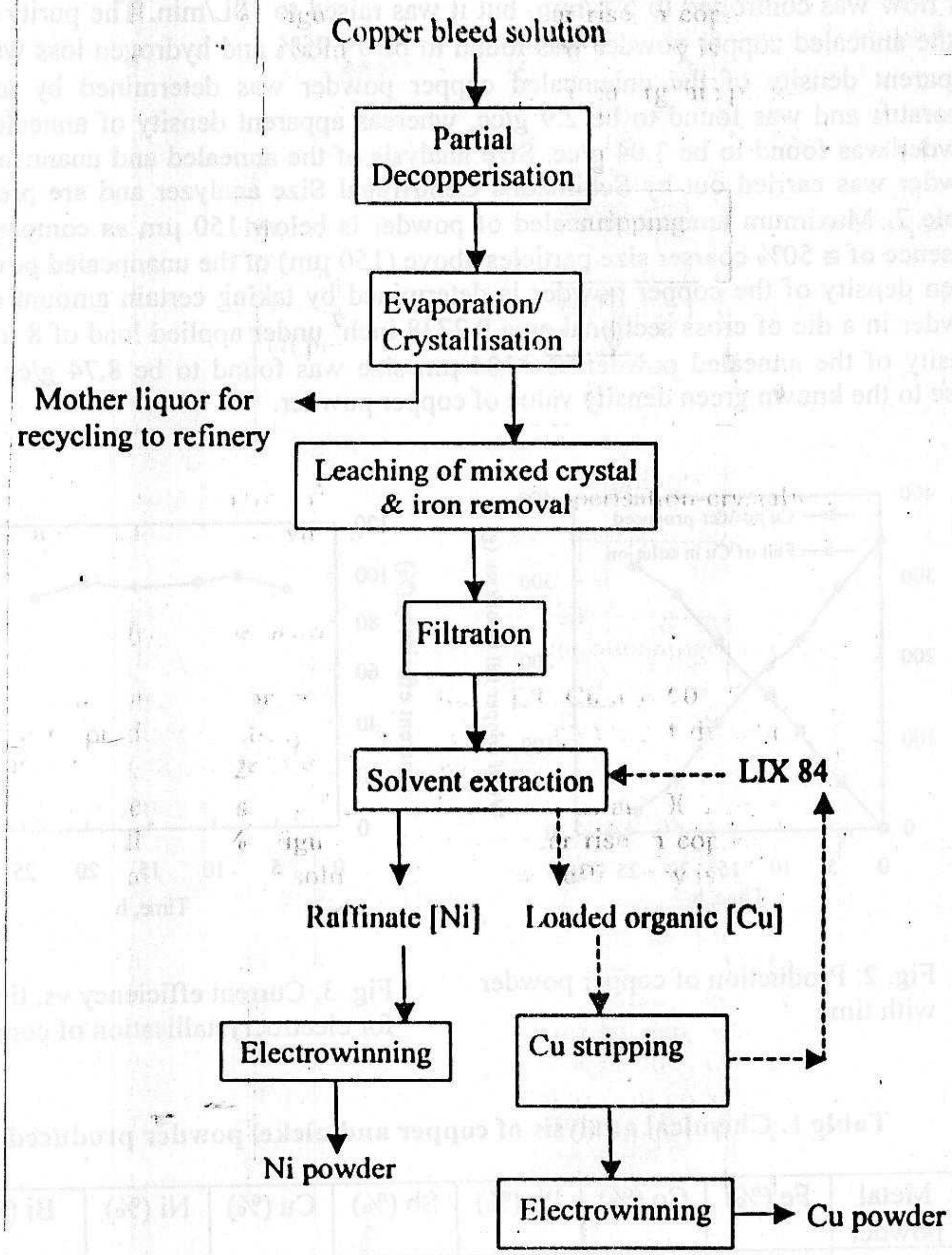


Fig. 1. Copper bleed solution treatment following decopperisation-crystallisation-solvent extraction-electrowinning

