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The electrodeposition of copper–silver and copper–nickel alloy powders from aqueous ammoniacal solutions

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The electrodeposition of copper–silver and copper–nickel powders from aqueous ammoniacal solutions at a continuously scraped rotating cylinder cathode is described. Ag–Cu powders can be prepared under these conditions, but the individual particles are inhomogeneous and the extent of this inhomogeneity is examined. Surface areas (from BET) and particle size distributions are reported, and the morphology is considered. Cu–Ni powders deposited under these conditions are heavily contaminated with oxide/hydroxides and this is attributed to an increase in near-cathode pH.

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1. Introduction

It is well known that finely divided metal powders can be prepared by electrolysis and indeed this method forms the basis of some industrially-scaled preparative routes. Both scientific and technological aspects of the subject are well covered in the monograph of Calosaru [1]. It is perhaps less well known that alloys, as well as single metals, can be made by the same method. Calosaru does not mention this, and the only general publication on the subject is a short review by Walker [2]. Since then a few further alloys have been made in powder form, for example Ag–Sn [3], and Ag–Cu-Sn [4]. It is perhaps surprising in the light of these publications that a major experimental drawback in the electrolytic manufacture of alloys, as opposed to single metals, has never been pointed out in the literature. This concerns the fact that the alloy particles, as soon as they have been detached from the cathode, constitute a miniature exchange couple which, in many cases, corrodes extremely rapidly in the electrolyte. The problems arising from this phenomenon were discussed and exemplified with data obtained from the electrolytic preparation of Ag–Cu powders from cyanide baths [5]. It was shown that within a minute or so significant changes in composition of the particles had taken place, with the less noble component being substantially depleted from the surface of the aggregates. In theory, corrosion inhibitors can be added to arrest or delay such attack. In practice, however, especially in solutions such as cyanide baths, both Walker [6] and ourselves [5] have failed to find an effective inhibitor.

In this paper attempts to prepare two alloy powders, both of potential technological interest are reported. Copper–nickel is well known as a useful material to prevent marine fouling, and is applied to the exterior of ships and used in other marine applications. Recently [7] it was announced that a means had been found for incorporation of the alloy, in finely divided powder form in paints

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or resins, again for marine applications. Copper–silver alloys in finely divided form are used for brazing processes in the aero-engine industry. Mixed with a flux in paste form, they are applied through a nozzle onto the surface of the metals to be joined.

There appears to be virtually no literature relating to the electrolytic preparation of these materials in powder form. Their deposition as a bright coating has been described, and the literature relating to this was reviewed prior to commencement of the experimental study.

2. Review of literature

2.1. *Electrodeposition of Cu–Ag*

Brenner [8] suggests that no practicable bath has been found for the deposition of bright Cu–Ag alloys and reviews deposition from a cyanide bath where alloys containing from 50–100% Ag were obtained whilst reporting the effect of current density and temperature. He suggests that the difference in standard of em.f.s is so great that the two metals can only be deposited from a complexing bath such a cyanide, though reference is made to work where mossy deposits were obtained from nitrate baths. It is interesting to note that in the former case, data on the electrodeposition conditions is incomplete both in respect to cyanide content and current density. However, the effect of increasing free cyanide is stated by Brenner to favour silver and discourage copper deposition, and it thus would not appear to be a parameter capable of independent variation. The effect [8] of silver on the structure of Cu deposited from a cyanide bath is also described. The deposits consisted of trees with dark cores, in contrast to other reports [8] of powdery deposits. Pushpavanam and Shenoi [9, 10] reviewed the electrodeposition of Ag and its alloys. For the Cu–Ag alloys after commenting on their superior hardness, they mention their colour, which progresses from white to red passing through rose and violet-grey, and they are fine-grained and coherent. They re-iterate Brenner's claim that no practical bath exists, but appear to misquote him on cyanide bath results. Other work using a nitrate bath with thiourea and LiCl and NaI is also described by Brenner [8]. Burkat [11, 12] referring to the early cyanide work in the Russian literature, shows that pyrophosphate baths can be successfully used to give the total compositional range of Cu–Ag alloys. Two papers by Ahuja and Banerjee [13, 14] report deposit composition, X-ray studies of phase structure and the effect of cathode potential on composition for six different bath compositions. Current efficiency is also reported in each case, though no particular conclusion emerges. Their data show a tendency for the composition to become potential-independent at higher potentials, as if both components were diffusion limited. A few other publications exist [15, 16] including one based on sulphates (but restricted to a maximum of 5% Ag) [17], a nitrate bath with methanolamine [18] and a bath based on secondary amines. Succinimide is given as an example [19]. Perhaps because the work described above is relatively old, it falls short of presently demanded standards in that the work is done at constant current and true current–potential data are not included. It is usually found that potentiostatically obtained data elicit the underlying mechanisms more clearly, and this was the aim in the present work.

