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Growth of electrodeposited copper on anodized titanium

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Copper electrocrystallization at high current density was studied in a pure copper sulphate–sulphuric acid bath. Besides the influence of the current density and electrolyte flow rate, the influence of the titanium substrate pretreatment on the nucleation and growth of copper is emphasized. The 100 μm thick copper deposits give two different layers. The layer in contact with the substrate shows a high density of very small crystals and corresponds to the unoriented dispersion (UD) type in the Winand diagram. The structure of the layer in contact with the electrolyte is, on the contrary, mainly controlled by the electrodeposition parameters (current density and electrolyte flow rate) and corresponds to a field oriented (FT)–UD type in this diagram. It is shown that the thickness of the transition zone between the substrate influenced deposit and that controlled by the electrodeposition parameters depends on the anodic oxidation conditions of the substrate pretreatment. The copper deposits were separated from their substrate and analysed by TEM (including cross-sections), SEM and X-ray diffraction. Some copper foils recrystallize at room temperature.

1. Introduction

Electrolysis is one of the most important processes for the production of copper. Many papers and patents are devoted to copper electrodeposition. These deal mainly with the influence of bath composition, electrolysis parameters (temperature of the bath, current density, electrolyte flow rate, . . .) and cell design on the structure and the properties of the deposits [1–6].

In order to summarize the influence of the electrolysis parameters on electrocrystallization, Winand [7, 8] presented a diagram (see Fig. 1) giving the fields of stability of Fischer's main types of deposits [9] as a function of two main parameters: (a) the inhibition intensity, and (b) the ratio of the current density to the diffusion limiting current density. This diagram is now widely used in the electrowinning and the electrorefining industries where thick copper deposits are produced on copper substrates.

In the electroplating industry, two other parameters that are not taken into account in this diagram, may play an important role on the structure of the deposits. These are: (i) the thickness of the deposit, and (ii) the roughness and composition of the substrate. The influence of this last parameter was shown by Ives *et al.* [10] and Fraser *et al.* [11] for the early stages of copper growth on titanium substrates and is confirmed by recent studies [12–14] devoted to the nucleation of copper on anodized titanium substrates in an additive free copper sulphate bath.

The purpose of this paper is to extend these studies from the nucleation to the growth of thick copper deposits in order to investigate the influence of the thickness on the structure of the deposits.

2. Experimental details

2.1. *Substrate preparation*

Titanium electrodes were cut from a commercially pure titanium sheet (IMI 115), the major impurities being oxygen (0.07%), chromium (0.05%), manganese (0.05%), nickel (0.05%) and vanadium (0.05%). The electrodes were chemically polished in a hydrofluoric–nitric acid bath as described in a previous paper [14] and etched for 30 s in a 10% hydrofluoric acid solution in order to increase the surface roughness. Some of these electrodes were then anodized at constant current density ($50\,\mathrm{A\,m^{-2}}$) in 1 M sulphuric acid electrolyte at 25° C to different anode to cathode potential differences. Three types of anodic oxide film [14] correspond to the selected anodization conditions:

- thin epitaxial films;
- thick epitaxial films;
- microporous films.

These three types of anodic films, together with chemically polished substrates, were used for the growth of copper foils (maximum 100 μm thick).

2.2. *Copper deposition*

In order to control the hydrodynamics during the copper deposition, a channel cell was used. In this cell (see Fig. 2) an additive free electrolyte, containing $50\,\mathrm{g\,dm^{-3}}$ sulphuric acid and $125\,\mathrm{g\,dm^{-3}}$ $CuSO_4.5H_2O$ (0.5 M Cu^{2+}), flowed parallel to the electrodes. The flow rate ranged from 0.3 to $1.8\,\mathrm{m\,s^{-1}}$. The corresponding diffusion limiting current densities were esti-

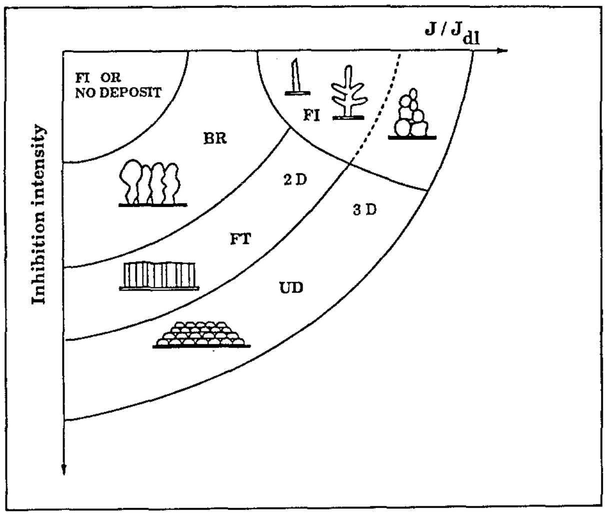


Fig. 1. Fields of stability of the main deposit structures [7, 8]. FI: field orientated crystals type (whiskers, dendrites or loose crystalline powder); FT: field oriented type (coherent deposits, small grain size, almost constant throughout the deposit); BR: basis reproduction type (coherent deposits, grain size and surface roughness increase with deposit thickness); UD: unoriented dispersed type (coherent deposits, small grain size, new crystals generated throughout deposit thickness). 2D: bidimensional nucleation, 3D: tridimensional nucleation.

mated by the tracer technique as described earlier [15, 16].

The temperature of the electrolyte was kept constant at 25° C. The anode is a pure copper electrode. The copper deposition current density ranged from 200 to 3500 A m^{-2}.