Preparation of electrolytic copper powder

Copper sulphate solution containing 36.07 g/L Cu and 90 g/L H_2SO_4 was used as electrolyte to produce electrolytic copper powder at current densities (CD) of 700 A/m^2 and 900 A/m^2. After 24h of electrolysis at a current density of 700 A/m^2 the overall current efficiency was found to be 88%, whereas at 900 A/m^2 CD the overall current efficiency fell to 69%. Figure 2 shows a linear rise in copper recovery at 700 A/m^2 and fall of metal content in solution. The current efficiency is highest (99%) at 8h

with energy consumption of 2.23 kWh/kg (Fig. 3). The copper produced at both the current densities were dendritic in nature. Copper powder produced was annealed in an electric furnace at 973 K under reducing atmosphere of hydrogen gas for 1h. Initially gas flow was controlled to 5 L/min, but it was raised to 10L/min. The purity (Table 1) of the annealed copper powder was found to be 99.95% and hydrogen loss was 0.89%. Apparent density of the unannealed copper powder was determined by using Hall apparatus and was found to be 2.9 g/cc, whereas apparent density of annealed copper powder was found to be 3.04 g/cc. Size analysis of the annealed and unannealed coper powder was carried out by Schimadzu Centrifugal Size analyzer and are presented in Table 2. Maximum amount annealed of powder is below 150 μm as compared to the presence of ≅ 50% coarser size particles above (150 μm) of the unannealed powder. The green density of the copper powder is determined by taking certain amount of copper powder in a die of cross sectional area 0.2738 inch^2 under applied load of 8 tonne. The density of the annealed powder of <104 μm size was found to be 8.74 g/cc which is close to the known green density value of copper powder.

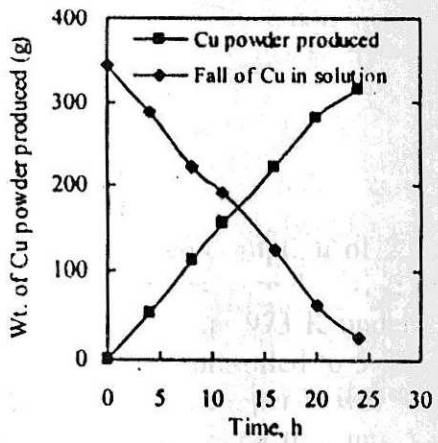


Fig. 2. Production of copper powder with time

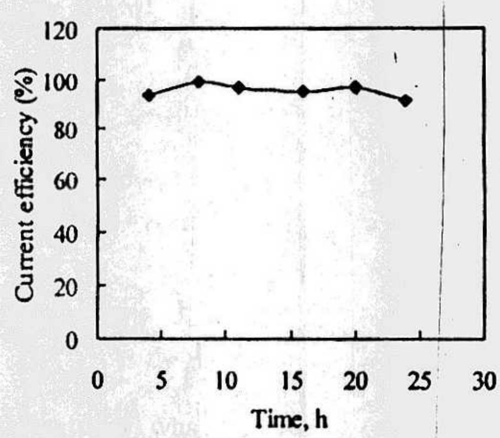


Fig. 3. Current efficiency vs. time for electrocrystallisation of copper

Table 1. Chemical analysis of copper and nickel powder produced

Metal powder	Fe (%)	Co (%)	Pb (%)	Sb (%)	Cu (%)	Ni (%)	Bi (%)
Copper	0.0072	NF	0.0025	0.037	**99.95**	NF	0.007
Nickel	0.017	0.032	0.434	NF	0.0148	**99.89**	NF

Table 2. Sieve analysis of the copper powder

Size range (μm)	Wt. of the powder (g) (Annealed)	Wt. of the powder (g) (Unannealed)
500-300	11.8	19.5
300-250	5.0	8.8
250-150	12.4	22.5
150-100	11.4	10.8
100-75	6.5	5.2
75-50	1.9	0.9
50-40	2.3	1.1
40-30	4.3	1.9
30-20	9.8	4.1
20-10	21.9	12.7
10-5	9.9	1.3
5-0.2	2.8	1.4
0.2-0.0	-	0.3