2.2. *Structure of Cu–Ag electrodeposits*

In all the foregoing, the word 'alloy' has been used in the loosest sense, implying only that more than one single component was present. The actual structure of electrodeposited 'alloys' has scarcely been investigated, and their variability (see below) causes experimental difficulties in this respect. Thus, Burkat [11, 12] reports the microhardness, electric resistance and wear resistance of his Ag–Cu alloys. After six months of storage, the microhardness values of the low-silver alloys had virtually halved. X-ray data showed supersaturated solid solutions at either end of the compositional range, with a mechanical mixture in the middle. However, re-examination after one week showed that the supersaturated state had disappeared, and the authors suggest they had decomposed. That change can occur so rapidly gives rise to implications for the chronology of experimental work both in reported and proposed studies. A very detailed X-ray study of bright plate Ag–Cu deposits from a cyanide bath is reported by Ahuja and Banerjee [13, 14]. Initial deposits are normally non-equilibrium and even annealing appears not to restore these, in every case, to the equilibrium state. It would have been useful, bearing in mind the extreme lability of the deposits shown by Burkat, had Ahuja and Banerjee stated the times involved between the making of their various measurements.

In a non-electrochemical examination of the formation of Cu–Ag alloys, Gruhl and Kramer [20] examined the phase structure of various alloys after different annealing times and temperatures. The generalized theory concerning the formation, or otherwise, of equilibrium phases, has been considered by several authors, including Polukarov *et al.* [21] who (briefly) used Cu–Ag to illustrate their arguments. They mentioned, without details, that a nitrate bath failed to give the supersaturated mixed crystal structure expected on the basis of galvanostatic transient work where Cu was deposited on a pure Ag surface. The role of the point of zero charge potential of the metals is also considered in a later paper [22].

2.3. *Electrodeposition of Cu–Ni alloys*

Brenner [8] gives an excellent summary of the situation up to about 1960, and the same corrosion-resistant properties are emphasized as were discussed by us above. As with copper and silver, the separation of the deposition potentials is held to prohibit co-deposition of the metals from simple solutions. Sulphate baths, pyrophosphates, cyanides and citrates, as well as tartrates ('Rochelle Salts') are discussed, as are oxalate and ammoniacal baths. Some work on thiosulphates is also mentioned. These themes can be seen to have been followed in more recent years: AEI in UK Patent 957 808 (1964) use citrate with saccharin. Galinker *et al.* [23] described a pyrophosphate bath, while one slightly more novel approach is the sulphate bath with L-aspargine additive of Sadana *et al.* [24]. UK Patent 1 422 296 (1976) describes a sulphate–tartrate–borate bath. Citrates or EDTA are mentioned as possible alternatives. The patent, unusually, presents polarization data both for sulphate alone and in the presence of the complexants. Kurachi and Suyama [25] showed polarization data using ammoniacal solutions. Another bath was described by Sadana and Venkatachalam [26]. Raj and Acharyyuku [27] have considered the preparation of Cu–Ni powders from a sulphate–citrate–borate bath. However, it would appear, that in common with so many other small laboratory scale studies, these powders were formed on a stationary electrode, which was then removed from solution. Thus the problems arising from galvanic actions of detached powders were avoided.

In the present work therefore, an attempt has been made to find more suitable electrodeposition baths in which these two powders might be prepared. In line with current thinking, every effort was made to avoid the environmentally undesirable cyanide bath. However, in the case of the silver-containing alloy, the choice was very restricted, and there have been many searches for non-cyanide silver baths. Knowing that a simple nitrate solution is commercially used to manufacture silver powders [28] some preliminary studies were carried out with such a solution. However, it became clear that (as Brenner himself suggested [8]) a complexing bath was called for and that nitrate alone would not serve. The ammoniacal nitrate bath reported in this work is readily managed, can operate at room temperature and, under these conditions, does not present environmental problems. With respect to the Cu–Ni alloys, after reviewing the literature, a similar bath was used, bearing in mind the cost and relatively poor stability of citrates and related organic complexants.

The results of this work are reported here.

