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Reflection and structural analyses of mirror-bright metal coatings

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Abstract Reflection and structural analyses of different copper and zinc coatings were performed. The copper coatings were electrodeposited from a sulfate solution in the presence of thiourea, as well as in the presence of modified polyglycol ether, PEG 6000 and 3-mercaptopropanesulfonate. The zinc coating was electrodeposited from a sulfate solution in the presence of a dextrin/salicylaldehyde mixture. They were examined by STM and X-ray diffraction analysis, and measurements of the reflection of light from their surfaces were taken. The mean sizes of atomically flat parts of these surfaces were estimated by the STM software measurements, using options for the determination of the autocovariance function and the power spectral density function. It was shown that the mean sizes of atomically flat parts of the copper coatings were several times greater than the mean size of atomically flat parts of the zinc coating. This difference probably leads to the difference in the maximum degrees of mirror reflection between copper and zinc coatings.

Keywords Copper · Electroplating · Scanning tunneling microscopy · X-ray diffraction · Zinc

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Introduction

The reflection and structural criteria which must be fulfilled in order for a metal surface to exhibit mirror brightness were recently defined [1]. Then, it was shown, by comparison of the reflection and structural characteristics of different copper surfaces with those of a silver mirror surface [1, 2], that mirror brightness of metal surfaces is determined by: (1) flat and mutually parallel parts of a surface which are smooth at the atomic level, and (2) the distances between adjacent flat parts which are comparable with the distances between adjacent flat parts of a silver mirror surface as the reference standard. In the same investigation it was also shown that mirror brightness could not be associated directly with the preferred orientation of a surface. Also, a mathematical model was proposed which treated brightness from the point of view of geometrical optics.

It was shown recently that these criteria can also be applied to the nickel coating obtained in the presence of both basic and top brightening addition agents [3]. On the basis of the same criteria, the nickel coating obtained in the presence of a basic brightening agent only was characterized as a semi-bright metal surface.

Also, the STM technique, with the application of an accompanying software package, offers the convenience for a quantitative analysis of the structure of metal surfaces [4]. Calculations commonly applied to STM data are: root-mean-square roughness (a measure of the variation in heights [5]); the autocovariance function (ACVF; a measure of the spatial correlation of heights [5, 6]); and the power spectral density function (PSD; a measure of the wavelength of periodic features [7, 8, 9, 10]).

In this work, in order to test the importance of proposed reflection and structural criteria, different metal coatings were examined. A copper coating electrodeposited from a solution containing thiourea, a copper coating electrodeposited from a solution containing a modified polyglycol ether, PEG 6000 and 3-mercaptopropanesulfonate, as well as a zinc coating electrodeposited from a solution containing dextrin and salicylaldehyde were examined by STM and X-ray diffraction (XRD) analysis. Reflection of light from these surfaces was also measured. Quantification of the structural characteristics of these metal surfaces was carried out by STM software measurements, using options for the determination of ACVF and PSD functions.

Experimental

Copper was galvanostatically deposited from:

1. 240 g L^{-1} $CuSO_4.5H_2O$ + 60 g L^{-1} H_2SO_4 + 0.050 g L^{-1} thiourea (solution I).
2. 240 g L^{-1} $CuSO_4.5H_2O$ + 60 g L^{-1} H_2SO_4 + 0.124 g L^{-1} NaCl + 1.0 g L^{-1} modified polyglycol ether (Lutron HF 1) + 1.0 g L^{-1} poly(ethylene glycol) [$M_n = 6000$ (PEG 6000)] + 1.5 mg L^{-1} 3-mercaptopropanesulfonate (solution II).

Galvanostatic deposition was carried out at a temperature of 21.0 ± 1.0 °C in an open cell, with a counter electrode of electrolytic copper (99.99%). The electrolyte was stirred. The thicknesses of the obtained copper coatings were 20 μm. The copper coatings were electrodeposited at $i = 60$ mA/cm^2 from solution I and at $i = 50$ mA/cm^2 from solution II onto nickel coatings (thicknesses of 15 μm) electrodeposited on polycrystalline copper cathodes.