Preparation of electrolytic nickel powder

A pregnant solution containing 10 g/L nickel, 10 g/L H_3BO_3, 40 g/L $(NH_4)_2SO_4$, 0.2 $CS(NH_2)_2$ was taken for the electrolysis of nickel at the current density in the range 4000-5000 A/m^2 at pH range 5.2-5.5. Boric acid acts as a buffering agent and it also helps in reduction of stress in the deposited metal whereas thiourea increases the brightness. Ammonium sulphate also helps in maintaining the pH of the electrolytic bath. It can be seen that the high current density leads to higher amount of nickel deposition. The nickel recovery is around 86% and current efficiency being in the range 39-44% with energy consumption of 20-21 kWh/kg. If we compare the current efficiency on the electrolysis of copper and nickel, the efficiency of later is almost half of the former. It is due to the fact that, current required in the case of nickel is excessively high which results in the decrease of the efficiency. The recovery of the nickel is maximum of 87% at 5000 A/m^2 at pH 5.25; the recovery is near to 90% at all other pH. But from the solution of 20 g/L nickel at pH 4.66, the recovery of the nickel goes up to 99% under the similar conditions (Table 2). Thus the higher nickel containing feed solution is beneficial to achieve high metal recovery with simultaneous decrease in the energy consumption to 19 kWh/kg from that of 21 kWh/kg consumed at low metal concentration.

A rise in nickel powder produced and fall in metal concentration are noticed which is more or less similar to data for copper (Fig 4). Voltage also descends with time but becomes almost constant at the later stage. Current efficiency also shows decreasing trend with time at a current density of 5000 A/m^2 (Fig. 5).

Table 3. Electrodeposition of the nickel powder

Composition (g/L): 19.37 Ni, 40 $(NH_4)_2SO_4$, 10 H_3BO_3, 0.2 $CS(NH_2)_2$

Volume of the electrolyte : 9.0 L

Cathode: Cylindrical rod (Stainless steel)

Parameters	Data
Time (h)	4.00
pH	4.66
Current densities (A/m^2)	5000
Average voltage (V)	9.30
Average current (A)	87.00
Energy consumption (kWh/Kg)	19.05
Volume of the spent electrolyte (L)	8.5
Nickel in the spent electrolyte (g/L)	0.15
Wt of the dry nickel powder	168.18
Current efficiency (%)	44.47
Recovery of the nickel powder (%)	99

