ELECTRODEPOSITION OF COPPER-TIN ALLOY (BRONZE) POWDERS FROM ACID CITRATE BATHS

R. K. Dube* and P. M. Prasad

Department of Metallurgical Engineering, Institute of Technology, Banaras Hindu University, Varanasi-221005.

** Presently at Department of Metallurgy and Technology, University College of Swansea, Swansea, SA2 8PP, U.K.*

(Received and accepted 20 Jan. 1977)

Cathode polarisation studies of normal salt baths of copper and tin with the addition of sodium citrate complexing agent, indicate the feasibility of codepositing them from such baths in the powder form. Investigations on the electrodeposition of copper-tin alloy powders from complex $CuCl_2$-$SnCl_2$ baths containing citrate additions show that the per cent tin in the powder is increased with the concentration of sodium citrate in the bath, decrease in the metal ion ratio $(Cu^{++})/(Sn^{++})$ of the bath and increase in the cathodic current density. For the preparation of a 92% Cu—8% Sn alloy (a typical bronze) powder using insoluble anodes at 30°C and a pH of 2.0, a current density of 10 asd, metal ion ratio $(Cu^{++})/(Sn^{++})$ = 1.065 and sodium citrate addition of 40 g/l have been found to be optimum. 'True bronze' powders thus prepared possess a dendritic shape and a good size distribution and may be considered suitable for the powder metallurgical fabrication of porous components, especially filters.

Although alloy plating has been the subject of several hundred investigations over the past few decades and electrodeposition of numerous binary and ternary alloys has become an established practice, preparation of alloy powders by electrodeposition has received only limited attention. In recent years some studies have been reported on the preparation of powders of a few binary alloys like copper-zinc (from an alkaline glycerate bath[1]), copper-nickel (from a bath with citrate addition[2]) and iron-nickel, iron-cobalt and cobalt-nickel (from sulphate baths[3-6]). The potentialities of citrate as a powerful complexing agent for the successful electrodeposition of some alloys (e.g , Fe-W, Co-W, and Fe-Co-W) — whose constituent metals are far removed from each other in the standard e.m.f. series— has long been realised [7,8]. But its exploitation for the electrodeposition of alloy powders has been most limited. So far electrodeposition of only copper-nickel alloy powders appears to have been realised from baths containing citrate as the complexing agent.

In an earlier paper, the authors[9] (from their investigations on the cathode polarisation behaviour of copper, zinc, cadmium and tin in complex baths containing citrate or tartrate as additives) reported that only copper exhibits tremendous polarisation in these baths and the other metals are not significantly polarised. Of the two complexants—citrate and tartrate—the former was found to be the more effective complexing agent capable of inducing greater cathode polarisation decidedly beneficial for the electrodeposition of some copper-base alloys. The present work is concerned with the possibility of codepositing copper and tin from acid citrate baths. Experimental results on the effect of various parameters influencing the deposition process were utilised to prepare one typical bronze (92% Cu-8% Sn alloy) powder.

EXPERIMENTAL

Materials: All the chemicals used in this investigation ($CuSO_4.5H_2O$, $CuCl_2.2H_2O$, $SnCl_2.2H_2O$, $Na_3C_6H_5O_7.2H_2O$, NaCl, KCl and NH_4Cl for electrodeposition studies and KI, CH_3COOH, HNO_3, H_2SO_4, NH_4CNS, Hypo etc. for analytical work) were of A.R. Grade.

Cathode plates were of electrolytic copper and chemical purity tin. Graphite plates were used as anode.

Procedure: The experimental arrangement consisted of two graphite anodes (covered with a thick cloth) on either side of the cathode of the chosen metal immersed in an appropriate electrolyte (1N $CuSO_4.5H_2O$ for copper and 1N $SnCl_2.2H_2O$ for tin with or without the desired citrate additions) contained in a rectangular 'Perspex' tank. D C. current was drawn from a 12V battery eliminator connected to the 220V A.C. supply. For cathode polarisation measurements, the metal electrode (whose cathode polarisation was to be measured) was electrolytically contacted via a salt bridge against a standard saturated calomel electrode. Terminals of the two electrodes were joined to a 'Philips' high impedence microvoltmeter through a contact key. The instantaneous e.m.f. developed was then measured at various current densities ranging from 0-20 asd.

