STUDIES ON ELECTROLYTIC PREPARATION OF IRON-COPPER POWDERS

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Factors affecting the physical characteristics and chemical composition of iron-copper powder deposits obtained by electrolysis, have been investigated. Effect of process variables such as current density, *p*H, temperature, time, concentration of electrolyte and agitation, has been studied over a wide range, for theoretical interest and to obtain powder deposits of a definite composition. Metallographic examination of iron-copper powder thus prepared after compacting and sintering, has revealed uniform and homogeneous dispersion of the two metals. The technique of preparation presented in this paper is a better substitute to the conventional practice of preparing binary metal powders by mixing and tumbling.

Binary metal powders prepared electrolytically show distinctive benefits and features not attainable by mechanical mixing of elemental metal powders[1]. In general one can expect electrolytically prepared mixtures of two metals to be denser, and more homogeneous than mixtures of metal powders prepared by conventional techniques after subsequent pressing and sintering. This electrolytic method has an added advantage over the other methods because of its simplicity of operation coupled with the attainment of higher degree of control over critical factors like chemical composition, particle size etc.

Simultaneous electro deposition of two metals depends on their individual single electrode potentials[2] which should be fairly close for achieving co-deposition of the two metals. The concentration of the complexing agent and the individual metal salts, the composition of the supporting electrolyte i.e., addition agents, *p*H and temperature are vital factors which also influence the co-deposition of two metals. Generally a modification of the bath composition, addition agents and variation of the process conditions lead to the formation of electro-deposit in the form of powder. This formation of powder is generally attributed[3] to the special features surrounding the electro-crystallisation of the metal when the layer of the metal adjoining the cathode is suddenly impoverished by the discharging metal ions, coupled with other factors like the various kinds of disruption of the crystal lattice and the electro-crystallisation of the metal at a greater number of places on the depositing surface.

In the present investigation co-deposition of Iron and Copper has been tried in the presence of various complexing agents and it has been found that in the presence of sodium citrate the deposition potentials are very near each other which facilitates satisfactory co-deposition. In the electrolysis of solutions containing ferrous ions, it is necessary to separate anode and cathode compartments[4] in order to avoid oxidation of the electrolyte, since ferric ions cause the deposit characteristics to change, consequently affecting the acidity of the cathode solution which will decrease steadily throughout the run of the experiment. To avoid the danger of ferric salt hindering the electrolysis, the authors have resorted to the use of an electrolytic cell with separate anode and cathode compartments.

EXPERIMENTAL PROCEDURE

The electrolyte (catholyte) contains the two metals iron (ferrous) and copper as their sulphates, sodium citrate as the complexing agent, ammonium chloride as the addition agent to increase the ionic concentration of the solution. The ionic concentration of copper and iron is maintained throughout the investigation in the fixed ratio of 1 : 2. (Subsequently some experiments were also carried out with ionic ratios 1 : 8, 1 : 26, 1 : 32 and 1 : 52). The compositions of the catholyte and anolyte are as follows :

Catholyte :	$CuSO_4 \cdot 5H_2O$	7·86 g/l
	$FeSO_4 \cdot 7H_2O$	19·92 g/l
	$Na_3C_6H_5O_7$	30·0 g/l
	NH_4Cl	20·0 g/l
Anolyte :	Na_2SO_4	(saturated solution)

The electrolytic cell consists of an outer vessel (capacity 1000 ml) in which is placed a porous vessel (capacity 500 ml). The latter acted as the cathode compartment and it is filled with the catholyte prepared as described above. The outer or anode compartment is filled with the anolyte. 18 : 8 stainless steel sheet 0·3175 cm thick is used as cathode with an area of 5·08 cm square. Graphite anodes of the same dimensions are placed symmetrically on either side of the outer compartment, their surfaces being parallel to the cathode face. The source of current is a selenium metal a c to d c rectifier, the output voltage of which can be controlled precisely. The investigation was carried out under different values of the various process variables like current density, *p*H, temperature, ionic concentrations, period of deposition and agitation of the electrolyte. The powders prepared are brushed off the cathode, washed free from the traces of electrolyte and dried in vacuum. The particle size of the powder has been determined by Fischer subsieve sizer which employs gas permeability technique. The chemical composition of the alloy powder is evaluated by conventional analytical methods[5].

RESULTS AND DISCUSSION

Process conditions influence the ultimate composition of the powder in which the metals co-deposit. These independent variables like current density, temperature, *p*H, rate of agitation etc. also influence the physical characteristics of the powder and the overall efficiency of the process. Since there is no comprehensive theoretical basis for interlinking the effects of these variables, only some salient features of the individual factors have been brought out in this paper.