Zinc was electrodeposited from: 300 g L^{-1} $ZnSO_4.7H_2O$ + 30 g L^{-1} $Al_2(SO_4)_3.18H_2O$ + 15 g L^{-1} NaCl + 30 g L^{-1} H_3BO_3 + 3.0 g L^{-1} dextrin + 2.8 mL L^{-1} salicylaldehyde. The deposition was carried out galvanostatically, at a temperature of 30.0 ± 1.0 °C, in an open cell, with a stirred electrolyte, on polycrystalline copper cathodes. The deposition current density was 130 mA/cm^2. The anode was 99.99% pure zinc. The thickness of the obtained zinc coating was 20 μm.

The reflection was determined using a reflectance spectrophotometer (Beckman UV 5240), i.e. the specimen was illuminated by a beam normal to the specimen [normal/total (abbreviation, 0/t): normal/diffuse (abbreviation, 0/d)]. The reflected flux was collected by means of an integrating sphere. This type of reflectance spectrophotometer gives the dependences of total reflection and diffuse reflection as a function of the wavelength of visible light [1].

The topography of the surface was determined ex situ using a STM NanoScope III in air (maximum scan size 880 nm×880 nm). The STM images were obtained in the constant current mode using a W tip electrochemically sharpened in 1 M KOH solution. The bias voltage ranged from 20.0 to 26.0 mV and the tip current from 7.0 to 8.8 nA for the copper surfaces and from 100 to 110 mV and the tip current from 11 to 13 nA for the zinc coating.

XRD analysis was performed for characterization of the copper and zinc surfaces. A Siemens instrument (type D 500) with Ni-filtered Cu Kα radiation (35 kV and 20 mA) was used at a continuous scan speed of 0.02° 2θ s^{-1}. The preferred orientation of the copper surfaces was determined according to the ASTM standard for copper powder and for the zinc surface according to the ASTM standard for zinc powder.

Results

Analyses of copper coatings

The ideal reflectance of copper [11] and the degrees of total reflection for the wavelength of light in the visible range for the copper coating obtained in the presence of thiourea (solution I) and the copper coating obtained in the presence of modified polyglycol ether, PEG 6000 and 3-mercaptopropanesulfonate (solution II) are shown in Fig. 1a. The degrees of mirror and diffuse reflections of the same copper coatings as a function of the wavelength of visible light are shown in Fig. 1b.

It can be observed from Fig. 1a and Fig. 1b that both copper coatings exhibit high degrees of mirror reflection, which approach very nearly the ideal reflectance of copper for the wavelength range above 600 nm. The degrees of diffuse reflection of these copper coatings are approximately the same values.

The 3-D (three-dimensional) STM images (300×300 nm^2) of the copper coating obtained from solution I and the copper coating obtained from solution II are shown in Fig. 2a and Fig. 2b, respectively. It can be seen from these figures that the copper surfaces are relatively smooth.