Based on a large number of preliminary experiments conducted in this study and drawing up on the experience of Prithviraj et al on the preparation of copper-nickel alloy powders from citrate baths[2], an electrolytic bath consisting of the following constituents was chosen for further systematic studies on the electrodeposition of copper-tin alloy powders:

$CuCl_2.2H_2O$	...	30 g/l
$SnCl_2.2H_2O$	...	20 g/l
NaCl	...	20 g/l
NH_4Cl	...	20 g/l
$Na_3C_6H_5O_7.2H_2O$	...	40 g/l

Since the insoluble anodes were used, composition of the electrolytic bath was maintained by periodic addition (every 2-3 mins) of the required quantities of copper and tin salts in the form of their standard concentrated solutions. To determine the proportions of additions of the metal salts, preliminary electrodeposition studies were conducted in which the compositions of the electrolyte and the alloy powder were determined in typical experiments under varying conditions for short durations.

The influence of metal ion $(Cu^{++})/(Sn^{++})$ ratio, concentration of the sodium citrate additive current density on the composition of the alloy deposit was then investigated in some detail. In all the experiments a temperature of 30°C and a pH value of 2.0 were maintained. No agitation was employed and electrolysis conducted for 12 mins in each trial, maintaining the bath composition as mentioned earlier.

In all the alloy powder deposition experiments, the powder which was found to have settled at the bottom of the tank, was collected, washed with distilled water and then preserved under 2% soap solution to minimise surface oxidation. Whenever required the powder was water-washed, washed with alcohol, dried in the atmosphere and chemically analysed by standard analytical procedures.

Based on the optimised bath composition and current density, electrolysis was conducted for over 6 hours to prepare about 25 gms of 92% Cu-8% Sn alloy powder add some of its properties were examined.

RESULTS AND DISCUSSION

Influence of Citrate on the Cathode Polarisation of Copper and Tin: From the results of the cathode polarisation measurements presented in Fig. 1, it is obvious that while the polarisation behaviour of copper is tremendously influenced by the addition of sodium citrate, the tin electrode is not significantly polarised by this additive. Citrates from a variety of neutral cationic or anionic complexes[10,11] with common metals depending on the concentration of the reagents, nature of the bath, its pH and temperature etc. In the present case the very high stability constant of copper citrate (1.6×10^{14} at 25°C), which is several orders of magnitude higher than that of copper sulphate (2.0×10^{2} at 25°C), is responsible for the high degree of cathode polarisation of copper induced by the citrate addition to the simple copper salt bath. Generally noble metal complexes are known to be more stable (in other words very poorly dissociated) than the base metal complexes and this leads to a tremendous decrease in the effective concentration of the free noble metal ion, whereas the free ionic concentration of base metals is not changed significantly by the addition of such complexing agents. Now in our case it appears that the addition of sodium citrate to the electrolyte leads to a drastic reduction in the free copper ion concentration while the free tin ion concentration does not seem to be much effected thus leading to an overall decided cathode polarisation of copper. Details of the influence of the concentration of sodium citrate on the cathode polarisation behaviour of copper, tin and a few other common metals have been discussed elsewhere by the authors[9].

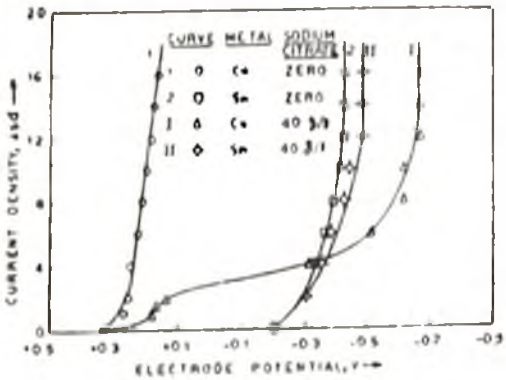


Fig. 1 Cathode polarisation curves for copper and tin at 30°C in normal solutions of their respective salts with and without sodium citrate addition

