

The structure of bright zinc coatings

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The structures of bright zinc coatings obtained from acid sulfate solutions in the presence of dextrin/salicyl aldehyde mixture were examined. It was shown by the STM technique that the surfaces of bright zinc coatings are covered by hexagonal zinc crystals, the tops of planes of which are flat and mutually parallel and which exhibit smoothness on the atomic level. X-Ray diffraction (XRD) analysis of the bright zinc coatings showed that the zinc crystallites are oriented in the (110) plane only.

Keywords: bright zinc coating, STM technique, X-ray diffraction analysis.

INTRODUCTION

The structure of bright metal surfaces has been the subject of many investigations.^{1–11} However, the conditions which must be fulfilled in order for the metal surfaces to exhibit mirror brightness have not been classified and systematized yet. Progress in the investigation of the structure of bright metal surfaces has accelerated recently, thank to the development of the scanning tunnelling microscopy (STM) technique.¹²

It has been shown by this technique that the reason of the mirror brightness of electropolished copper surfaces might be that large parts of the surface consists of small, flat and mutually parallel metal crystals, which exhibit smoothness on the atomic level.¹² For this reason, it was considered necessary to examine whether this conclusion about the structural features of electropolished mirror bright metal surfaces is also valid and for bright metal coatings obtained by electrodeposition.

Hence, the structures of bright zinc coatings, obtained by electrodeposition from acid sulfate solutions in the presence of dextrin/salicyl aldehyde mixtures as brightening agents, were examined by the STM technique and X-ray diffraction analysis.

EXPERIMENTAL

Zinc was electrodeposited from:

$1.300 \text{ g L}^{-1} \text{ ZnSO}_4 \cdot 7 \text{ H}_2\text{O} + 30 \text{ g L}^{-1} \text{ Al}_2(\text{SO}_4)_3 \cdot 18 \text{ H}_2\text{O} + 15 \text{ g L}^{-1} \text{ NaCl} + 30 \text{ g L}^{-1} \text{ H}_3\text{BO}_3$

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2. 300 g L⁻¹ ZnSO₄ · 7 H₂O + 30 g L⁻¹ Al₂(SO₄)₃ · 18 H₂O + 15 g L⁻¹ NaCl + 30 g L⁻¹ H₃BO₃ + 3.0 g L⁻¹ dextrin + 2.8 mL L⁻¹ salicyl aldehyde.

The depositions were 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 a 99.99 % pure zinc.

The thicknesses of the zinc coatings obtained from solution (II) were 20, 25 and 60 μm, approximately. The thickness of the zinc coating obtained from solution (I) was 25 μm, approximately.

The preparation of the copper cathodes consisted of alkaline degreasing at 70 °C, followed by acid etching (20 % H₂SO₄) at 50 °C. After each phase, the copper surfaces were rinsed with distilled water. This pretreatment of the electrode is important in order to obtain the same initial electrode surface prior to each experiment.

The zinc deposits were characterised by X-ray diffraction (XRD) analysis using a Siemens apparatus (type D 500) with Ni filtered Cu Kα radiation (35 kV and 20 mA) and a continuous scan speed of 0.02° 2θ s⁻¹.

The reflection was determined using a Reflectance Spectrophotometer Beckman UV 5240, *i.e.*, the specimen was illuminated by a beam whose axis was at an angle not exceeding 10° from the 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.

The topography of the surface was determined by a STM NanoScope III in air (maximum scan size was 880 × 880 nm²). The STM images were obtained in the constant current mode using a W tip electrochemically sharpened in 1 M KOH solutions. The bias voltage ranged from 100 to 110 mV and the tip current from 11 to 13 nA.

The average roughness of the surfaces of the samples along a special direction was calculated from the surface profiles for different scan sizes.¹³ The surface roughness obtained from the STM images is dependent of the scan size. With increasing scan size it initially increases, approaching a constant value for larger scan sizes. In our case, a constant value was obtained for scan sizes larger than 650 nm.

RESULTS AND DISCUSSION

The zinc coatings electrodeposited from the acid sulfate solution containing a dextrin/salicyl aldehyde mixture were bright, while the zinc coating obtained in the absence of these additives was mat.

The degrees of mirror and diffuse reflection as a function of visible light wavelength for the zinc coatings are shown in Fig. 1. The mirror reflection is an indicator of the surface brightness while the sum of the mirror and diffuse reflection represents the total reflection from the metal surface.

The degrees of mirror and diffuse reflection as a function of visible light wavelength for the mat zinc coating obtained from the acid sulfate solution in the absence of additives are shown in Fig. 1a. It can be seen from Fig. 1a that the reflection of light from this coating is mostly diffuse reflection. The mirror reflection from this coating is negligible.