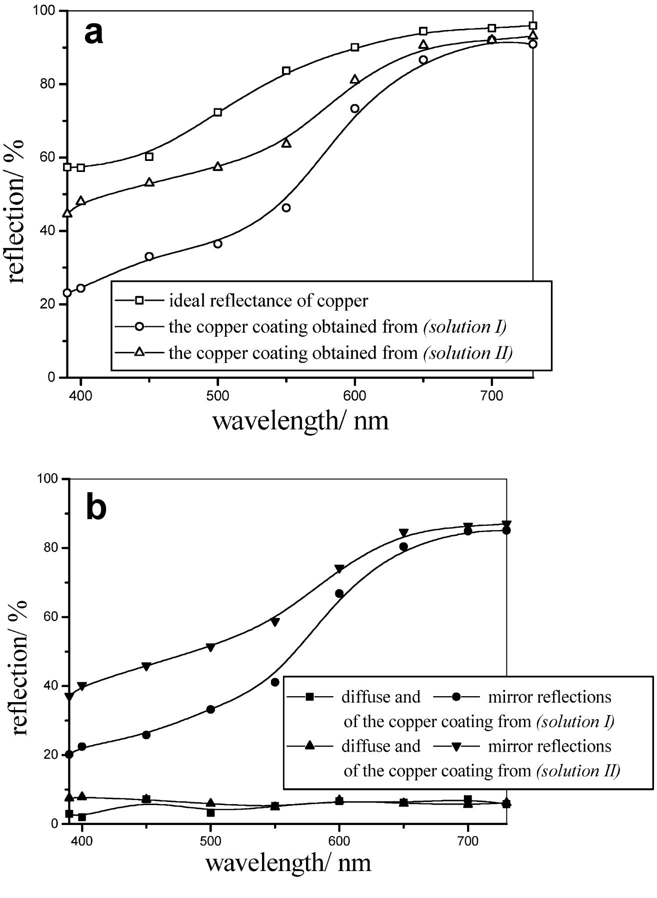


Fig. 1 The dependence of the degrees of reflection on the wavelength of visible light for: (**a**) the ideal reflectance of copper (*open squares*) and the total reflections of the copper coating electrodeposited from solution I (*open circles*) and the copper coating electrodeposited from solution II (*open triangles*); (**b**) mirror (*filled circles*) and diffuse (*filled squares*) reflections of the copper coating electrodeposited from solution I, and mirror (*filled down triangles*) and diffuse (*filled up triangles*) reflections of the copper coating electrodeposited from solution II

Figure 3a and Fig. 3b show that the surfaces of these copper coatings consist of flat and mutually parallel parts of a surface. The distances between adjacent flat

Fig. 2 3D STM images of copper coatings electrodeposited from: (**a**) solution I, (**b**) solution II. Scan size: 300×300 nm^2

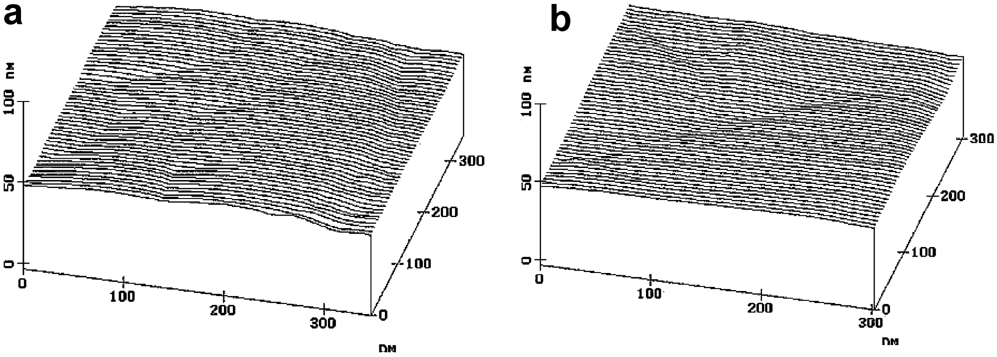
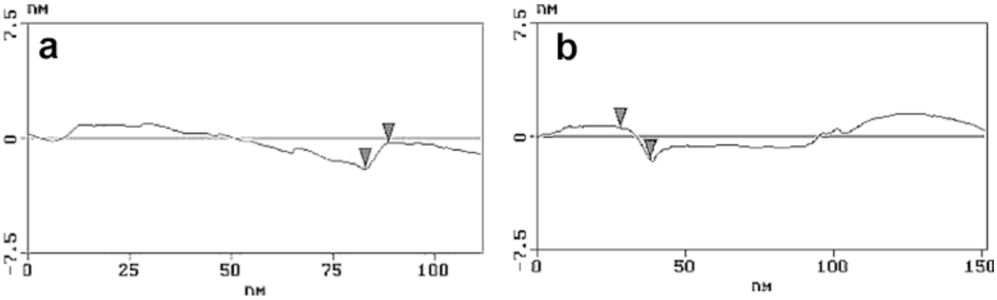


Fig. 3 Line section analysis from the portion of the STM surfaces shown in Fig. 2: (**a**) the copper coating electrodeposited from solution I; (**b**) the copper coating electrodeposited from solution II. The vertical distances between markers are: **a** 1.656 nm, **b** 2.136 nm



parts of the analysed copper surfaces were several atomic diameters of copper [12].

Figure 4a and Fig. 4b show flat parts of these copper surfaces. It was shown by the STM software measurements that the roughness of the flat parts was less than the atomic diameter of copper, i.e. the flat parts of the surfaces were smooth at the atomic level.