3. Experimental details

3.1. *Copper–silver powders*

These alloys were deposited from an ammoniacal nitrate bath. This was made up using $AgNO_3$ and $Cu(NO_3)_2$ (BDH AnalaR grade) in deionized water and adjustment of the bath pH to 9.6 by addition of 0.880 s.g. ammonia solution. The actual concentrations of metal ions are stated in Table 1. All deposition experiments were carried out using the potentiostatically controlled 100 A scraped rotating cylinder which has been described elsewhere [4, 5]. Cathode area was either 40 or 80 cm^2 depending on conditions. Solution analyses were controlled with atomic absorption spectrometry

Table 1. Electrodeposition of silver–copper powders

	A. *Deposition voltage* – 1.2 V, 200 r.p.m. 80 cm² *cathode area*					B. *Deposition voltage* – 1.8 V, 200 r.p.m. 40 cm² *cathode area*									
	1	*2*	*3*	*4*	*5*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
Mean current (A)	45	52	23	67	62	20	25	17	22	22	24	32	26	30	38
Mean Ag concentration (g dm^{-3})	4.1	3.5	2.2	1.2	0.3	3.8	3.6	3.5	3.4	3.25	2.8	2.2	1.5	0.9	0.4
Mean Cu concentration (g dm^{-3})	19.2	19.0	18.7	17.7	16.0	16.0	15.9	15.9	15.8	15.8	15.6	15.2	15.0	14.6	14.2
Powder composition															
Ag (%)	82	86	61	46	14	76	62	82	67	66	74	62	68	61	43
Cu (%)	18	14	39	54	86	24	38	18	33	34	26	38	– 32	39	57

	C. *Deposition voltage* – 1.5 V, 1000 r.p.m. 40 cm² *cathode area*										D. *Deposition voltage* – 1.5 V, 230 r.p.m. 80 cm² *cathode area*					
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*1*	*2*	*3*	*4*	*5*	*6*
Mean current (A)	17	15	13	13	17	15	21	13	22	14	25	30	22	55	27	26
Mean Ag concentration (g dm^{-3})	4.1	3.7	3.4	3.25	2.7	1.9	1.1	0.5	0.2	0.03	1.8	1.3	0.6	0.4	0.3	0.2
Mean Cu concentration (g dm^{-3})	21	21	21	21	21	21	21	21	21	20.5	18	18	17	15	15	13
Powder composition																
Ag (%)	92	78	86	91	92	91	84	84	75	41	65	90	81	53	3	2
Cu (%)	8	22	14	9	8	9	16	16	25	59	35	10	19	47	97	98

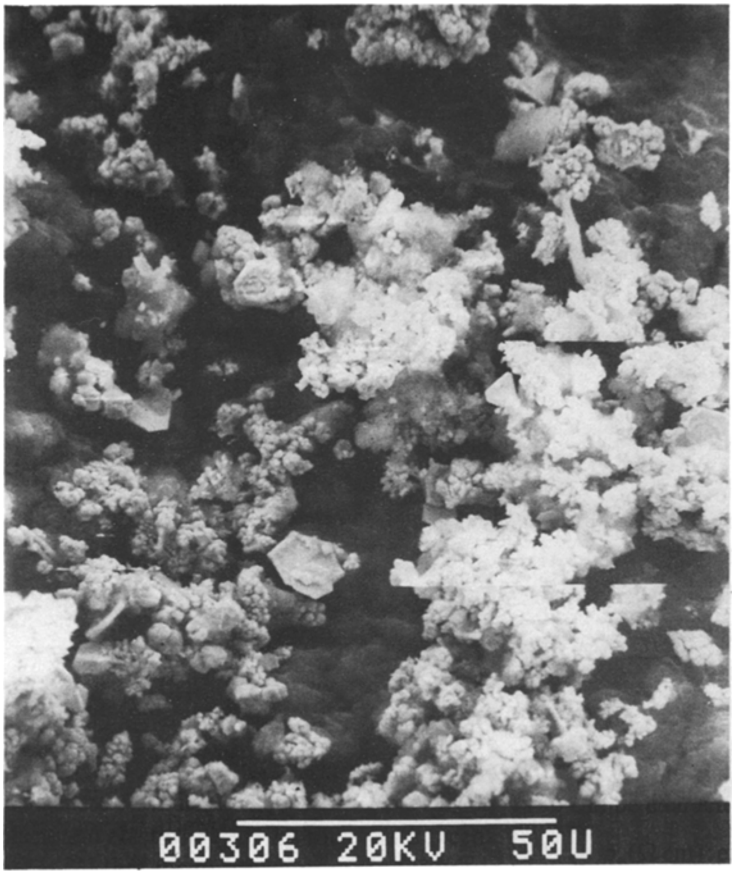

Fig. 1. Ag–Cu powder (60 Ag–40 Cu) produced from ammoniacal solution, and showing both nodular and tabular morphologies.

