JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 309–314

The continuous deposition of metal powders in a pump cell

R. E. W. JANSSON, G. A. ASHWORTH*

Chemistry Department, Southampton University, UK

Received 13 July 1976

Metal powders have been obtained continuously from dilute feedstocks (about 10^{-3} mol l^{-1} metal) in an unoptimized electrochemical pump cell at an electrolysis cost of about 1·8 kWh kg^{-1}. Particle sizes ranged from about 10 to 250 μm depending on metal and conditions. Good quality copper, tin, copper/tin ('bronze'), and zinc powders have been obtained.

1. Introduction

Conventionally, metal powders have been obtained electrolytically by deposition at high current densities in a plate cell. The dendritic growths have either broken off, or have been scraped off periodically, and have subsequently been recovered from the cell and segregated in size. The process is labour-intensive and therefore costly. Recently a cell has been introduced [1] with a cylindrical cathode about 1 m in diameter which rotates slowly, the dendritic deposit being scraped off as in a drum filter. High current densities are required to promote dendritic growth, leading to quite a large *iR* drop despite the high cation concentration. Electrolytic power consumption is of the order of 3 kWh kg^{-1} of deposited metal and the cost of segregation substantially as before.

The electrochemical pump cell [2] is a device which produces very high mass transfer rates while maintaining a small interelectrode gap (hence a small *iR* drop) and therefore, in principle, offers a method of sustaining high current densities with metal concentrations typical of those found in many industrial effluents.

Preliminary experiments [3] have shown that it is feasible to produce copper powder of good purity continuously from dilute feedstocks. In the present paper this work is reported more fully, together with the extension of the study to other metal systems.

2. Electrochemical pump cell

Fig. 1 shows a schematic drawing of one version of the pump cell [2]. An annular disc electrode is separated by a small (adjustable) gap from another and can be rotated, if necessary at high speed. Electrolyte flows radially outwards through the annular gap at a rate dependent on rotational speed; the cell is thus also its own pump. Strong swirl is induced by the rotation and a complex velocity/pressure field is generated [4], which can be exploited to good advantage. Particles produced in the cell are centrifuged outwards and can be caught in a suitably-constructed spillway.

In the work reported here the electrodes were discs 84 mm o.d. × 48 mm i.d. (the length of electrode in the radial direction then being only 18 mm and the transit time in the region of 3–5 ms), however in other applications [4] electrodes of 230 mm diameter have also been used successfully.

The experimental aim was to produce as high a rate of mass transfer, hence current density, as possible while still obtaining dendritic or nodular deposits. Therefore the stator rather than the rotor was used as the cathode, since, under otherwise similar conditions, the mass transfer rate to the rotor was so great that the deposits were always coherent [4]. An additional benefit of a cathodic stator is that the growing dendrites experience the high tangential velocity gradient in

---

* Present address: Chloride Alcad Ltd., Ponthenry, Dyfed.