The atomically flat parts of these copper coatings are shown in Fig. 5. The mean size of these atomically flat parts was estimated by STM software measurements, using the option for the determination of the ACVF and PSD functions. The estimated mean size of the flat parts was approximately 160×200 nm^2 by the ACVF function and 229 nm by the PSD function for the copper

Fig. 4 Line section analysis of the flat parts of surfaces: (**a**) the copper coating electrodeposited from solution I; (**b**) the copper coating electrodeposited from solution II

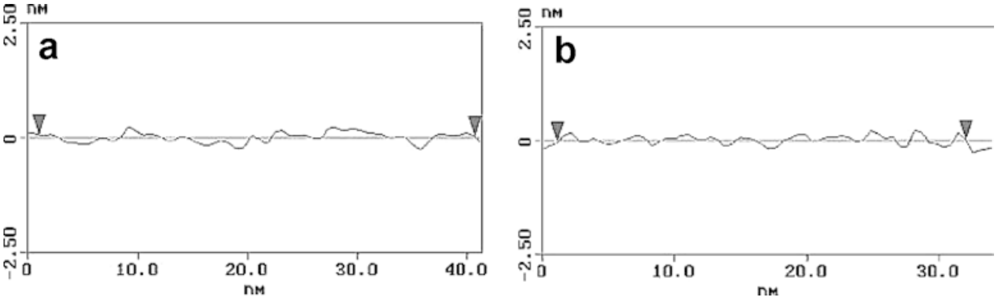
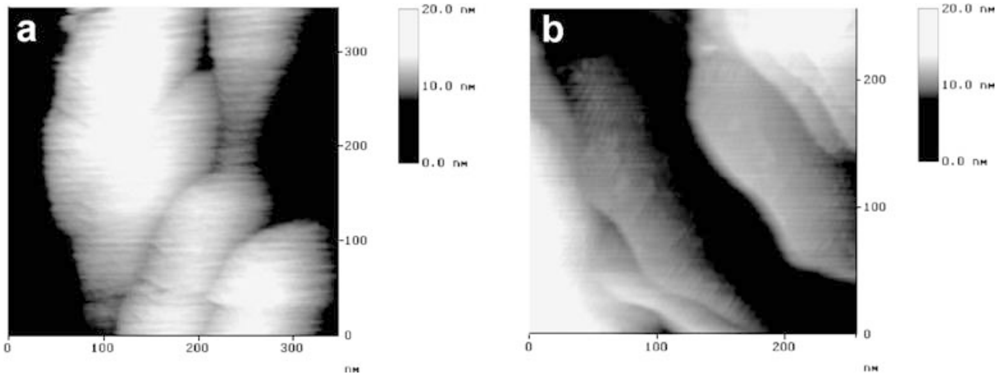


Fig. 5 STM images of copper coatings electrodeposited from: (**a**) solution I; (**b**) solution II



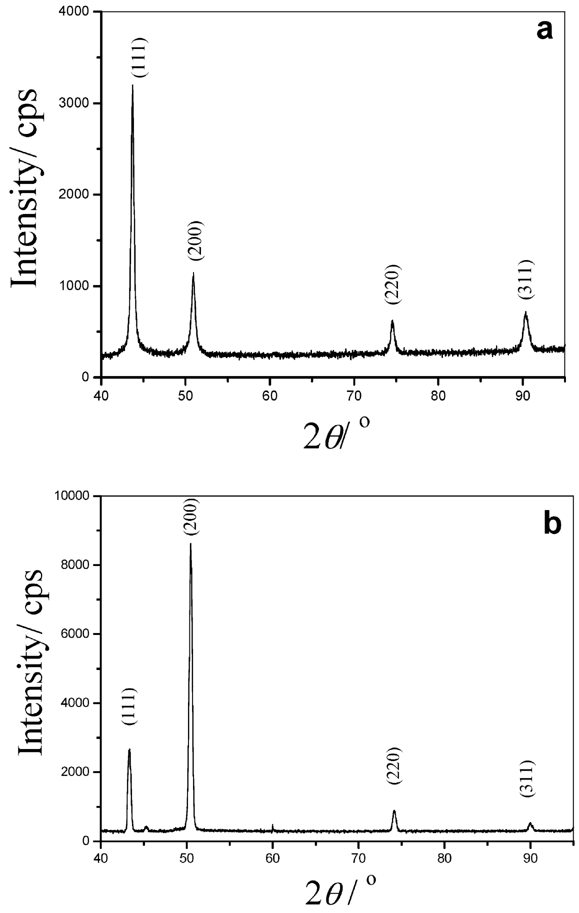


Fig. 6 XRD patterns of copper coatings electrodeposited from: (**a**) solution I; (**b**) solution II