Possibility of the Electrodeposition of Copper and Tin Alloy Powders: Fig. 1 further reveals that the current density vs cathode potential curves of copper and tin in baths without citrate addition are far removed from each other and no codeposition is possible from such baths. On the other hand, the polarisation curves for copper and tin in citrate baths overlap at current densities beyond 3.5 asd indicating the theoretical possibility of codepositing them by chosing appropriate experimental conditions. The dynamic potentials for the deposition of copper and tin from these baths become equal at a current density of 4.5 asd. At high current densities tin even appears to behave as a more noble metal as compared to copper in such baths.

In the individual normal salt baths containing the sodium citrate additive (40 g/l), as is to be expected, metal plating was observed at low current densities and the concerned metal powders were formed at high current densities. The transition plating→powder was characterised by a relatively large and sudden increase in polarisation with only a slight increase in

current density. In each case, current densities beyond a certain value had no perceptible effect on the cathode polarisation and thus the electrode potential remained constant after a critical value of current density. The transition plating→powder in the normal copper and tin baths containing 40 g/l sodium citrate was found to occur, respectively, at current densities of 2 and 8 asd. Since the plating→powder transition lies at a relatively low current density in the case of copper deposition and the current density vs cathode potential curves for copper and tin (in citrate baths) do not overlap until a much higher current density (3.5 asd), electroplating of copper-tin alloys is not considered feasible from these baths. However, at current densities beyond 8 asd where tin plating distinctly changes to over tin powder in this baths, electrodeposition of copper-tin alloy powders may be achieved at suitable current densities from their mixed salt baths containing sodium citrate as the addition agent. This fact has been confirmed in actual electrodeposition experiments (of the present studies) where it was observed that copper-tin alloy powder deposition is possible even at 4 asd, a current density which is in between that required for the preparation of individual metal powders in their respective citrate baths.

Effect of Concentration of Sodium Citrate on the Composition of the Cu-Sn Alloy Powder : Fig. 2 shows

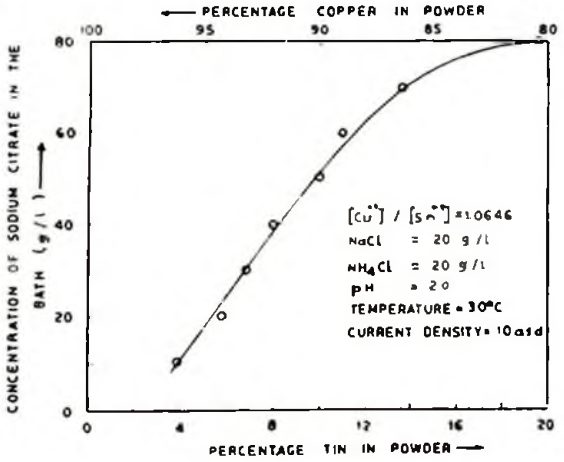


Fig. 2 Effect of concentration of sodium citrate on the tin content of the powder

the influence of sodium citrate on the percent tin in the alloy powder. It is evident that upto 60 g/l of sodium citrate in the bath, the tin content of the alloy powder varies linearly with the quantity of the citrate additive. Beyond this value (60 g/l citrate), the increase in percent tin in the powder is obviously rapid. This behaviour may be attributed to the fact that the effect of increasing the concentration of sodium citrate is to make the deposition potentials of copper less noble (or more negative) so that copper becomes less readily deposited at excessive concentrations of the complexing agent. On the other hand, since there is no significant effect on the cathode polarisation characteristics of tin (with increasing amount of citrate), it (Sn) behaves as an increasingly noble metal with respect to copper with increased addition of sodium citrate to the mixed electrolytic bath. The net result is an increase in the tin content of the alloy deposit with increasing amount of citrate in the bath.