Effect of Current Density

The proportion of copper in the deposited powder decreases with increase in current density (CD) and this trend is more significant at lower *p*H values (Table 1). It is also observed that the rate of decrease with increasing current density is less marked at higher CD and lower *p*H.

Increase in CD tends to increase the cathode potential favouring an increase in deposition of iron. This tendency is however counteracted by certain other factors. The deposition potential of copper is subsequently lowered since the deposit tends to become poorer in copper. Added to this, the electrolyte surrounding the cathode will become

TABLE 1

INFLUENCE OF *p*H AND CURRENT DENSITY ON PERCENTAGE OF COPPER IN IRON-COPPER POWDER (AT 29°C)

Current density (amp/sq cm)	Copper (%)			
	*p*H 4	*p*H 6	*p*H 8	*p*H 10
0·0155	71·36	71·00	70·52	70·58
0·0310	57·38	57·54	62·11	65·70
0·0465	45·87	51·93	52·70	55·88
0·0620	37·53	40·30	48·13	53·00
0·0775	35·34	37·41	43·13	43·46

relatively richer in copper ions since the deposit contains more Fe. This tends to retard the increase in Iron content, hence the rate of decrease of copper with increasing CD becomes less significant at higher current density and it is quite possible that a balance point will be reached at which the factors neutralise one another and a steady composition is reached, as seen at *p*H value 4 (Table 1, Fig. 1).

*Influence of p*H

At a particular CD, increase in *p*H tends to increase the copper content in general (Table 1). It is observed that at very low CD, the compositions more or less remain constant with increase in *p*H and also that the increase of copper content is maximum at a current density of 0·0620 amp/sq cm. These changes are perhaps due to variations in cathode potentials and the rate of deposition for a given CD with increase in *p*H.

Effect of Temperature

At a given CD and *p*H the increase in temperature increases the copper content although in the more alkaline solutions (namely *p*H 10) a reverse trend has been observed (Table 2, Fig. 2). The decrease in copper content with increase in CD is more striking at *p*H 8 for higher temperatures whereas the same phenomenon has been observed at *p*H 6 and *p*H 10 for lower temperatures. It is apparent that the increase in temperature tends to bring about a change in the composition which is quite opposite to that observed with increasing CD. The temperature changes can bring about a reversal in the relative mobility of the two co-depositing metals, thus increase in temperature tends to have an effect opposite to that of increase in CD.

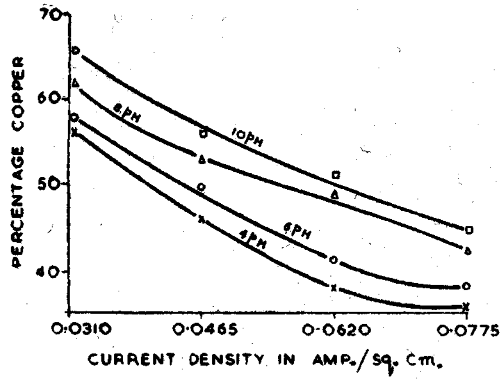

Fig. 1—Influence of *pH* and current density on percentage of copper (in iron-copper powder) at 29°C.

TABLE 2

EFFECT OF TEMPERATURE ON PERCENTAGE OF COPPER IN IRON-COPPER POWDER FOR DIFFERENT VALUES OF *p*H AND CURRENT DENSITY

*p*H	Current density (amp/sq cm)	Copper (%)		
		Temp (29°C)	Temp (55°C)	Temp (75°C)
	0·0310	57·50	62·15	64·91
6	0·0465	51·90	60·20	62·11
	0·0620	40·70	47·00	54·70
	0·0310	62·10	68·88	72·80
8	0·0465	52·70	54·62	57·20
	0·0620	48·10	50·37	53·00
	0·0310	65·70	53·98	48·90
10	0·0465	55·90	44·96	41·00
	0·0620	53·00	42·70	39·40

TABLE 3

INFLUENCE OF STIRRING ON PERCENTAGE OF COPPER IN IRON-COPPER POWDER

Current density (amp/sq cm)	Copper (%)					
	*p*H 6		*p*H 8		*p*H 10	
	Stirred	Unstirred	Stirred	Unstirred	Stirred	Unstirred
0·310	72·25	57·80	62·00	62·10	50·10	65·7
0·465	61·70	51·40	59·60	52·70	48·81	55·8
0·620	49·91	40·30	54·40	48·10	45·10	53·4