(AA) and powder composition was determined using a semi-quantitative EDX procedure (Hitachi Link SEM–microprobe analyser). In a series of calibrational experiments, the metal content as determined with the EDX was found to agree within ± 10% with the AA-determined values.

3.2. *Copper–nickel powders*

These were deposited from an electrolyte based on 3 g Cu and 3 g Ni per dm^3, based on the appropriate weights of $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$ respectively (BDH AnalaR grades). As before, final bath pH was adjusted to pH 9.5 by addition of 0.880 s.g. ammonia solution. It was found that without such additions, the metals were not fully complexed.

4. Results

4.1. *Silver–copper alloys*

The composition of powders formed under various conditions of potential, rotation speed and metal ion concentration (Cu^{2+}, Ag^{+}) is shown in Table 1 (all potentials vs SCE).

4.1.1. Morphological observations. It is evident (Fig. 1) that the particles formed from the ammoniacal bath are much more nodular with less dendritic character, than the Ag–Cu powders formed by deposition from a cyanide bath reported recently [5]. This can be explained by the observation that, after deposition, the powders from the ammoniacal bath detach themselves readily from the cathode. The dendritic material formed in cyanide baths coheres by an inter-locking action and is readily removed from solution together with the cathode, when the latter is withdrawn. The particle size distribution of some typical Ag–Cu powders, obtained using a Malvern laser-light scattering particle sizer, is shown in Fig. 2. It should be borne in mind that though the light-scattering method is capable of measuring smaller-sized particles than the Coulter counter technique,

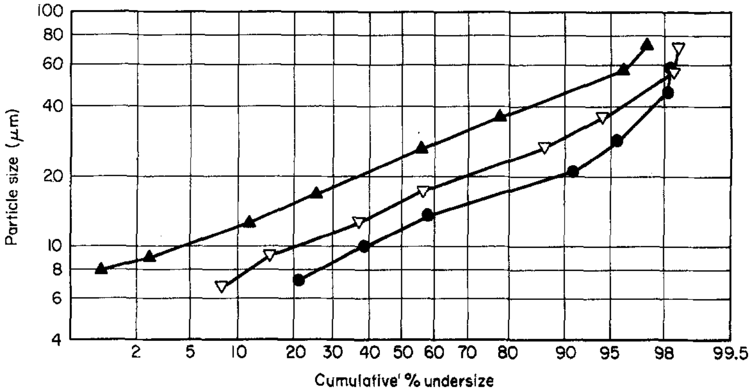

Fig. 2. Particle size distribution of the Ag–Cu powder obtained with a 'Malvern' laser light-scattering particle size analyser. ▲ – 43% Ag–Cu; ▽ – 33% Ag–Cu; ● – 67% Ag–Cu.

for asymmetrical particles (where the meaning of particle size in any case requires qualification) the data given represents the area swept out when a particle spins through the solution. This comment is of special importance in the light of the tabular nature (see Fig. 1) of some of the particles observed under the SEM. Typical surface area measurements obtained with a 'Monosorb' single point BET apparatus are shown in Table 2.

It has been previously noted [5] that the composition of electrodeposited alloy powders shows great variability, even within single dendrites which must have been formed as single phases. Such results are attributable either to variation in deposition conditions, a surface effect due to post-deposition galvanic exchange or variation in the take-off angle for the X-rays from the irregular surfaces. In order to eliminate the second and third possibilities a powder was prepared from an ammoniacal nitrate silver–copper solution and the deposit on a flat electrode was washed immediately after formation and was mounted in acrylic resin and sectioned. Fig. 3 shows the locations of a series of spot analyses and the accompanying Table 3 shows the compositional results obtained. It is noted that there is still considerable variation of composition, indicating this to be a real characteristic of the as-formed alloy.

Table 2. Typical surface areas of some Ag–Cu powders

Composition (wt %)		*Deposition potential (V)*	*Surface area ($m^2 g^{-1}$)*
Ag	*Cu*		
43	57*	−1.8	3.49
67	33†	−1.8	3.33
67	33	−1.5	4.35
88	12	−1.5	0.49
98	2	−1.1	0.39

Notes: Measured with 'Monosorb' single-point BET Apparatus; rotation rate was 200 rpm in all cases.
*Sample B10 in Table 1; †Sample B4 in Table 1.