2.3. *Analysis*

Surface micrographs of the copper deposits were obtained by means of a JEOL JSM 820 scanning electron microscope (SEM) while their textures were analysed by X-ray diffraction with a SIEMENS D 5000 apparatus. Higher magnifications of the deposit grain structures were observed with a PHILIPS EM 30 transmission electron microscope (TEM). The copper foils were thinned in a classical STRUERS TENUPOL double jet apparatus.

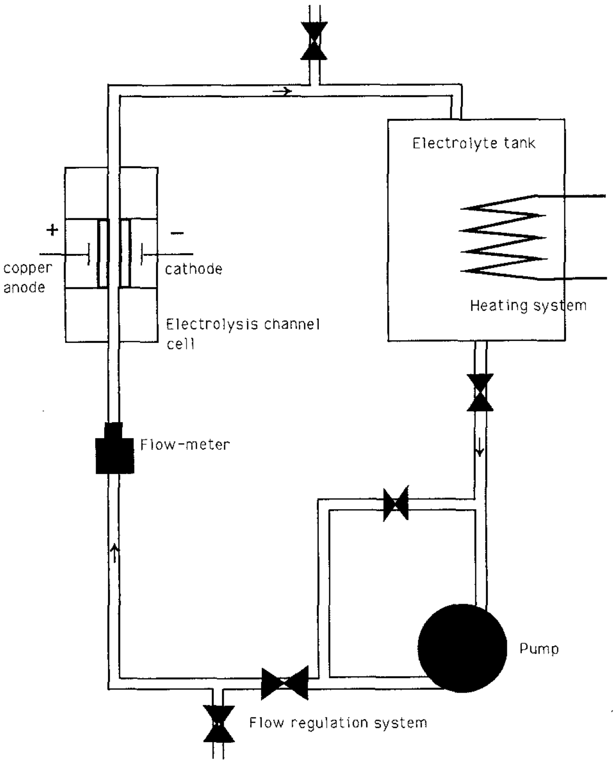


Fig. 2. Description of the electrolysis cell for the copper deposition.

The metallographic structure of the deposits was observed either with an optical microscope REICHERT-JUNG MeF3A (after embedding the copper foils in Mecaprex resin, polishing the cross sections with 1200 SiC paper and etching in a NH_4OH–H_2O_2 solution) or by TEM. The preparation of the cross-sections for the TEM experiments was based on the technique developed by Amblard *et al.* [17] for nickel deposits. The main problem here was the thin starting samples (maximum 100 μm). The copper foils were thus first thickened by electrolysis at low current density (200 A m^{-2}) and room temperature for 5 days in an electrolyte containing 1 M Cu^{2+} ions, 50 g dm^{-3} H_2SO_4 and 5 g dm^{-3} ethanol. 500 μm thick slices perpendicular to the substrate were then cut by means of a BUEHLER ISOMET diamond saw. These slices were thinned to 100 μm by electrolysis in a H_3PO_4–CrO_3 bath [18]. 3 mm diameter samples were cut from these slices and thinned in the double jet apparatus. Accordingly, TEM micrographs were obtained in planes perpendicular to the starting sheet.

3. Results and discussion

3.1. *Influence of electrolysis parameters on thick deposits structure*

In the channel cell, a fully developed forced turbulent flow was obtained in the studied flow rate range. A linear relationship between the diffusion limiting current density (J_{dl}) and the electrolyte velocity to the power 0.8 ($v^{0.8}$) was observed (see Fig. 3). Accordingly, the diffusion limiting current density for the copper deposition ranged, in this study, between 2000 and 10 000 A m^{-2}.

At low and medium constant current density (200 to 2000 A m^{-2}), three types of copper growth structure

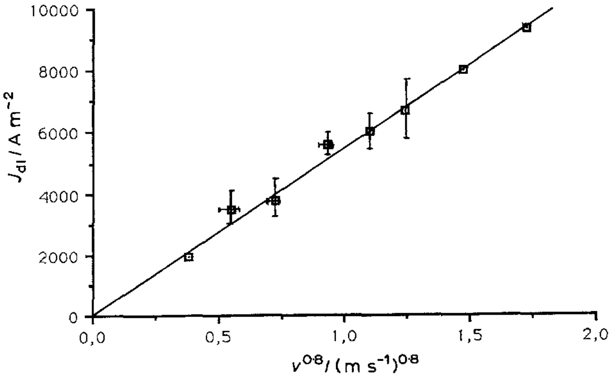


Fig. 3. Dependence of J_{dl} on $v^{0.8}$.