TABLE 4

VARIATION IN PERCENTAGE OF COPPER WITH TIME OF DEPOSITION IN IRON-COPPER POWDER

*p*H	Current Density (amp/sq cm)	Time (min)	Copper (%)
6	0·0465	10	59·40
		20	55·90
		30	55·00
		40	55·30
8	0·0465	10	55·80
		20	55·06
		30	54·90
		40	54·10

TABLE 5

INFLUENCE OF DILUTION ON PERCENTAGE OF COPPER IN IRON-COPPER POWDER AT pH 8

Current density (amp/sq cm)	Copper (%)		
	Undiluted	Diluted to 2 volumes	Diluted to 3 volumes
0·0310	62·11	47·1	37·6
0·0465	52·70	46·7	36·8
0·0620	48·13	44·3	35·5

Effect of Stirring

At a given CD the increase in pH increases the copper content under static conditions of the electrolyte, while a reverse trend is observed if the electrolyte is agitated (Table 3). The effect of increase in CD is similar in both the cases (stirred and unstirred). In general the copper content at a given CD and pH is more in the stirred bath than in the static one. However, this change is not so marked at pH 8 while a reverse trend has been observed at pH 10. A theoretical interpretation for these changes is difficult since this is a complex phenomenon involving various factors like degree of ionisation, the concentration of primary salts and complex ions and relative ion diffusion velocities.

Effect of Time of Deposition

Studies on the variation in percentage of copper in the deposit with time of electrolysis indicate that the copper percentage tends to decrease while the electrolysis proceeds and tends to attain a balance point after which the change in the composition of the powder is almost negligible (Table 4). The initial variations are perhaps due to changes in the concentration of the electrolyte in the immediate vicinity of the electrode. As electrolysis proceeds, the changes in diffusion rate maintain the near consistency of the composition of the powder.

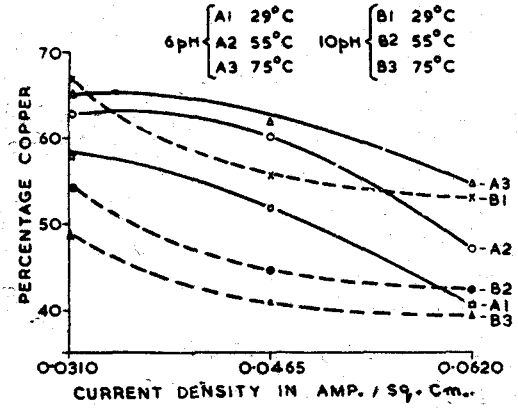

Fig. 2—Effect of temperature on percentage of copper (in iron-copper powder) for different values of pH and current density.

Influence of Bath Concentration

At a given CD and pH, the increase in dilution of the electrolyte decreases the copper content (Table 5). The tendency to reach the consistency with increase in CD in the composition of the powder is faster at higher dilutions. This is due to the compatible rates of deposition and diffusion attained at higher dilutions.

Powder Characteristics

The average particle size of the powder prepared is 2μ. The powder is very pure and the impurities are in trace level. Preliminary metallographic analysis of

TABLE 6

OPTIMUM CONDITIONS FOR ATTAINING TYPICAL COMPOSITIONS AT 30°C

Type Cu/Fe	Bath comp	pH	CD (amp/sq cm)	Agitation
5/95	V	4	0·0465	Unstirred
10/90	IV	8	0·0465	Unstirred
20/80	III	8	0·0620	Unstirred
30/70	II	6	0·0310	Unstirred
40/60	I	6	0·0620	Stirred
50/50	I	6	0·0620	Unstirred
60/40	I	8	0·0310	Unstirred
70/30	I	8	0·0155	Unstirred

BATH-COMPOSITION (g/l)

No.	$CuSO_4 \cdot 5H_2O$	$FeSO_4 \cdot 7H_2O$	$Na_3C_6H_5O_7$	NH_4Cl
I	7·86	19·92	30·0	20·0
II	4·0	40·0	60·0	20·0
III	2·0	80·0	100·0	20·0
IV	1·2	40·0	60·0	20·0
V	0·6	40·0	60·0	20·0

compacted and sintered samples of the powder confirmed that the two elements are distributed uniformly and the dispersion is homogeneous.

CONCLUSION

The present investigations have shown that by a selective choice of the levels of the operating parameters, it is possible to obtain electrolytically the iron-copper powders of the desired composition (Table 6). From the metallographic studies it is confirmed that the distribution of the two metals is uniform and the dispersion is homogeneous, which is rather difficult to attain by conventional methods.

Thus, this method of electrolytic preparation of iron-copper powders is a better substitute to the conventional practice of mixing and tumbling in the manufacture of powder metallurgical components.

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