Effect of Metal Ion Ratio of the Bath on the Cu-Sn Alloy Powder Composition : The influence of metal ion ratio of the bath on the composition of the Cu-Sn alloy powder at 10 asd is shown in Fig. 3. The percent

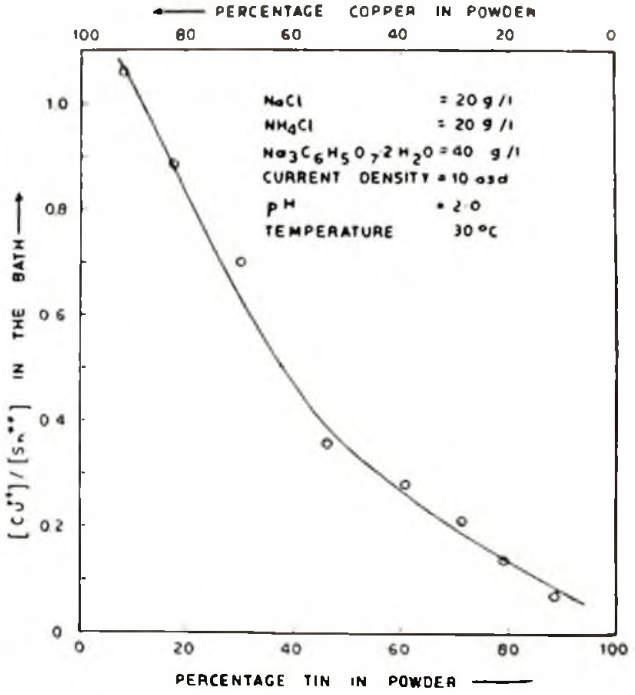


Fig. 3 Effect of metal ion ratio on the tin content of the powder

copper in the alloy powder is seen to be effected by even relatively small variations of the metal ion ratio of the bath and copper-tin alloy powders of any desired composition can be obtained by simply varying the metal ion ratio of the bath.

Effect of Current Density on the Composition of the Cu-Sn Alloy Powder : From Fig. 4 it is seen clearly that the per cent tin in the powder increases (linearly) with increase in current density. In other words copper content of the powder decreases with increasing current density. This may be qualitatively explained from two viewpoints: diffusion control and cathode potential. With regard to cathode potential, an increase of current density causes the cathode potential of copper to be

more negative (i.e., less noble) (see Fig. 1) and hence the deposition conditions approach more closely to those represented by the current density vs cathode potential curve of the less noble metal (tin). This condition amounts to an increase in the proportion of tin deposit. "According to the simple diffusion theory, the rate of deposition of a metal has an upper limit which is determined by the rate at which its ions can move through the cathode diffusion layer. At a given current density, the rate of deposition of the more noble metal is relatively much closer to its lin iting value than that of the less noble metal. An increase in current density, therefore, must be borne mainly by an increase in the rate of deposition of the less noble metal[12]" (in our case tin). It is also probable that the rate of diffusion of tin is more than of copper in the cathode diffusion layer.

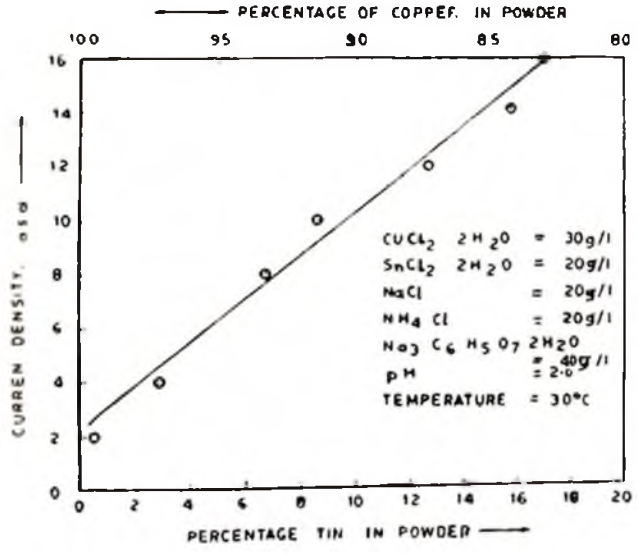


Fig. 4 Effect of current density on the tin content of the powder

Preparation of Bronze Powders of Low Tin Content:— From the preceding results an electrolytic bath containing 40 g/l of sodium citrate as the complexing agent, with a metal ion $(Cu^{2+})/(Sn^{2+})$ ratio of 1.03 and a current density of 11 asd are considered suitable for the preparation of bronze powders of the nominal composition 90% Cu and 10% Sn.