coating obtained from solution I and approximately 140×160 nm^2 by the ACVF function and 166 nm by the PSD function for the copper coating obtained from solution II.

XRD patterns of the copper coating electrodeposited from solution I and the copper coating electrodeposited from solution II are shown in Fig. 6a and Fig. 6b, respectively. From these figures it can be seen that the copper surfaces exhibited different preferred orientations. The copper coating electrodeposited from solution I showed a (111) preferred orientation (Fig. 6a), while the copper coating obtained from solution II showed a (200) preferred orientation (Fig. 6b).

Analyses of the zinc coating

The degrees of total, mirror and diffuse reflections as a function of visible light wavelength for the zinc coating obtained from a solution containing a dextrin/salicylaldehyde mixture are shown in Fig. 7. This figure shows that the degree of mirror reflection reached 80%, while the degree of diffuse reflection is very small (up to 5%).

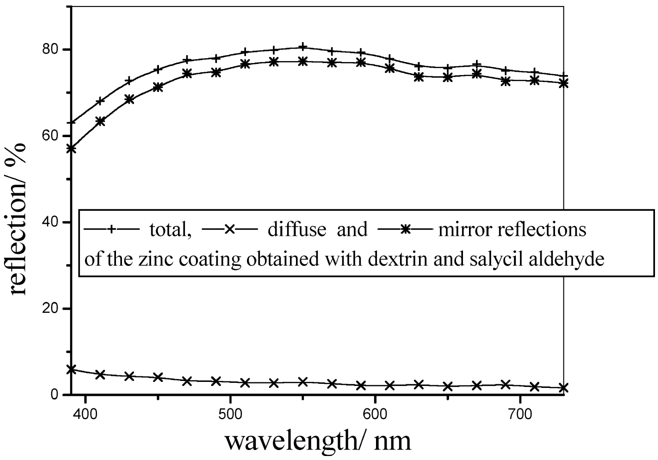


Fig. 7 The dependence of the degrees of total (*plus signs*), mirror (*asterisks*) and diffuse (*crosses*) reflections on the wavelength of visible light for the zinc coating electrodeposited from a solution containing a dextrin/salicylaldehyde mixture

The 3-D STM image (300×300 nm^2) of the zinc coating is shown in Fig. 8. It can be observed that the surface of the zinc coating is relatively smooth, but without large flat and mutually parallel parts which were characteristic for the previously analysed copper surfaces. Figure 9 shows analysis of this coating at higher magnification (i.e. smaller scan size). It can be observed from Fig. 9a that the zinc surface is very fine-grained. From Fig. 9b it can be seen that the surface of the zinc coating is covered with relatively hexagonal zinc crystals.

Figure 10a shows the line section analysis of a part of the surface of the zinc coating. It can be observed from this part that the top surfaces of the hexagonal zinc crystals are relatively flat and mutually parallel. The distance between the top plane of a hexagonal zinc crystal and the boundary with the adjacent zinc crystal is several atomic diameters of zinc [12]. Figure 10b shows the line section analysis of a zinc crystal surface. The roughness of the hexagonal zinc crystals was less than the atomic diameter of zinc, i.e. these zinc crystals were smooth at the atomic level. The mean size of the zinc crystals was also estimated by STM software measurements, using the option for the determination of the