4.2. *Copper–nickel alloys*

Very high overpotentials (− 3 V SCE) were required before significant amounts of metal deposited. At these potentials, where the cd was *c.* 1.2 A cm^{-2}, metal deposits were 'treed' and no fine powder was obtained. In subsequent experiments *c.* 1 g dm^{-3} gelatine was added in an attempt to suppress 'tree' formation. While this was apparently successful in that powder formation was observed, a number of side effects were noted, including a high degree of frothing.

The powders as formed (see Fig. 4) were very dark, somewhat lustrous and did not have a metallic appearance. This was confirmed when they were dried, weighed and dissolved in a known volume of dilute HCl. Subsequent electrogravimetric analysis showed that only some 50% by weight of the material was metal, the rest being presumably hydrated oxide. In the light of this, further work on this alloy was abandoned.

5. Discussion

It is believed that the observations reported here are illustrative of the limitations which presently apply to the manufacture of electrodeposited powders of any alloy. The inhomogeneity reported previously [5] has been demonstrated in greater detail. In many applications, for example as a

Fig. 3. Ag–Cu alloy powder mounted in acrylic resin and sectioned. The numerals indicate locations of EDX analyses and should be read in conjunction with Table 3.

brazing alloy, such inhomogeneity is unimportant. For others, such as catalysis, it may even be desirable. However, it is clear that unless an efficient means of continuously removing the electrolytic particles can be achieved, these particles, during their residence time on the cathode, will be subjected to continually varying polarization, current and solution concentration gradients in the surrounding electrolyte.

In respect of the use of an ammoniacal bath, it is clear that the manufacture of Cu–Ni powders is not straightforward. There was a distinct suggestion that the addition of gelatin, while not altering the total current value, tended to suppress metal deposition, simultaneously enhancing hydrogen evolution. The formation of oxides during electrodeposition is a well-known phenomenon, though it has not been reported for this particular system. It is due to the increase of pH in the near cathode region, caused by co-evolution of hydrogen, a topic (with examples of oxide formation during electrodeposition) which has recently been studied and reviewed [29]. Any increase in i_{H_2} caused by gelatin addition would

Table 3. Composition of silver–copper alloy in Fig. 3
Readings from whole dendrites chosen at random.

				Spots																		
	A	*B*	*C*	*1*	*1*	*2*	*2*	*3*	*3*	*4*	*4*	*4*	*4*	*4A*	*5*	*5*	*6*	*6A*	*6B*	*7*	*7A*	*7B*
% Ag	27	27	29	41	39	23	23	29	31	34	27	24	21	28	30	29	41	36	19	22	39	35
% Cu	73	73	71	59	61	77	77	71	69	66	73	76	79	72	70	71	59	64	81	78	61	65

Note: Where spots are shown repeated the spot was moved slightly from its previous position but not enough for a separate location to be indicated on the figure.

