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Structural effects during the electrodeposition of silver–antimony alloys from ferrocyanide–thiocyanate electrolytes

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Self-organization phenomena are observed during electrodeposition of silver–antimony alloys. On increasing the current density, black regions (assumed to be an antimony-richer phase) appear on the electrode surface. Under certain conditions these black regions are shaped as spirals with different topological charges. The width of the black and white regions depends on the current density and the antimony content in the electrolyte. Quantitative characterization of the phase composition in the black regions is a problem which still remains to be solved.

1. Introduction

Investigations of the structure and phase composition of silver–antimony alloys plated from ferrocyanide–thiocyanate electrolytes [1] have shown that the incorporation of antimony into the silver crystal lattice (formation of solid solution) exerts a depolarizing effect and leads to a significant expansion of the lattice and increased microhardness of the deposit, thus offering the possibility of obtaining semi-bright coatings in the absence of organic additives. It has been shown that at high antimony concentrations in the electrolyte it is possible to deposit not only the α-phase but also the other phases of the silver–antimony system.

This paper presents several structural and spatial time effects observed during the deposition of the alloy in the region of high antimony content, i.e. deposits which are of no interest for practical applications due to the probable deterioration of the electrical parameters of the coatings.

2. Experimental details

The experimental techniques and bath composition are described in [1]. The antimony concentration in the electrolyte was 5 and $10\,\mathrm{g\,l^{-1}}$. The deposits were plated under galvanostatic conditions, the cathode potential being measured against a platinum wire spiral reference electrode, silver-plated from the same basic electrolyte in the absence of antimony.

3. Results and discussion

As previous studies [1] have shown, during the deposition of alloys from electrolytes containing $5\,\mathrm{g\,l^{-1}}$ antimony the following phenomena are observed when the cathodic current density is increased. Within the co-deposition range of antimony, a depolarization of the cathodic process occurs, the parameter of the silver crystal lattice increases and at an antimony content in the alloy of about 7 wt % and a current density of $1\,\mathrm{A\,dm^{-2}}$ the curve reaches a plateau. The deposits are light coloured, semibright and a substantial increase of microhardness is observed up to a level of 2–3% antimony in the alloy. Further increase in antimony content exerts no effect. The X-ray investigations show no other phases appearing up to a current density of $1.25\,\mathrm{A\,dm^{-2}}$.

Within the current density range 1.0–$1.25\,\mathrm{A\,dm^{-2}}$ and potentials 580–620 mV versus the silver reference electrode the initiation and propagation of dark bands with irregular shapes is observed on the surface of the electrode (Fig. 1). This is directed from the bottom to the

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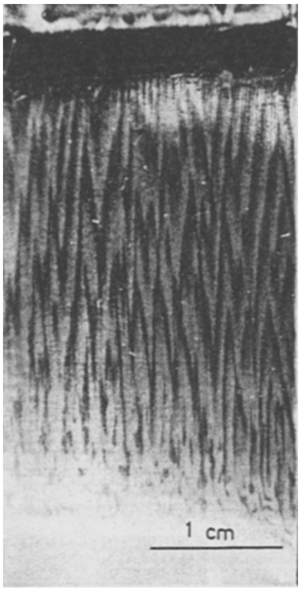

Fig. 1. Electrodeposit showing antimony-rich phase plated at 1.2 A dm^{-2} with 5 g l^{-1} antimony in the electrolyte.

top, probably due to the natural convection of the electrolyte in the vicinity of the electrode. Within this layer the discharge of the ions of both metals reduces the density of the electrolyte and the buoyant force causes an upward flow. A reverse phenomenon is observed in the vicinity of the anode. These convective flows resulting from the changes in the density of the electrolyte in the vicinity of the anode and cathode are readily visible with the naked eye. It must be mentioned that these effects are observed within a region where silver is deposited at the limiting current density, hence any increase in the current would only enhance the content of antimony in the alloy.

As the current density reaches 1.5 A dm^{-2} the entire plate becomes grey and matt and the deposit is rough. At higher current densities the entire deposit is black, spongy and shedding.