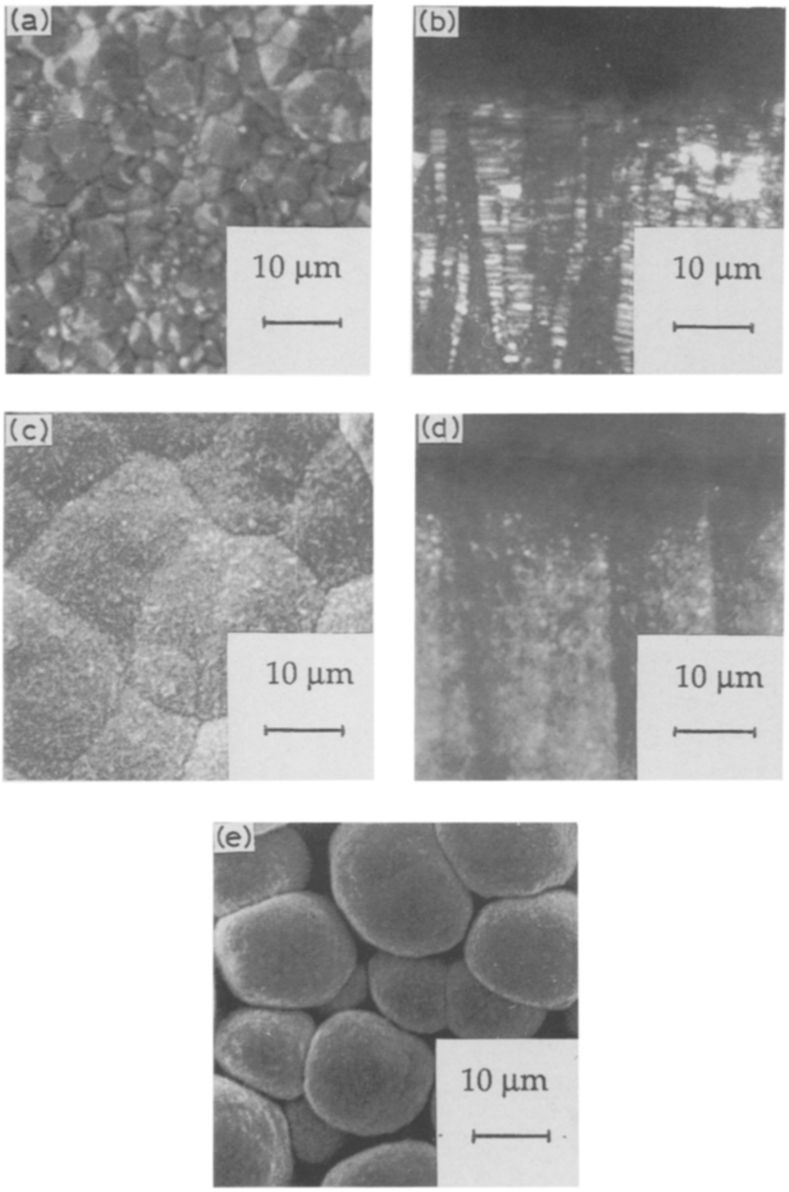


Fig. 4. Copper growth structures. FT–UD structure ($J = 800\,\mathrm{A\,m^{-2}}$, $J_{dl} = 4300\,\mathrm{A\,m^{-2}}$): (a) surface SEM, (b) cross-section; UD structure ($J = 2000\,\mathrm{A\,m^{-2}}$, $J_{dl} = 5400\,\mathrm{A\,m^{-2}}$): (c) surface SEM, (d) cross-section; powder structure: (e) surface SEM.

(Fig. 4) are observed, depending on the electrolyte flow rate and thus on the ratio between the current density and the diffusion limiting current density. They correspond respectively, for increasing values of this ratio, to a FT (field oriented texture)–UD (unoriented dispersion) type, a pure UD type and a powdery type in the Fischer classification. This succession is in agreement with the Winand diagram. For increasing values of the current density, the stability domain of the pure UD type increases and that of the FT–UD type decreases. At high current density (higher than $2000\,\mathrm{A\,m^{-2}}$) only the UD and the powdery types of deposits are observed.

The transition between the 2D (bi-dimensional) nucleation, corresponding by definition [7] to the FT type of deposit and the 3D (three-dimensional) nucleation corresponding to the UD type of deposit, is not perfectly observed in this study due to the formation of new crystals (3D nucleation) in the FT structure. Nevertheless, these results demonstrate that the 2D to 3D nucleation transition does not occur in the additive free electrolyte, for a well defined value of the ratio between the current density and the diffusion limiting current density, as believed earlier [19], but in a range of values that decrease with increasing current density. This fact was already suspected at high current density [20, 21].

In order to study the influence of the surface pretreatment, two sets of electrolysis parameters are selected. The first corresponds to the growth of FT–UD type deposits ($800\,\mathrm{A\,m^{-2}}$, $0.68\,\mathrm{m\,s^{-1}}$) and the second to UD type deposits ($2000\,\mathrm{A\,m^{-2}}$, $1\,\mathrm{m\,s^{-1}}$).