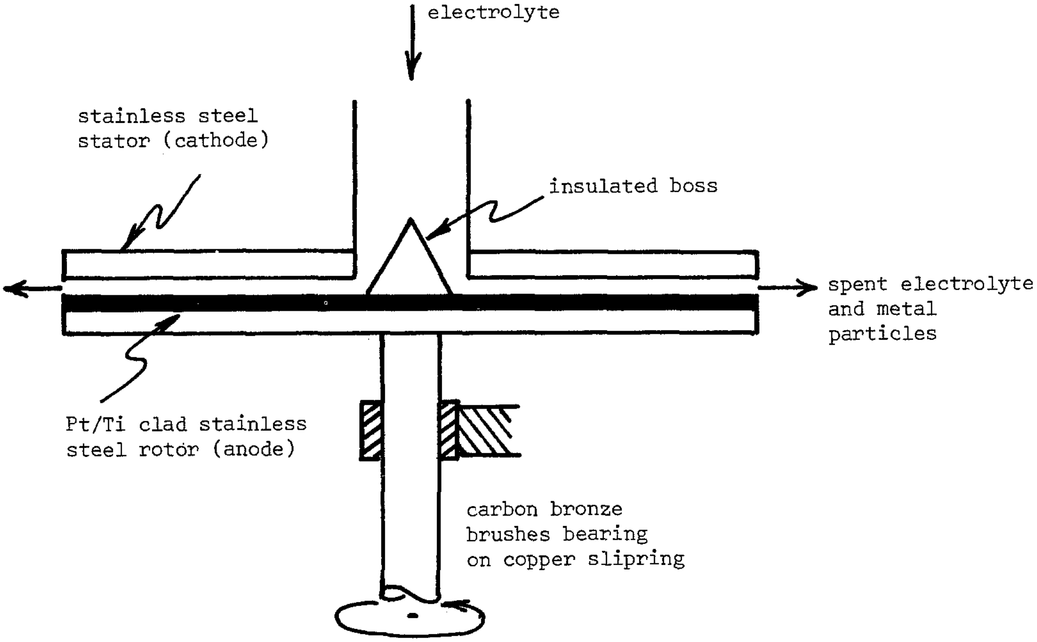

Fig. 1. Schematic diagram of cell (not to scale).

the electrolyte near the rotor, and hence shear off before bridging the gap. The possibility of growing a billet by withdrawing a cathodic rotor was not explored, although clearly feasible.

Other studies [3, 4] with the ferri/ferrocyanide couple and a smooth electrode suggested that, in this small cell, 4000 rev min^{-1} was a rotational speed giving a reasonable compromise between mass transfer rate and power consumption. 4000 rev min^{-1} was then chosen as the standard speed for the work reported here, although, in view of the higher mass transfer coefficients observed during metal deposition (probably due to roughness), it can in no way be regarded as optimal. In a larger cell it would, in any case be lower, decreasing by the reciprocal of the square of the scale factor to preserve similarity.

Initial experiments with dilute solutions (about 10^{-3} mol l^{-1}) were carried out under active potentiostatic control, but for currents greater than 20 A a Westinghouse 125A d.c. power supply was used, the voltage at first being controlled by hand at 5 min intervals with respect to a saturated calomel electrode. After the first half-hour the voltage was usually perfectly stable. A recirculating electrolyte system was used with an inventory of 30 l of solution.

3. Copper deposition

Fig. 2 shows a polarization curve for copper depositing on smooth stainless steel. It is seen that current density increased with rotational speed. At − 400 mV (SCE) and 4000 rev min^{-1} the average mass transfer coefficient, k_M, is about 0·021 cm s^{-1}, equivalent to a Nernst diffusion layer thickness of about 0·0005 cm, or twice the surface roughness of the original stainless steel electrode. The current progressively increased over the first 28–30 min as more copper was deposited, probably partly due to a change in surface roughness, and then showed a fairly stable mean value. The instantaneous value fluctuated periodically as dendrites grew and broke off. Whatever the initial value of the gap, a decreasing flow-rate at otherwise constant conditions showed that the spongy/dendritic layer on the cathode grew until the gap was reduced to a value where the hydrodynamic shear was sufficient to break off the dendrites from the weak substrate; an equilibrium was then established. Occasionally a current pulse was observed as a bunch of dendrites shorted the cell, but, provided the initial gap was much larger than the equilibrium gap, this did not happen frequently (Fig. 3). Ultimately k_M reached a value of about 0·4 cm s^{-1}.