When the alloy is deposited within the range 1.0–1.5 A dm^{-2} and 7–12 wt % antimony the change in the plating pattern may be observed visually. Since within this range the silver crystal lattice parameter is no longer changed and the amount of antimony in the alloy surpasses the saturation limits of the silver crystal lattices, the formation of a new phase could be presumed. According to the diffraction patterns, peaks are registered which could be attributed to the hexagonal phase at current densities higher than 1.25 A dm^{-2}, i.e. more than 9–10 wt % antimony, while the bands appear and the plateau of the lattice parameter versus percentage of antimony curve is reached at 1 A dm^{-2}, i.e. 7 wt % antimony. Therefore we can claim that the new phase is formed at antimony contents lower than those given by the phase diagram of the alloy, i.e. 9.6 at %, but the quantities of this phase are probably inadequate to produce a detectable reflection on the X-ray patterns. Another uncertainty is caused by the fact that the antimony content in the deposit is determined by routine volumetric analysis and reflects the value of the average content in the entire mass, which may be quite different from the local amounts. Finally, the deposition pattern is not static – the dark zones shift on the surface of the plate, and presumably as the coating thickness increases it will comprise alternating layers with lower or higher antimony content.

Other structural effects are visible within the current density range 1.25–1.4 A dm^{-2}, where the observed bands are dense and appear on the lower part of the sample. Microscopic studies also reveal other structural effects. Within this range the macrobands are transformed into growth microfronts. Regions with irregular spots are observed on the plate, which are transformed into regular fronts with a fairly stable period (Fig. 2), as well as more complex patterns, i.e. straight, rounded or spiral (Fig. 3). The spiral waves are either left-handed or right-

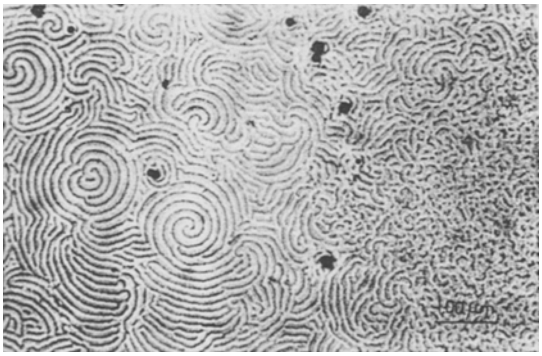

Fig. 2. Transition from dark spot regions of antimony-rich phase to regular fronts and spirals, at 1.3 A dm^{-2} with 5 g l^{-1} antimony in the electrolyte.

Fig. 3. Spiral waves with different topological charge with connected and disconnected arms, plated at 1.5 A dm^{-2} with 6 g l^{-1} antimony in the electrolyte.

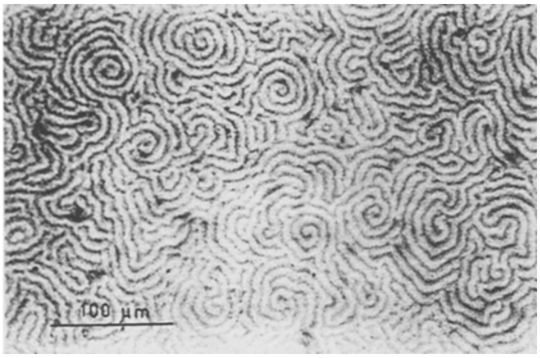

Fig. 5. Surface morphology of a deposit plated at 1.4 A dm^{-2} with 5 g l^{-1} antimony in the electrolyte.

handed and can have different topological charges. We observed spirals with up to five or more arms (Fig. 4), but in contrast to other authors [2] who investigated a chemical system obtaining spirals with topological charges up to four, we were unable to observe these waves during their initiation, development and propagation. They illustrate the momentary condition on the surface of the electrode when the current is switched off. When the electrolyte is agitated or the electrode removed, the picture disappears. The increase in current density leads to an enhancement of the chaotic character of the wave fronts and a transition to black deposits (Figs 5, 6). In this case microdendrites are formed. The cross-cut of a similar deposit is shown in Fig. 7, where it can be noted that the layer has grown in such a manner that a columnar structure is formed.

When the antimony concentration in the electrolyte is 10 g l^{-1}, within the current density range 1.75–2.1 A dm^{-2} (19 wt % antimony in the alloy), similar effects are observed but the wave fronts are chaotic (Fig. 8). These fronts resemble wide black bands, separated by white lines. If we consider the fact that within this region not only the ζ- and ε-phases were observed, but also the pure antimony phase, it is very difficult to evaluate, even qualitatively, the phase composition of the dark bands. Attempts at microprobe analysis proved fruitless, at least for the present, since the antimony content in both regions proved identical. This result in turn suggests that the waves shift rather fast, so that the thickness of the layer deposited during the time required for the passage of two waves through the same point is less than the depth of penetration of the electron beam, i.e. the thickness of the excited bulk of the deposit. Thus a reliable measurement of the antimony content in the black and white regions is a problem which still remains to be solved.