Twenty two grams of a typical low tin bronze powder of the nominal composition 92 Cu–8 Sn has been prepared by electrodeposition from a mixed $CuCl_2$–$SnCl_2$ bath containing sodium citrate additive. The exact experimental conditions employed for the same (standardised from the preceding results) and some of the properties of the resultant alloy powder are summaraised in the Table 1. It analysed 8.1% tin and balance copper. The current efficiency for the deposition of this copper-tin alloy, calculated by employing the formula given by Brenner[12].

Table 1 Bulk Preparation of a Typical Copper-Tin Alloy Powder and its Properties

Composition of Electrolyte*	...	$CuCl_2.2H_2O$ = 30 g/l $SnCl_2.2H_2O$ = 20 g/l NaCl = 20 g/l NH_4Cl = 20 g/l $Na_3C_6H_5O_7.2H_2O$ = 40 g/l
pH value	...	2.0
Temperature	...	30°C
Anode Current Density	...	9.7 asd
Cathode Current Densits	...	10 asd
Voltage During Electrolysis	...	4.0 V
Duration of Electrolysis	...	736 mins
Weight of Alloy Powder	...	22.3 gms
Composition of Alloy Powder	...	8.1% Sn and balance Cu
Lattice Parameter of the Alloy Powder	...	a = 3.655 Å
Cathode Current Efficiency for the Alloy Deposit	...	74%

Sieve Analysis of the Bronze Powder

Mesh sive	Fraction retained wt. %
+100	18.8
−100, +150	13.8
−150, +200	6.6
−200	60.8

Shape of the Bronze Powder ... Mostly dendritic, some of it irregular and rounded.

* $(Cu^{++})/(Sn^{++})$ ratio = 1.065

$$\text{Cathode Current Efficiency of Alloy Deposition} = \frac{P_1.W}{e_1 it} + \frac{P_2.W}{e_2 it}$$

(where P_1 and P_2 are the percent by weight of each metal in deposit of W gms, e_1 and e_2 are their respective electrochemical equivalents expressed in gms per coulombs, i is the current in amps and t the time in seconds), has been found to be 74%.

The bronze powder prepared as above was mostly dendritic in shape (some of it was rounded and irregular) and consisted of coarse, medium as well very fine particles (Sieve analysis included in Table 1) which appears to be a good blend for powder metallurgical (PM) compaction. X-ray powder diffraction pattern of this alloy powder showed only reflections corresponding to

the characteristic f.c.c. solid solution of tin in copper (metastable α phase). Its lattice parameter has been calculated to be 3.655 Å which is good agreement with that expected for a metastable 92% Cu-8% Sn alloy phase[13].

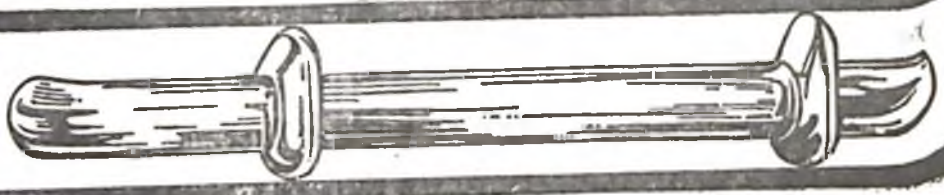
Probable Uses for These Bronze Powders: PM bronze components are used because of their corrosion resistance, stability, relatively good mechanical strength, high damping capacity, good wear resistance and their self lubricating feature[14,15]. Dense as well as porous bronze PM products generally contain 5-12% tin[15,16] (with or without addition of graphite up to 6%, and for certain special applications up to 6% of iron and lead). The straight copper-tin bronze powders such as those prepared in the present study appear to be suitable for the PM fabrication of porous bronze filters which find applications involving filtration of various types of oils, waxes and dyes, water and caustic solutions. They may also be used as diaphragms in control instruments and distributors for fermentation process[15]. It is also noteworthy that for the PM fabrication of porous components, especially filters, sintering of alloy powders is considered to be more efficient[15] (and therefore preferred) as compared with the sintering of mixtures of elemental powders (e.g., copper and tin) which is the conventionally used method for the manufacture of porous bearings. Atomisation is the most widely used method of producing the "true bronze" (copper-tin alloy) powders[17]. It is believed that the present attempt opens out another attractive method of preparing these bronze powders.