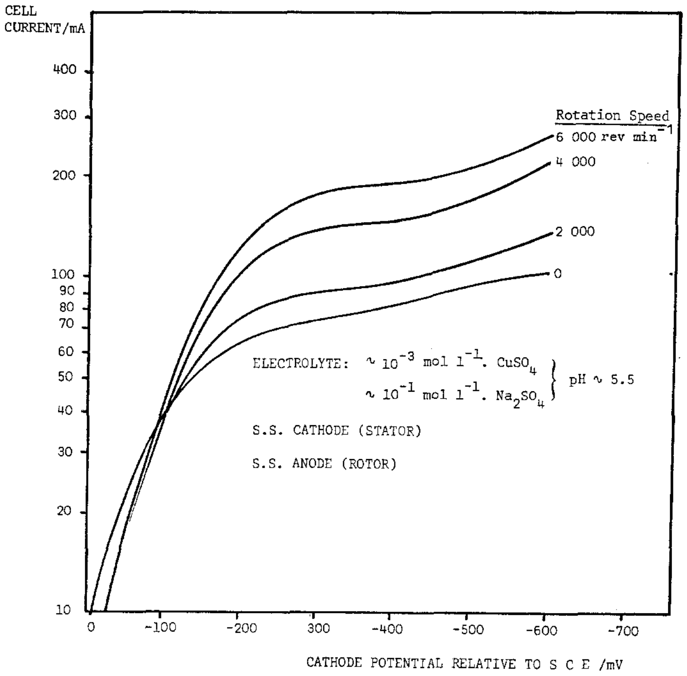

Fig. 2. Polarization curves for deposition of copper on smooth stainless steel.

The effects of pH were studied in the range 2–7. Both pH and potential were found to be critically important related parameters; below about pH 2 the deposit was coherent, and at about 5·5 the product was extremely fine (about 10 μm) and partially oxidized. Naturally the best power efficiency would be expected at a potential near that of the limiting current, however this potential gave rise to hard, flaky deposits at all but the highest pH and caused both serious arc-over and corrosion of the stainless steel anode, which was replaced with one of platinized titanium. Similar deposits were obtained at the lowest pH's for a range of potentials. Powder was most easily obtained at potentials of 500–700 mV (SCE) when the current was slightly higher than the diffusion limited value and powder formation was probably assisted by hydrogen evolution. Analysis

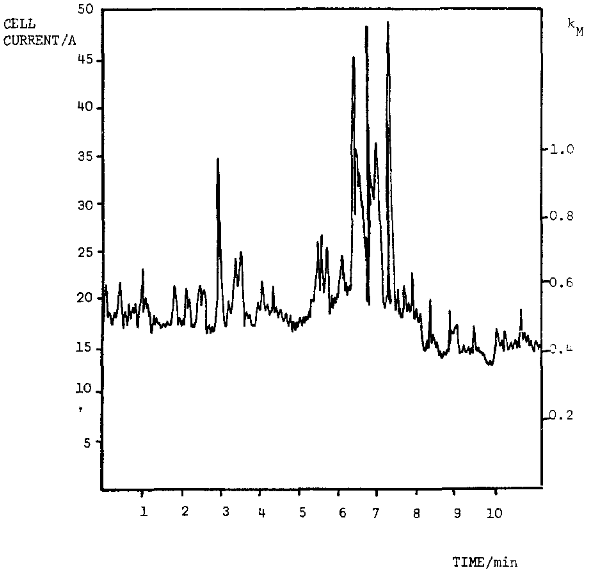

Fig. 3. Cell current versus time. Nominal gap setting 0·375 mm; equilibrium gap ~ 0·05 mm; cell voltage ~ 3·5 V; electrolyte 5 × 10^{-3} mol l^{-1} $CuSO_4$, 10^{-1} mol l^{-1} Na_2SO_4, pH 3·5–4.

showed a copper content of up to 97% at pH 3, the balance being oxygen, falling to 85% at pH 5·5.

During the early stages of deposition the current efficiency was nearly 100%; however after about 90 min this had usually fallen to 30–45%, depending on conditions, particularly the frequency of arc-over. A Pt/Ti rotor/anode was tried with a slightly protruberent polycarbonate 'fence' along a diameter to act as a mechanical scraper, but this so increased the mass transfer rate to the stator/cathode that dendritic deposits could not be obtained under any conditions. (This would be the ideal case for growing a billet on the stator.) Taking the worst case of a current efficiency of 30%, the power consumption was 1·8 kW h kg^{-1} copper, which compares well with more conventional systems. To this, however, must be added the rotational power, which was high in our unoptimized, small-electrode cell with its overlarge motor [3]. A more realistic estimate [5] is 3 kW h kg^{-1} (overall) which is comparable with the electrolysis plus pumping power of more conventional systems. There is, therefore, no particular advantage in power, but the product is obtained continuously from dilute feedstocks and in a narrower size range (typically 50–150 μm). The morphology of the deposit will be discussed later.