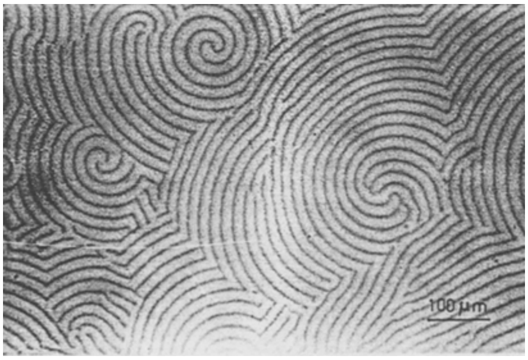

Fig. 4. Spiral waves with enhanced topological charge, plated at 1.3 A dm^{-2} with 5 g l^{-1} antimony in the electrolyte.

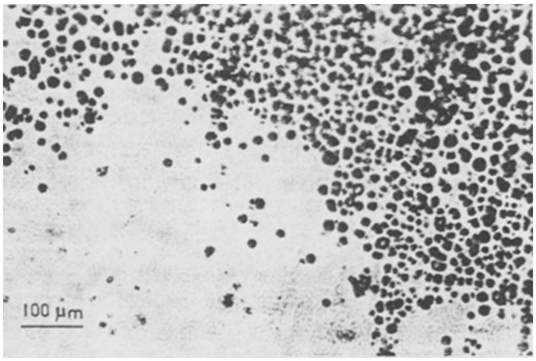

Fig. 6. Transition to a black deposit plated at a current density of 1.5 A dm^{-2}, from an electrolyte containing 5 g l^{-1} antimony.

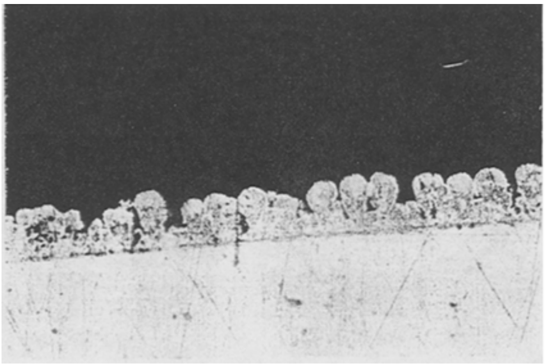

Fig. 7. Cross-cut of a black deposit plated at a current density of 1.7 A dm^{-2}, from an electrolyte containing 5 g l^{-1} antimony. The figure represents a region of area 275 × 425 μm.

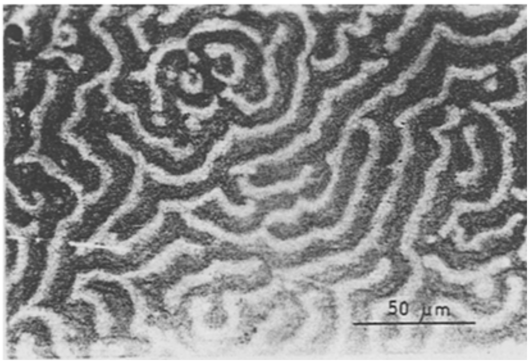

Fig. 8. Surface morphology of a deposit plated at a current density of 2 A dm^{-2} with 10 g l^{-1} antimony in the electrolyte.

It must be noted that these phenomena are observed in both cases within the same potential range, i.e. 600–700 mV versus silver reference electrode, and this region is adjacent to the limiting current of the entire system. The co-deposition of both metals at the limiting current density is probably one of the factors leading to the observed phenomena similar to those observed by Raub and Schall [3] when plating silver–indium alloys at limiting current density. When the alloy is plated with the limiting current region a rapid increase of potential is observed in some cases, with the formation of a dark deposit followed by a decrease and formation of a light-coloured coating. In separate cases these phenomena are repeated many times. It is possible that these effects are due not only to the co-deposition of the two metals at limiting current density but also to a change in the deposition mechanism at each change of the phase composition of the substrate.

4. Conclusions

1. It is established that during the plating of silver–antimony alloys from ferrocyanide–thiocyanate electrolytes at high antimony content in the deposit, a new antimony-enriched phase is co-deposited with the α-phase, leading to the formation of black and white regions on the electrode surface.

2. When the deviation from equilibrium conditions becomes more substantial (increased cathodic current density leading to higher values of the cathode potential) an enhanced self-organization of the system is observed. The wave fronts become more regular and geometrically defined, forming straight, round and spiral waves, the latter with different topological charges.

3. At extreme deviations from the equilibrium conditions the chaotic character of the observed wave propagation is enhanced.

4. Self-organization phenomena during the electrodeposition of alloys are demonstrated. The pictures obtained remain stable and unchangeable over long periods of time.

References

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