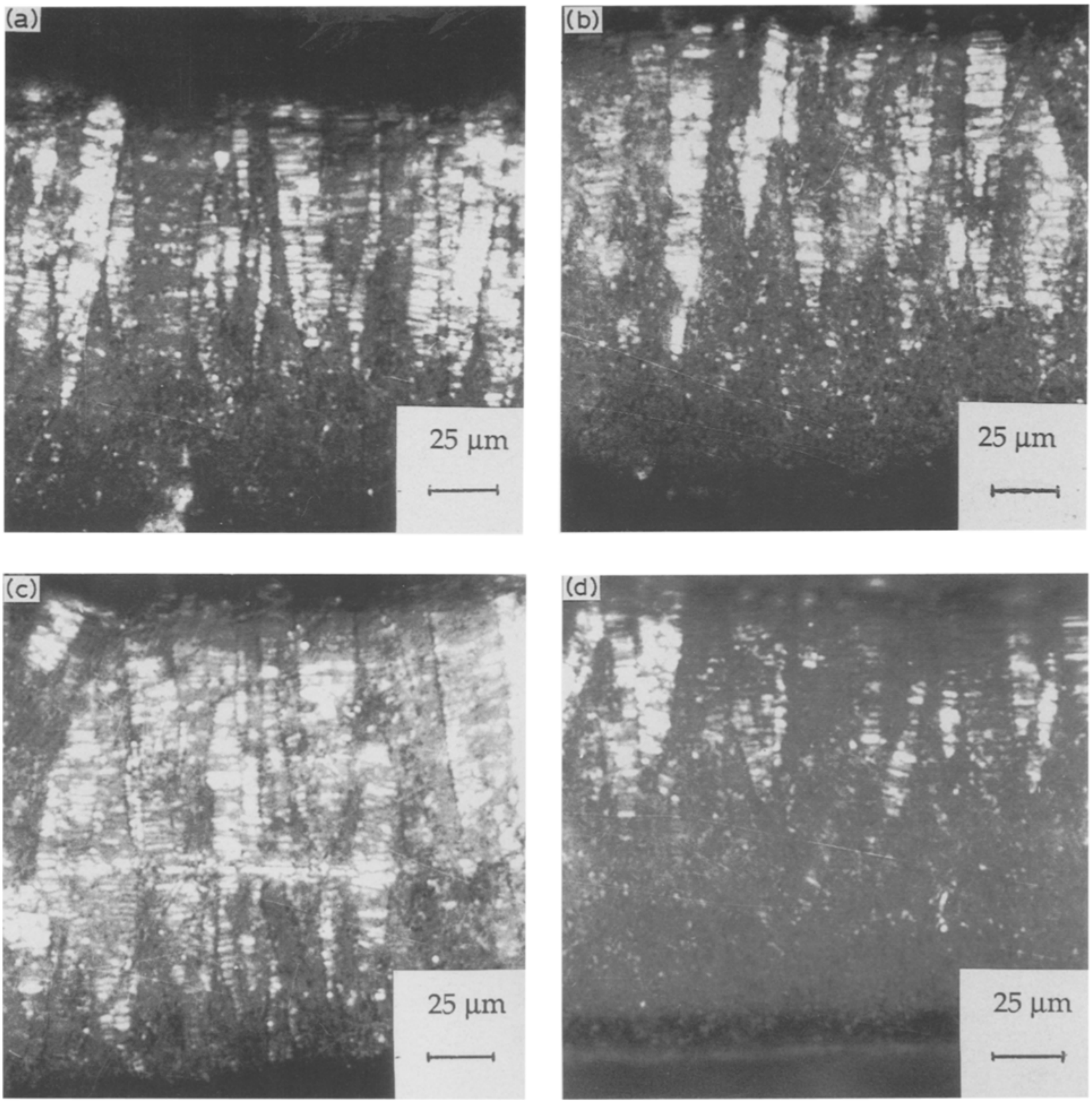


Fig. 5. Influence of the substrate pretreatment on the growth of a FT–UD type deposit (metallographic structures) for $J = 800\,\mathrm{A\,m^{-2}}$ and $J_{\mathrm{dl}} = 4300\,\mathrm{A\,m^{-2}}$. Substrates: (a) polished titanium, (b) thin epitaxial oxide film, (c) thick epitaxial oxide film and (d) microporous oxide film.

3.2. *Influence of substrate pretreatment on the growth of the FT–UD copper deposit structure*

Figure 5 shows the metallographic structures of $100\,\mu\mathrm{m}$ thick FT–UD copper deposits on the four different substrates. Two layers are observed whatever the substrate pretreatment. The first layer, in contact with the substrate, shows a high density of unoriented small crystals. On top of this layer, the FT–UD structure grows by selection of well oriented crystals.

The presence of a thin initial UD layer was observed by Ives *et al.* [10] and by Fraser *et al.* [11] on mechanically polished titanium substrates but was not observed on copper substrates after anodic activation [22]. Figure 5 clearly shows the influence of the substrate pretreatment on the thickness of this layer. On the thick epitaxial anodic oxide layer, this thickness is very small and the copper growth is nearly immediately controlled by the current density and the electrolyte flow rate. On the contrary, for the microporous anodic oxide layer, the growth of the copper deposit is initially controlled by the substrate pretreatment. The thickness of the substrate-controlled UD layer is important and corresponds, in this case, to about half the thickness of the deposit ($50\,\mu\mathrm{m}$).

The evolution from UD to FT–UD structure is also confirmed by X-ray diffraction on copper foils of increasing thickness (see Fig. 6). For thin foils, all the orientations mentioned in the 4-0836 ASTM reference are observed. For increasing thicknesses, these orientations disappear except the (1 1 1) and (2 2 2) orientations. This preferential (1 1 1) FT–UD orientation corresponds to that observed earlier by Pauwels [7, 23] for copper electrodeposition on copper at room tem-