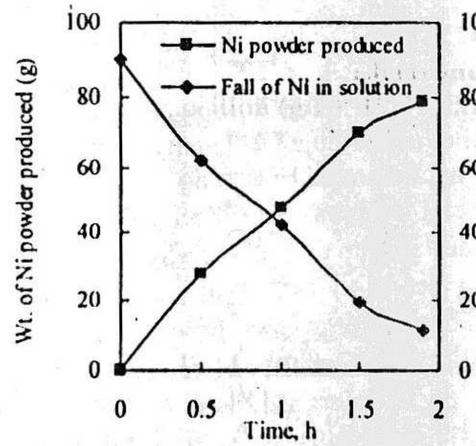


Fig. 4. Production of nickel powder with time

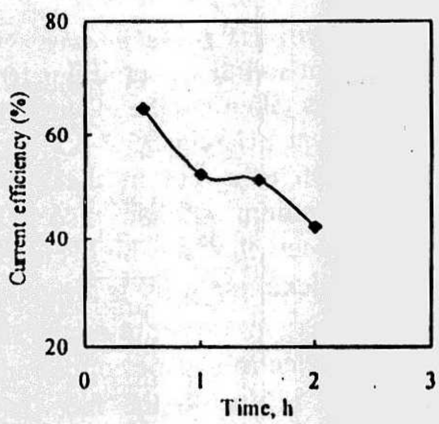


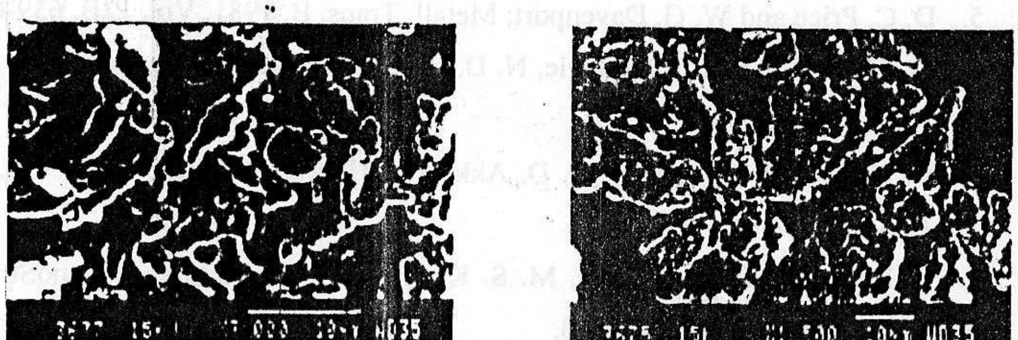
Fig. 5. Current efficiency vs. time for nickel powder deposition

With the objective of getting the powder for the P/M applications, electrolytic nickel powder is annealed in the electrically operated tubular furnace at 973 K for 1h under reducing atmosphere of hydrogen. A very bright powder was obtained upon annealing. The purity of the annealed nickel powder was found to be 99.89% (Table 1). The particle size of the nickel powder (Table 4) was within the range of 213 to < 38 μm with maximum amount of 212-150 μm size. Apparent density of the nickel powder was found to be 4.29 g/cc. The density of the annealed powder of the size < 104 μm was found to be 7.22 g/cc under the load of 8 tonne for the die size of 0.2738 inch^2.

Table 4. Sieve analysis of annealed nickel powder

Particle size (μm)	Percentage by weight
212	22.66
212-150	30.10
150-106	13.94
106-75	8.61
75-63	4.44
63-45	3.98
45-38	8.09
38	7.67

Fig. 6 presents the SEM pictures of annealed copper and nickel powder produced at 700 A/m^2 and 5000 A/m^2 respectively. Both the copper and nickel powders were found to be dendritic in nature, and have the advantage of better compaction for P/M application. The nickel powder dendrite showed well defined growth in thickness as compared to copper.



a. b.

Fig. 6. SEM pictures of annealed (a) copper and (b) nickel powder

Conclusion

1. A 95 % copper powder recovery is achieved at a current density of 700 A/m^2. The powder is dendritic in nature. The current efficiency for copper powder production by electrolysis is upto 88 % with energy consumption in the range 2.3-3.8 kWh/kg.
2. The purity of the annealed copper powder is found to be 99.95 %. The annealed powder has apparent density of 3.04 g/cc, hydrogen loss 0.72 % and acid insoluble is 0.27 % and green density of 8.7 g/cc on compaction of < 104 μm size powder.
3. At high concentration of nickel (20 g/L) with high current density of 5000 A/m^2, 99 % of nickel powder recovery is achieved. However, the lower nickel tenor of 10 g/L yields lower metal recovery of 86 %.
4. The current efficiency in nickel electrolysis is practically low (44 %) as compared to that of copper. On the other hand, energy consumption is high 19.05 kWh/kg with nickel feed of 20 g/L which increases to 20-21 kWh/kg with 10 g/L Ni feed.

5. Purity of the annealed nickel powder is found to be 99.89 %. Other properties of the annealed powder are: flow rate 20-21 s/50g; acid insoluble 0.13-0.37 %; hydrogen loss 0.3-0.88 %; green density 7.22 g/cc on compaction of < 104 μm size powder.

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