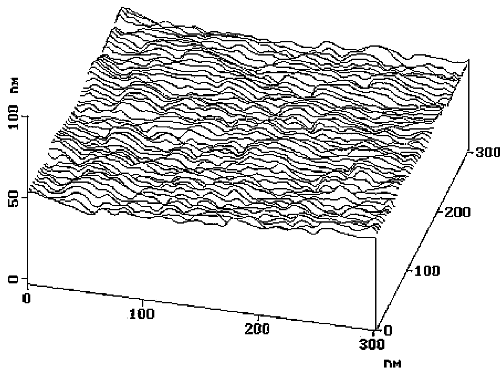


Fig. 8 3D STM image of the zinc coating electrodeposited from a solution containing a dextrin/salicylaldehyde mixture. Scan size: 300×300 nm^2

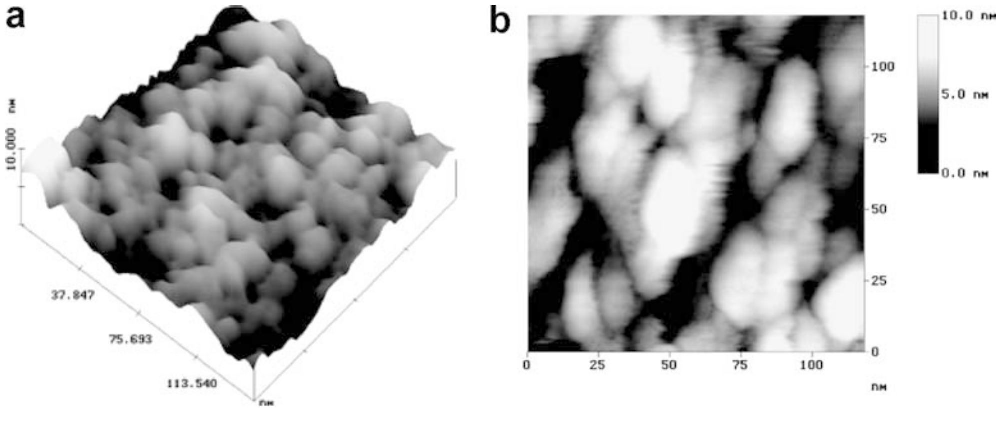


Fig. 9 STM images of the zinc coating electrodeposited from a solution containing a dextrin/salicylaldehyde mixture. Scan size: (**a**) 160×160 nm^2; (**b**) 120×120 nm^2

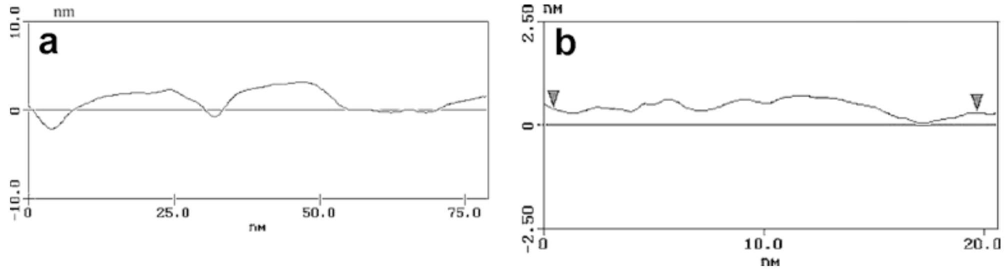


Fig. 10 Line section analysis: (**a**) the portion of the STM surface shown in Fig. 9a; (**b**) the surface of a hexagonal zinc crystal

ACVF and PSD functions. The estimated mean size of the zinc crystals was approximately 18×20 nm^2 by the ACVF function and 20 nm by the PSD function.

XRD analysis of the zinc coating obtained from a solution containing the dextrin/salicylaldehyde mixture (Fig. 11) showed that the zinc crystallites were oriented in the (110) plane only.

Discussion

On the basis of reflection and structural analysis of these copper coatings, it follows that both the copper coating obtained from solution I and the copper coating obtained from solution II fulfilled the conditions to be characterized as mirror-bright metal surfaces [1]. The degree of mirror reflection of these coatings approached the theoretical reflectivity of copper. The structural details which enabled this degree of mirror reflection are: flat and mutually parallel parts of the surface which are smooth at the atomic level, and distances between adjacent flat parts which are several atomic diameters of copper and which are comparable with the same distances of a silver mirror surface.