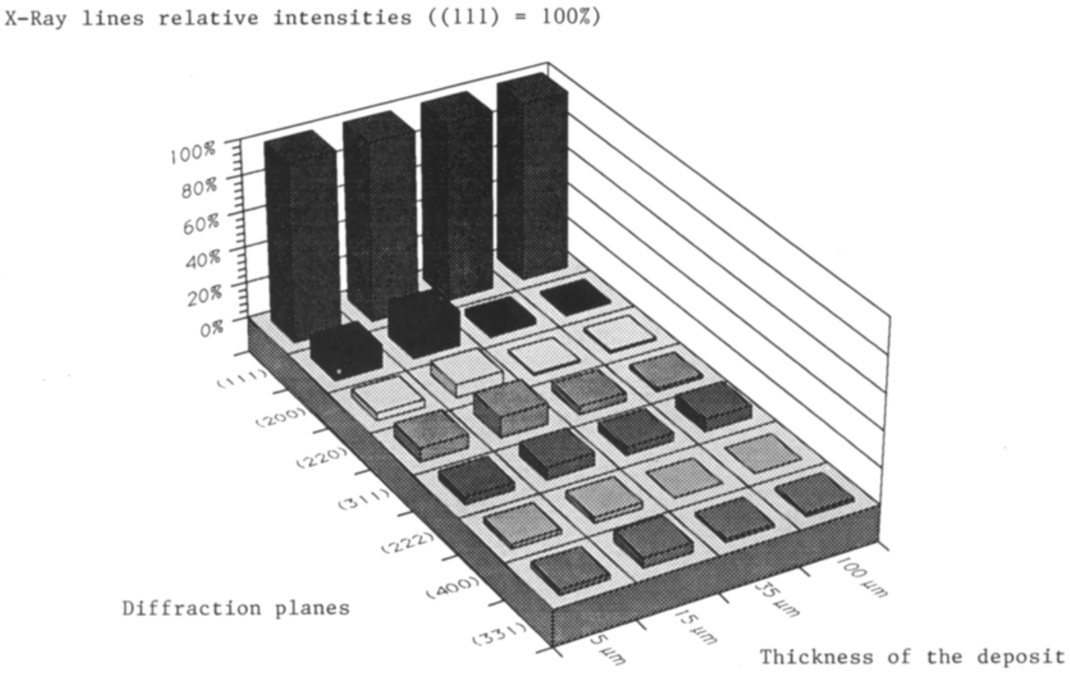


Fig. 6. Transition from UD to FT–UD structure for increasing thickness of the copper deposit on polished titanium. X-ray diffraction patterns.

perature. This evolution is observed whatever the substrate pretreatment is but for different values of the transition thickness.

The TEM cross section pictures, shown in Fig. 7(a), show that this (1 1 1) FT–UD orientation is stabilized by twinning planes. Large copper grains with a diameter of 1 μm or more are observed as shown in Fig. 7(b).

3.3. *Influence of the substrate pretreatment on the growth of the pure UD copper deposit structure*

Figure 8 shows the metallographic structures of 100 μm thick UD copper deposits on the four different substrates. Whatever the substrate pretreatment, these copper deposits are homogeneous and correspond to the UD type. Macrostructures corresponding to the dimensions of the underlaying titanium crystals are observed throughout the deposits. Buds are sometimes observed.

TEM analysis shows a large number of very small crystals (diameter less than 0.5 μm) throughout the deposits (Fig. 9). The UD type is confirmed by the X-ray diffraction experiments (Fig. 10). The X-ray diffraction patterns correspond to a copper powder pattern with sometimes a slight (1 1 1) preferential orientation. It thus seems that, for these values of the electrochemical parameters, the substrate-controlled deposition structure is identical to the deposition structure that is controlled by the current density and the electrolyte flow rate.

It should be noted that these very fine crystal UD deposits present a remarkable effect: they recrystallize at room temperature. The X-ray diffraction patterns of Fig. 11 show this recrystallization for samples left for 300 days at room temperature (25° C). The slight (1 1 1) preferential orientation gradually turns to a preferential orientation of (1 0 0) planes parallel to the surface. This recrystallization effect is confirmed by TEM experiments. Figure 12 shows the copper grains immediately after electrodeposition and 45 days after deposition. The initial small copper crystals recrystallize to form large square crystals with a low density of twinning planes. This recrystallization is not due to a heating effect in the microscope.

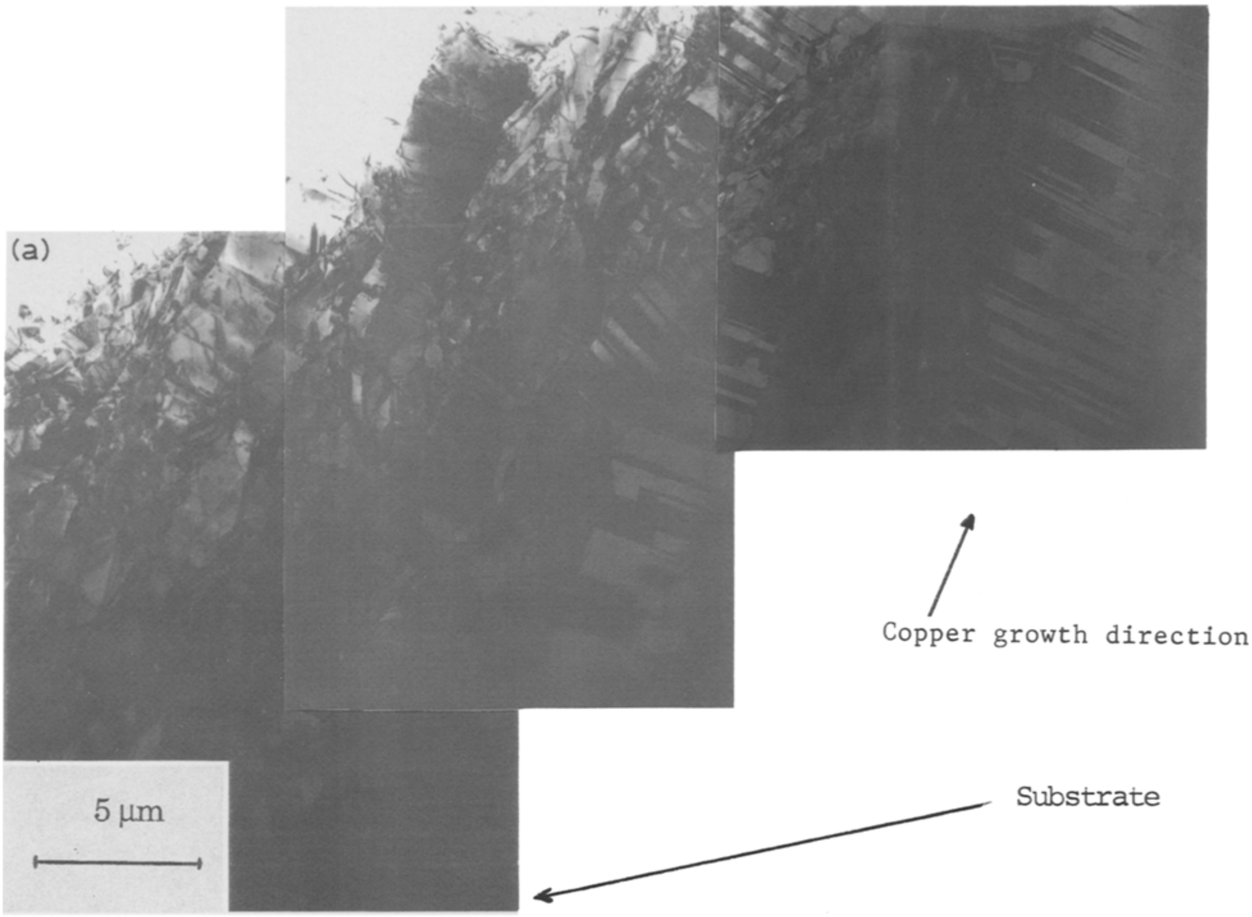
In the literature, copper recrystallization is observed, for bulk samples, at temperatures higher than 80° C [24]. For electrodeposits, this effect is not mentioned, except by Tomov *et al.* [25–27] who produced very fine deposits by addition of organic brighteners to the electrolytic baths. These authors consider that the observed room temperature recrystallization may be related to the small grain size of their deposits and to the large number of defects in the grain boundaries.