The degrees of mirror and diffuse reflection as a function of visible light wavelength for the bright zinc coatings, thicknesses of 20, 25 and 60 μm, obtained from the acid sulfate solution containing the dextrin/salicyl aldehyde mixture are shown in Fig. 1b. The degree of mirror reflection reached 85 %, while the degree of the diffuse reflection from these coat-

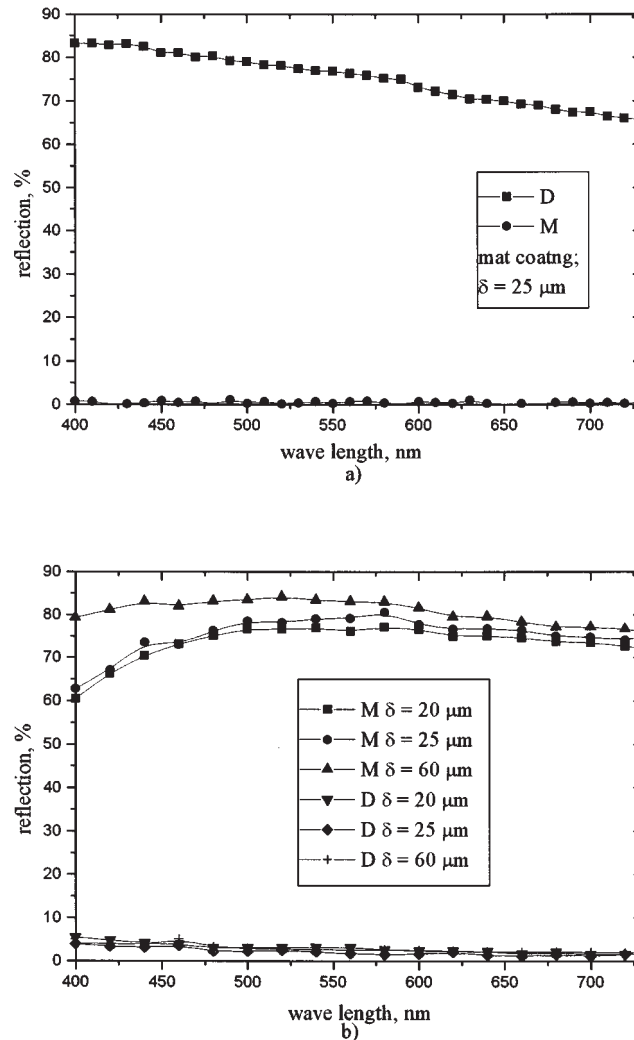


Fig. 1. The dependence of the degree of reflection on the visible light wavelength for zinc coatings: a) mat zinc coating, b) bright zinc coatings. M – mirror reflection, D – diffuse reflection.

ings is very small (up to 5 %). Also, it can be observed from this Figure that the degree of mirror reflection increases with increasing thickness of the bright zinc coatings.

The 3D (three-dimensional) STM images (880×880) nm² of the mat zinc coating and the 25 μm thick bright zinc coating are shown in Fig. 2a and Fig. 2b, respectively.

It can be seen from Fig. 2a that the surface of the mat zinc coating is very rough. The bright zinc coating, on the other hand, is relatively smooth (Fig. 2b), but without flat and mutually parallel parts of the surface, which were characteristic for electrochemically polished metal surface.

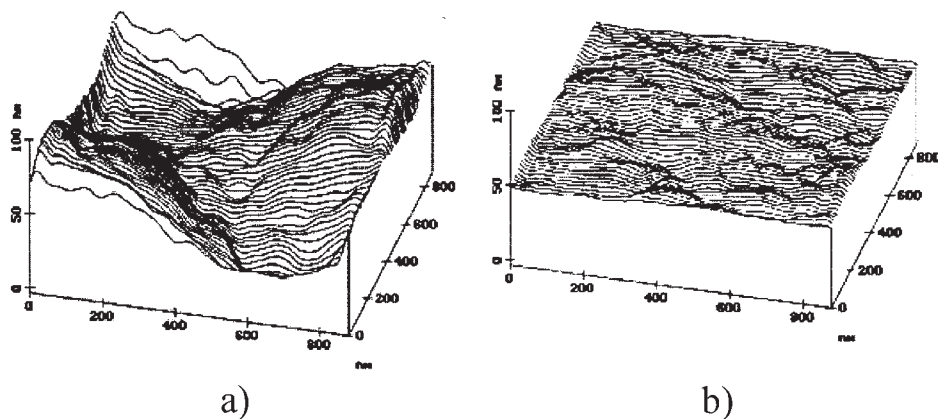


Fig. 2. 3D STM images of zinc coatings: a) mat coating of average roughness $R_a = 26.9$ nm, b) bright coating; $R_a = 5.2$ nm. The thicknesses of the observed zinc coatings were $25\ \mu\text{m}$. Scan size: $880 \times 880\ \text{nm}^2$.