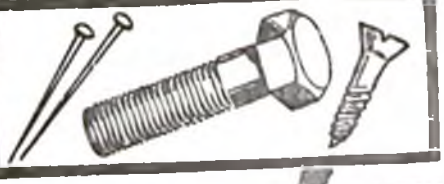
Further work on (1) the influence of the pH, temperature and agitation of the bath on the deposition of Cu-Sn alloy powders from the citrate baths, (2) the accurate control of electrolyte composition by the use of suitable soluble alloy anodes or individual metal anodes and (3) preparation of bronze powders on a large scale followed by their assessment for PM applications will be useful.

REFERENCES

1. B.P. Yura'v and L.A. Aladxhalov, Soviet Powder Metallurgy and Metal Ceramics, 5(77 (1969) 345.
2. V. Prithviraj, S.L.N. Acharyulu and R.V. Tamhankar, Trans. Ind. Inst. Metals 23(2) (1970) 51
3. A.V. Pomosov, I.B. Murashoza and V.P. Artamonov, Soviet Powder Metallurgy and Metal Ceramics, 5(77) (1969) 341.
4. B.P. Yure'v and S.A. Sviridova, ibid 7(79) (1969) 519.
5. B.P. Yure'v and L.P. Sukhanova, ibid, 6(78) (1979) 438.
6. B.P. Yure'v and L.A. Golubkov, ibid, 7(55) (1967) 425.
7. M.L. Holt and L.E. Vaaler, Trans. Electrochem. Soc., 90(1946) 43.
8. R. Bhat, R.D. Angal and K.M, Pai, J. Electrochem. Soc. (India), 25(2) (1976) 61.
9. R.K. Dube and P.M. Prasad, J. Electrochem. Soc., 122 (11) (1975) 1473.
10. K.B. Yatsimirskii and V.P. Vasil'ev, "Instability and Stability Constants of Complex Compounds" Van Nostr-and Co., Princeton, N.J. (1960).
11. "Stability Constants" Special Publication No. 17 The Chemical Society. London (1964).
12. A. Brenner, "Electrodeposition of Alloys" Vol. 1, Academic Press, London (1963) 123 & 149.
13. W.B. Pearson, "A Handbook of Lattic Spacing and Structures of metals and Alloys" Vol. 2, Pergamon, Press, London (1967) 612.
14. J S. Hirschhorn, "Introduction to Powder Metallurgy" Amerlcan Pow. Met. Inst., New York (1969) 322.
15. C.G. Goetzel, "Treatise on Powder Metallurgy" Vol. II, Interscience Publishers, New York (1950) 506, 509-13, 518, 532, 536-8 & 542.
16. P. Schwarzkopf, "Powder Metallurgy", McMillan and Co., New York (1947), 46, 161-5 & 252.
17. W.D. Jones "Fundamental Principles of Powder Metallurgy" Edward Arnold Publishers, London (1969) 233.

ELECTROPLATERS & ANODISERS





ELECTROPLATING :-

Chrome, Nickel, Silver, Bronze, Brass, Tin, Zinc, Copper, Cadmium, Chromate Processing, Barrel plating etc.

Auto Motor Bumpers & Guards a speciality. Remember, it is the quality that counts! Work carried out to I.S., B.S. & ASTM Specifications.



ALUMINIUM ANODISING :-

Specialists in Industrial & Structural Anodising.

KOHINOOR ELECTRO GILDERS

(Estd. 1932)

Khetwadi 10th Lane, Bombay-4. 'Phone : 351786