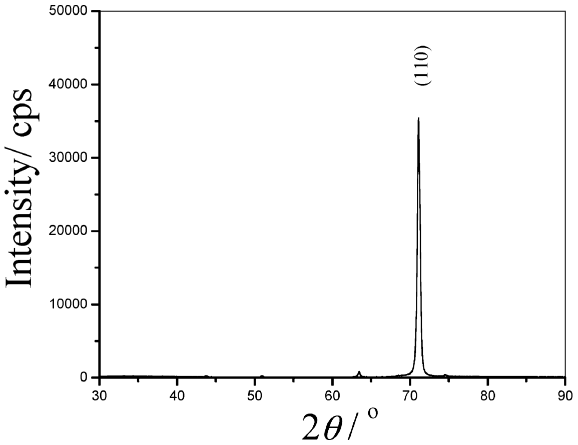


Fig. 11 XRD pattern of the zinc coating electrodeposited from a solution containing a dextrin/salicylaldehyde mixture

Structural details which enabled a high degree of mirror reflection of the zinc coating are relatively hexagonal zinc crystals, the base planes of which are flat and mutually parallel and which are smooth at the atomic level. The distance between the top plane of a hexagonal zinc crystal and the boundary with adjacent zinc crystals is several atomic diameters of zinc and is comparable with the distance between adjacent flat parts of a silver mirror surface. Hence, on the basis of these structural characteristics, it can be concluded that the zinc coating obtained from the solution containing dextrin and salicylaldehyde as brightening addition agents fulfilled the conditions to be a mirror-bright metal surface.

The zinc coating electrodeposited from the solution containing dextrin and salicylaldehyde was very fine grained, with the zinc crystallites oriented in the (110) direction only. The (110) plane of the h.c.p. crystal lattice is the plane where the most densely packed atom rows in the most densely packed lattice plane (basal plane) stand upright to the cathode surface [13]. According to Finch et al. [14, 15], when the crystallites of the deposits are oriented so that the most densely populated atom plane is perpendicular to the substrate, then the deposited metal adopts an outward type of growth. The structural characteristics of this zinc coating were very similar to the structural characteristics of the chromium coating electrodeposited from a sulfate solution [16]. Nielsen et al. [16] showed that the chromium coating consisted of a small grain size (20×80 nm^2), oriented in the (111) plane primarily. The (111) plane in a b.c.c. crystal lattice is the plane in which the crystallites of the deposits are oriented so that the most densely populated atom row, in the most densely populated atom plane, is perpendicular to the substrate. The deposited metal then adopts an outward type of growth.

The different preferred orientations of coatings which are characterized as mirror-bright metal surfaces clearly indicate that mirror brightness of a surface is not associated with a preferred orientation of the metal surface and that the preferred orientation depends on the type of brightening addition agents that are used.

The difference in the maximum degrees of mirror reflection between the copper coatings (above 85%) and the zinc coating (below 80%) can be ascribed to the different mean size of the atomically flat parts of the copper and zinc coatings. The smaller mean size of the atomically flat parts of a surface, the greater is the ratio of screened parts which do not have the ability to reflect light. In the both cases, the distances between adjacent flat parts are approximately the same values, and comparable with the same distances between adjacent flat parts of a silver mirror surface.

Conclusions

Reflection and structural analysis of the copper coating obtained in the presence of thiourea (solution I), the copper coating electrodeposited in the presence of polyglycol ether, PEG 6000 and 3-mercaptopropanesulfonate (solution II) and the zinc coating electrodeposited in the presence of dextrin and salicylaldehyde showed that these metal coatings fulfilled the criteria to be mirror-bright metal surfaces.

The estimated mean size of the atomically flat parts of the copper coating obtained from solution I was approximately 160×200 nm^2 by the ACVF function and 229 nm by the PSD function. The estimated mean size of the atomically flat parts of the copper coating obtained from solution II was approximately 140×160 nm^2 by the ACVF function and 166 nm by the PSD function. The estimated mean size of the zinc crystals was approximately 18×20 nm^2 by the ACVF function and 20 nm by the PSD function.

The different values of the estimated mean size of the atomically smooth copper and zinc crystals probably led to the difference in the maximum degrees of mirror reflection between the copper (above 85%) and zinc (below 80%) coatings.

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