4. Zinc deposition

Zinc could be deposited similarly to copper but only at low values of pH due to the solubility of the product. Again an 'initiation period' of about 30 min was observed, but the equilibrium gap was larger, the dendrites softer and more easily removed, leading to larger particle sizes (~ 0·1 mm). Deposits were grey/black in appearance when first formed, but the surface oxidized rapidly when dried, leading to difficulties in microscopic examination. Current efficiencies were generally high, 60–80%, reflecting the larger equilibrium gap and less frequent arc-over.

5. Copper/tin alloy deposition

Deposits were obtained from copper/tin solutions ranging from 10^{-2} to 10^{-3} mol l^{-1} in each metal. The addition of tin to the copper had a beneficial effect, increasing the equilibrium gap and current efficiency (50–70%). The equilibrium gap was also potential-dependent; this is associated with hydrogen being evolved on the tin at a lower potential than on copper. The pH could not be increased beyond 3 due to the formation of white tin oxide.

Normally powder settled in both the solution spillway and in the lower reservoir of the recirculation system, providing a crude method of segregation, which could well be refined in practice.

6. Morphology of deposits

6.1. *Copper*

Under most conditions the particles were porous spheres or plate-like structures in the size range 10 to 150 μm. Figs. 4 and 5 show particles of about 100 μm diameter produced at pH 4·5 and 2 respectively. The former have a soft, porous structure, while the latter form an agglomeration of hard crystallites with occasional powdery 'cauliflower' outgrowths. The difference in nature of these particles explains the increased shorting of the cell and abrasion of the anode when processing solutions of low pH. At the maximum achievable pH, 5·6, the powder becomes very fine due to the formation of star-like dendrites which are easily reduced to small fragments a few μm across. At this pH most of the powder consists of small, easily oxidized crystallites.

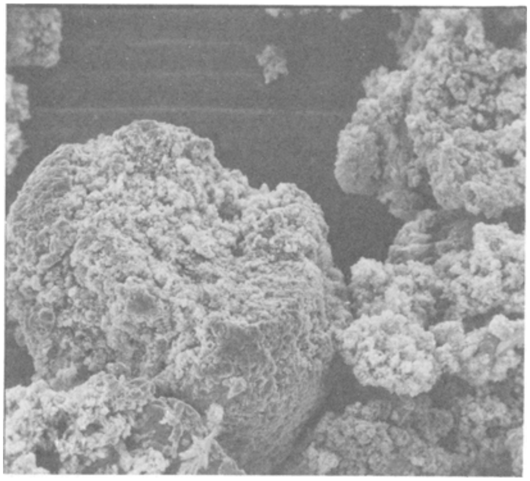

Fig. 4. Copper particles of about 100 μm diameter; pH 4·5.

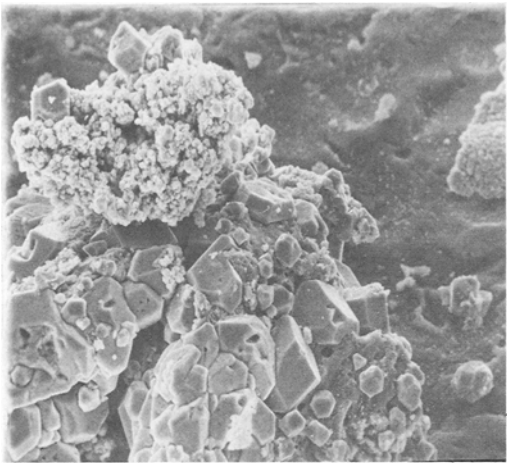

Fig. 5. Copper particles, pH 2.

6.2. *Copper/tin alloys*

The copper/tin mixtures took forms ranging from fine black suspensions to reddish dense deposits depending on the ratio of the metals in the electrolyte. Microprobe analysis, however, did establish that, in the main, they were co-deposits of copper and tin and not simply crystal mixtures. The finer, dark deposits oxidized on drying to give white powder, presumably tin oxide, which caused great problems with steroscan microscopy. It also appeared that the morphology changed on oxidation from compact particles to a light fluffy mass.