The UD deposits present the same characteristics as Tomov's deposits without addition of brighteners. The strain energy stored in these small grain electrodeposits could be high enough to promote, even at room temperature, dislocations, displacements and recrystallization.

This recrystallization effect is not observed for deposits obtained at low current density, even when the substrate initiates a thick UD layer. It thus seems that the presence of a surrounding FT–UD structure stabilizes the fine grains and prevents the motion of the dislocations and the subsequent recrystallization.

4. Conclusions

This study has shown that the results obtained for the



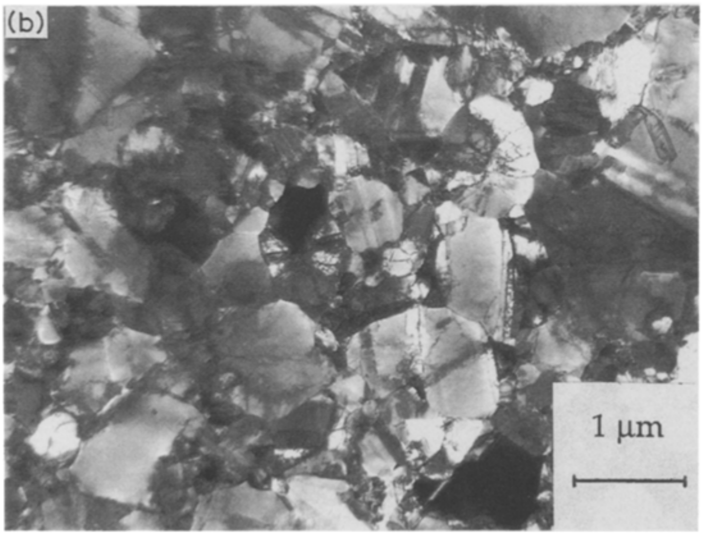


Fig. 7. TEM observation of a (1 1 1) FT–UD copper deposit on polished titanium. (a) Section perpendicular to the substrate and (b) section parallel to the substrate.

electrodeposition of thick (in the millimetre range) copper deposits on copper cannot automatically be transferred to the growth of thin deposits on foreign substrates. This raises the question whether the use of the Winand diagram is appropriate in the copper electroplating industry.

Looking at its fundamental background, Winand's diagram [8] was established for deposits undergoing steady-state growth under conditions of electrodeposition control, with no influence of the substrate. In electroplating, it should accordingly be necessary to check if these conditions are observed.