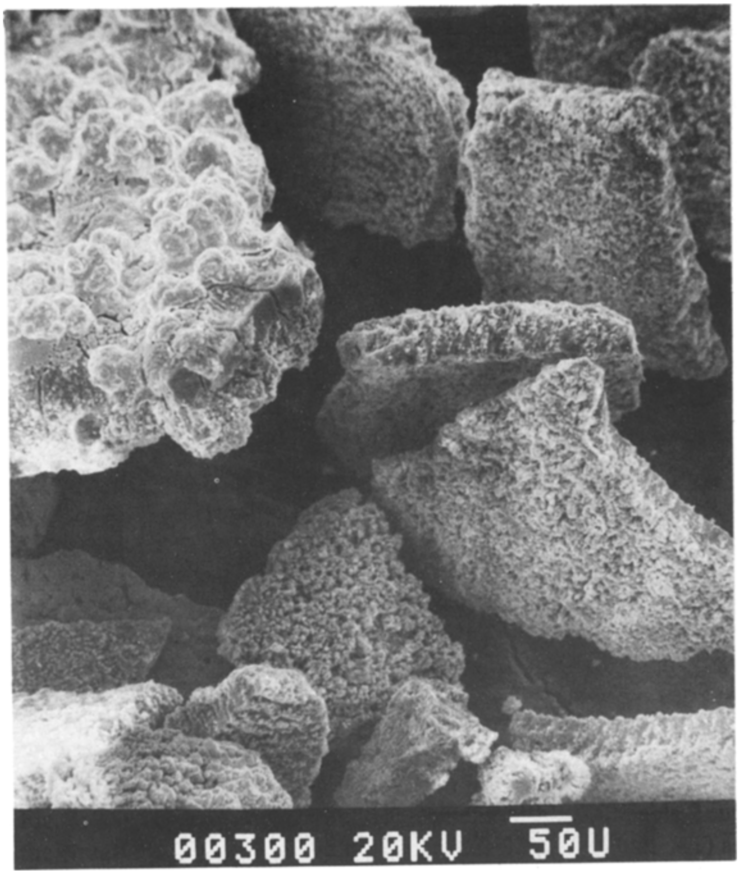

Fig. 4. Cathodically formed powder from Ni–Cu ammoniacal solutions showing its nonmetallic character.

most certainly have led to further increase in near cathode pH and greater ease of oxide formation. Further work on the preparation, by electrodeposition, of Cu–Ni alloy powders will have to be based on other electrolytes.

For the preparation of Ag–Cu powders we believe that further work using this electrolyte is well justified, once the mechanical problems of continuous powder removal have been overcome. The ammoniacal bath is finding increasing application and its use in the electrodeposition of Co [30], Mn [31], Cu [32, 33] and Ni [34, 35] as well as Ag [36] has been described in recent years. In this bath, pH and $[NH_4^+]$ may be independently

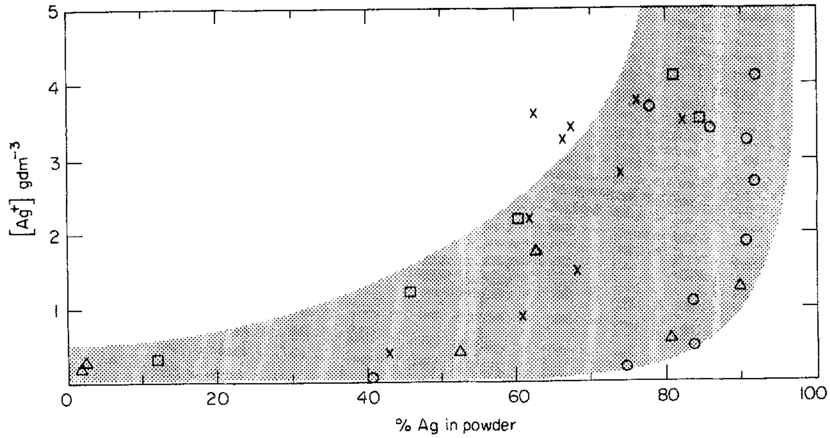

Fig. 5. Relationship between Ag concentration in solution and percentage Ag content of electrodeposited powders. ○ – — 1.5 V, 1000 rpm; × – — 1.8 V, 200 rpm; △ – — 1.5 V, 230 rpm; □ – — 1.2 V, 200 rpm.

varied using alkalis other than ammonia to alter the pH. This aspect of the problem was not examined in the present work, but clearly an ability to vary the degree of complexation while maintaining the desired pH presents another means of controlling the relative amounts of the two metals deposited from solution. To some extent, as seen in Fig. 5, a relationship does exist between the concentration of silver in solution, and the percentage content of the same metal in the electrodeposited powders. A high degree of scatter was observed, much of which can be associated with the anomalously high currents reported in Table 1. The reason for these high currents is as yet unexplained. For this reason, in Fig. 5, rather than attempting to draw curves through sets of data for individual runs, representing the various conditions of potential, rotation rate, etc., we have simply enclosed all data points within an envelope to indicate that a broad trend does indeed exist, between silver ion concentration in solution and the percentage of the same metal in the resulting powder that is deposited. Beyond this overall finding, the working of other effects, such as potential or rotation rate, can in at least some cases be discerned, and the use of different symbols (see legend to Fig. 5) allows the reader to pursue this. This emphasizes the undoubted importance of mass-transport in determining the composition of deposited powder. These observations tie in with what little is known about the mechanism of deposition from ammoniacal baths [32, 33]. We were aware, from various references in the literature, that the nitrate ion, employed for the Ag–Cu deposition work, can be cathodically reduced [37–40]. However, the reduction is a slow one and there were no indications that this reaction seriously affected the overall electrodeposition of the metals or that it led, over several weeks in each case, to the degradation of the bath.

In conclusion, it is felt that the most serious problems which presently prevent the large-scale electrodeposition of these and other metal alloy powders are now recognized, and work in progress is aimed at overcoming such problems.

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