Fig. 6. Copper/tin co-deposit.

Fig. 7. Co-deposit, high in copper.

Most particles had a leaf-like structure (Fig. 6) and were approximately 60 x 20 μm, although, when the copper concentration in the electrolyte was high, particles apparently containing only copper were also present (Fig. 7). Composition of the particles was dependent upon composition of the electrolyte, although not in a simple way, as Table 1 shows. The single experiment at a lower rotational speed (1600 rev min^{-1}) showed markedly different (Cu/Sn) ratios. Electrolytes containing more than 65% copper produced heterogeneous samples containing co-deposit and single crystals of copper. Particles from the lower reservoir in general were smaller than those from the spillway; composition is therefore also linked to particle size. By juggling the variables of the pump cell, tailoring of the product is clearly possible, but no systematic study has been made at this stage.

7. General remarks and conclusions

Metal powders of the order 100 μm (and smaller) can be produced continuously in the pump cell and roughly segregated by centrifugation. Copper, zinc, iron, tin and copper/tin alloy powders have all been produced. The size and morphology of the particles depend on metal, potential, pH and base electrolyte concentration. They probably also depend on rotation rate and electrode size,

Table 1. Composition of electrolyte and composition of co-deposit

Sample	*Standing concentration* (μg mol^{-1}) (%)		*Total metal concentration* (mol l^{-1} × 10^3)	*Composition of powder sample (%)*					
				Spillway			*Lower Reservoir*		
	Cu	*Sn*		*Cu*	*Sn*	*Cu/Sn*	*Cu*	*Sn*	*Cu/Sn*
AD4	334(32)	546(67)	9·8	63·9	29·4	2·2			
AD11	50(34)	97(65)	1·6	54·5	30·0	1·8			
AD3‡	309(38)	499(62)	9·0	43·2	35·1	1·2	12·8	41·4	6·3
AD51	314(38)	506(62)	9·2	64·2	30·6	2·1	65·1	25·7	2·5
AD6	449(59)	304(40)	9·6	65·8	20·5	3·2	68·9	25·9	2·7
AD7*	622(66)	326(34)	12·5	72·9	19·5	3·7	67·9	23·0	3·0†
AD8†	627(68)	294(32)	12·3	69·4	22·2	3·1			

* Heterogeneous sample; discrete copper particles formed.
† Small copper crystals apparent in mainly homogeneous sample.
‡ Rotation speed 1600 rev min^{-1}.

although these were not studied systematically. Current efficiencies vary in the range 30% + for copper to 80% + for zinc at 4000 rev min^{-1}, with a cell voltage of typically 2·7–3·0 V. Good quality single phase particles or co-deposits can be produced from electrolytes as dilute as 10^{-3} mol l^{-1} in metal at an electrolysis cost of about 1·8 kW h kg^{-1}. Power efficiency increases as metal concentration increases; the limit of our experiments was set by the capacity of the d.c. power supply (current densities of up to 8·7 kA m^{-2} were recorded in this work). Depending on the flow-rate, about 10% of the metal was removed per pass during the transit time (a few ms) of the small (18 mm length) electrodes. This could no doubt be increased with larger electrodes. It has been shown elsewhere [5] that a pump cell can be arranged to operate under depletion control, so that two or three cells in series, possibly with recirculation loops, would form an efficient effluent scrubber, the product being obtained continually. All the cells could run on a common shaft [2] requiring only one motor.

References

[1] D. L. Adamson, W. M. Tuddenham, *J. Metals.* **22** (1970) 32A.
[2] M. Fleischmann, R. E. W. Jansson, G. A. Ashworth and P. J. Ayre, Provisional Patent Application 18305 (1974).
[3] G. A. Ashworth, P. J. Ayre and R. E. W. Jansson, *Chem Ind.* (1975) 385.
[4] G. A. Ashworth, Ph.D. Thesis, Southampton University (to be presented).
[5] R. E. W. Jansson and G. A. Ashworth, *Electrochim. Acta.* (in press.)