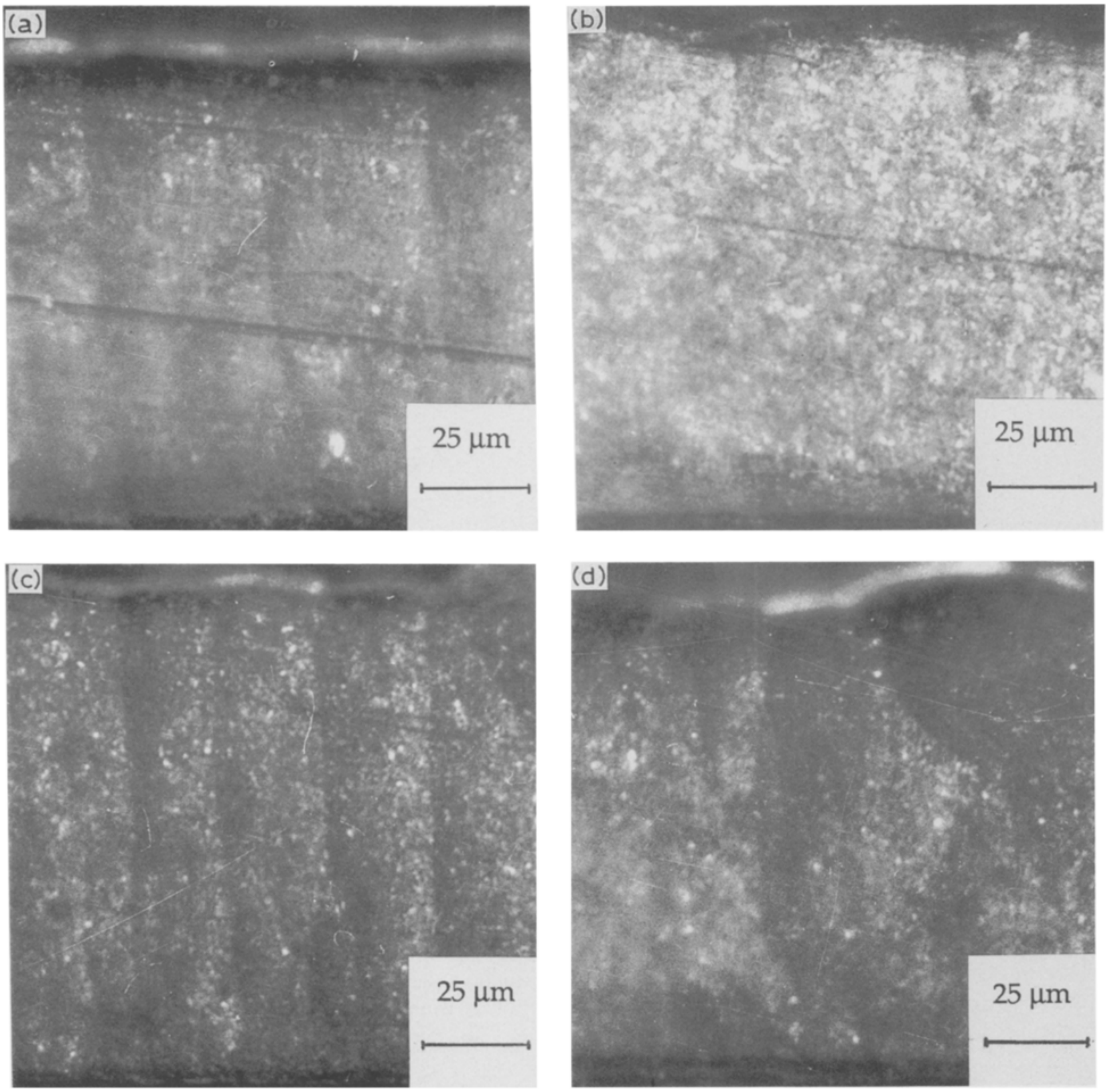


Fig. 8. Influence of the substrate pretreatment on the growth of a pure UD-type deposit (metallographic structures) for $J = 2000\ \mathrm{A\,m^{-2}}$ and $J_{dl} = 5400\ \mathrm{A\,m^{-2}}$. Substrate: (a) polished titanium, (b) thin epitaxial oxide film, (c) thick epitaxial oxide film and (d) microporous oxide film.

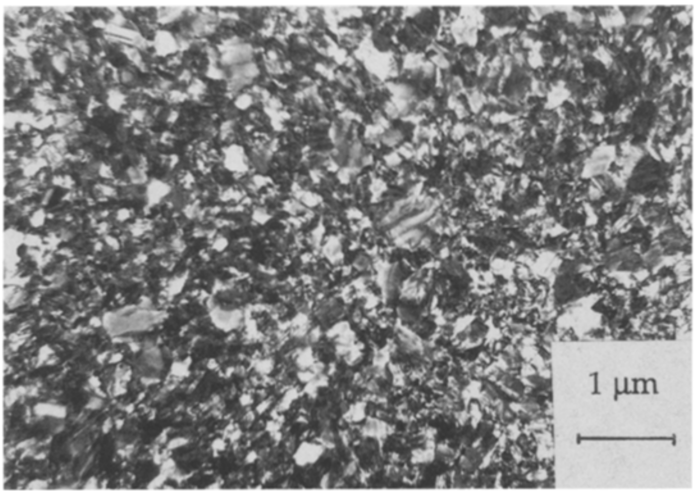


Fig. 9. TEM observation of the grain structure of a UD copper deposit on polished titanium. Copper growth direction ⊙.

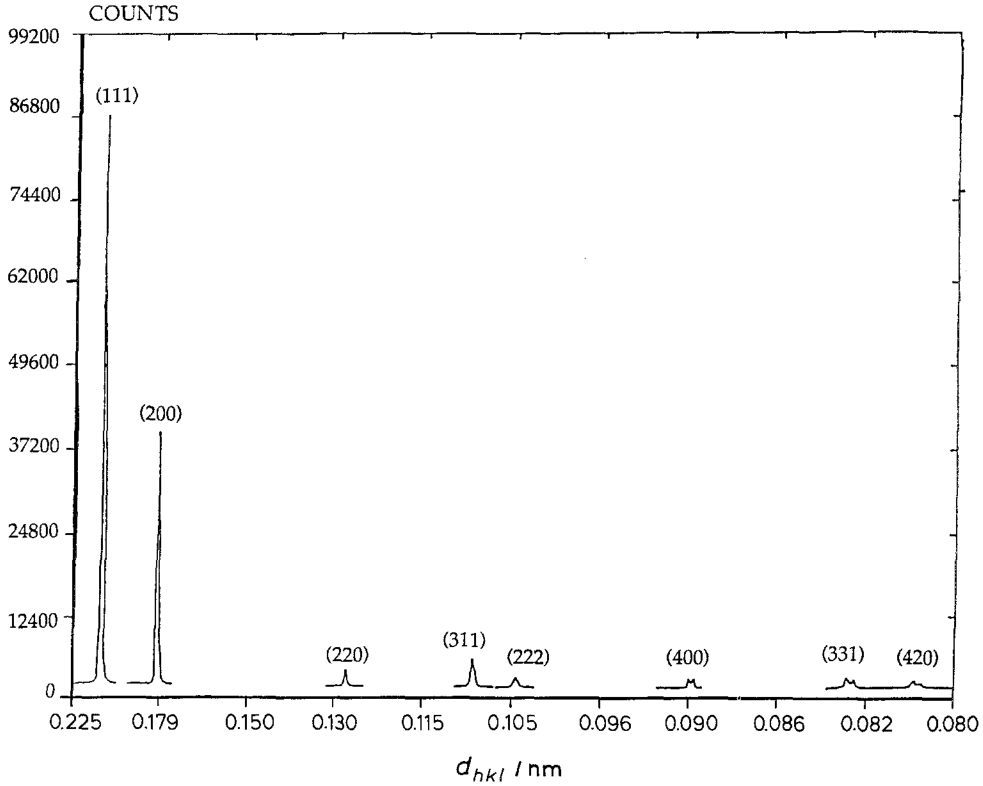


Fig. 10. X-ray diffraction pattern of a UD-type copper deposit on polished titanium.

These preliminary experiments can only provide a partial answer to this question. If the surface properties of the substrate do not influence the nucleation of the copper deposit, the use of the Winand diagram is probably valid whatever the thickness of this deposit. On the contrary, for substrates with a strong influence on the nucleation, the user has to be very cautious. More experiments are needed to understand how some substrates can influence the deposit structure even tens of micrometers far from the substrate-deposit interface.

In the industrial production of thin metallic foils by electrolysis, the control of the substrate surface treatment is essential. Poor control of this treatment may induce the production of a totally undesirable deposit structure that may change gradually by recrystallization at room temperature.

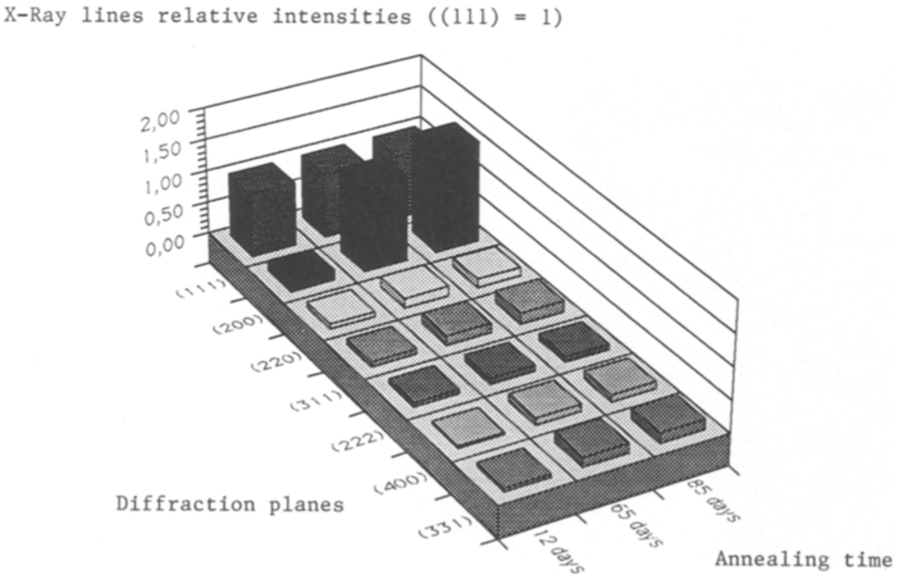


Fig. 11. Recrystallization of a UD-type copper deposit as a function of the annealing time at room temperature. X-ray diffraction patterns.

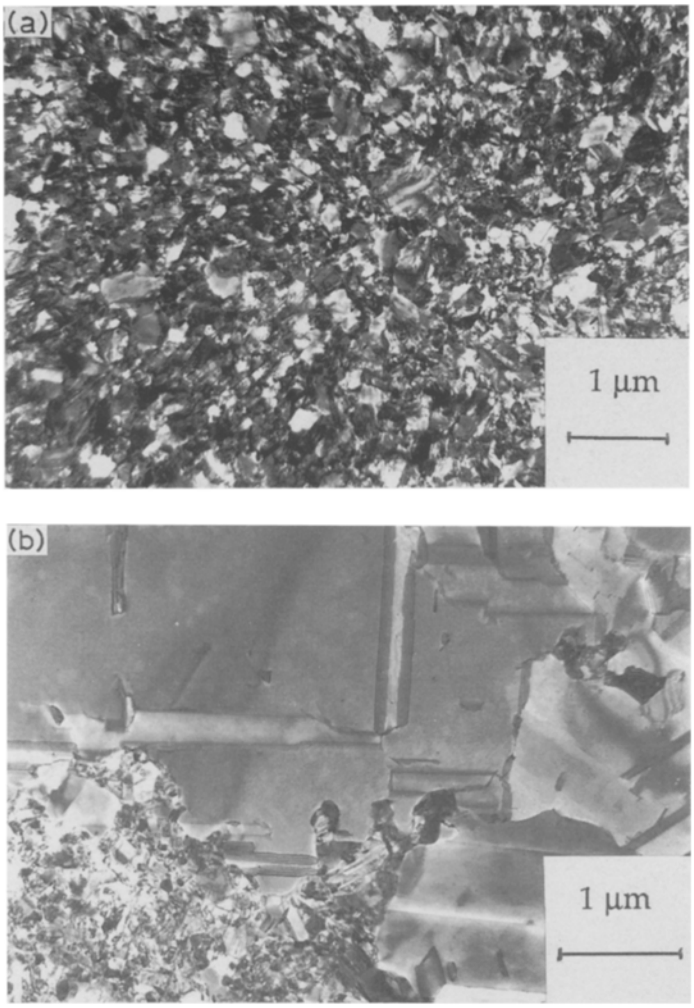


Fig. 12. Recrystallization of a UD-type copper deposit as a function of annealing time at room temperature: TEM pictures: (a) after deposition and (b) 45 days after deposition. Copper growth direction ⊙.

Acknowledgements

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