The average roughness of these zinc coatings can be estimated from the surface (880×880) nm^2 , which showed that the mat zinc coating has a considerably greater average roughness than the bright zinc coating. The surfaces of bright zinc coatings of thicknesses 20 and $60\ \mu\text{m}$ were very similar to the surface of the bright zinc coating of thickness $25\ \mu\text{m}$ and, consequently, the STM images of bright zinc coatings are not presented.

The absence of small, flat, mutually parallel and parallel to the base parts of the surface demanded new investigations of the structure of these bright zinc coatings. In order to establish which structural features determine brightness of these zinc coatings, the surfaces of bright zinc coatings and the mat coating were investigated under different magnifications.

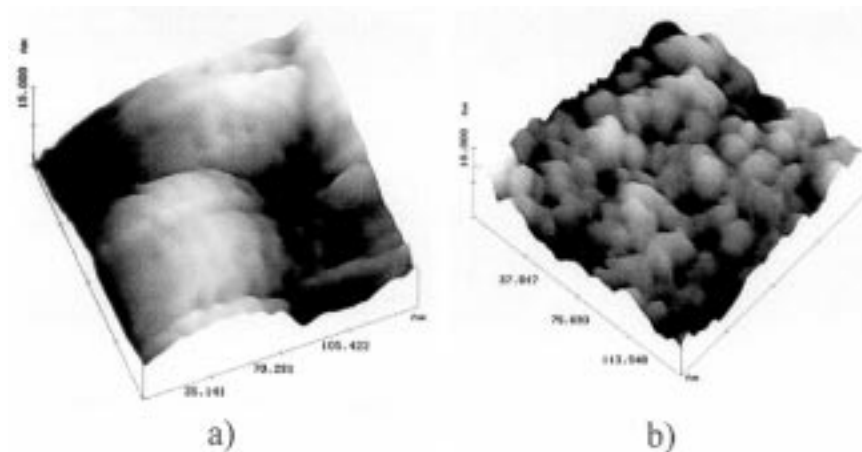


Fig. 3. 3D STM images of zinc coatings: a) mat coating, b) bright coating. The thicknesses of the observed zinc coatings were $25\ \mu\text{m}$. Scan size: $150 \times 150\ \text{nm}^2$.

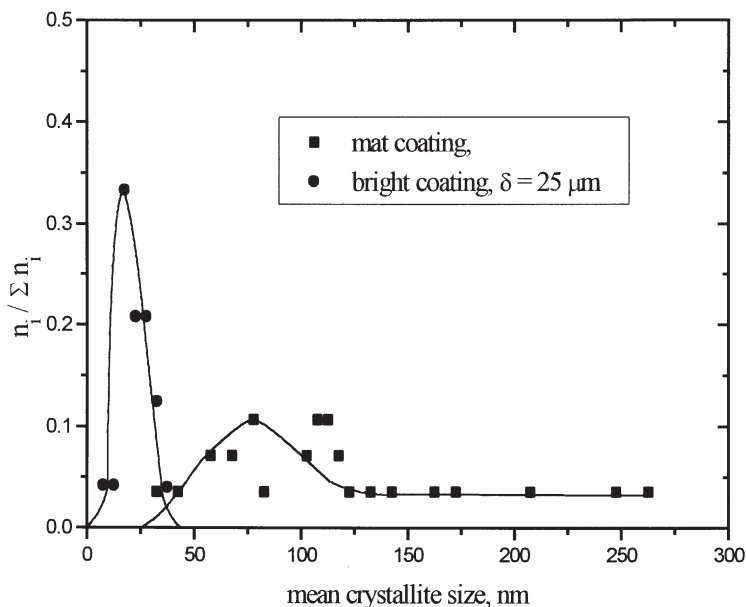


Fig. 4. Typical distribution of the zinc crystallites of the zinc coatings.

Analysis of the surfaces of zinc coatings showed that the bright zinc coatings are very fine-grained, while the mat zinc coating contained coarse crystallites. The STM images (150×150) nm² of the mat and the bright zinc coating of 25 μm thickness are shown in Fig. 3. The STM images are also presented in a three-dimensional form, where the light tones represent high areas in the image. STM analysis of the bright zinc coatings showed that the mean crystallite size was approximately 20 nm, and independent of the thickness of the coatings. The crystallite size of the mat zinc coating ranged from 50 to 300 nm in diameter. Typical size distributions of the zinc crystallites of the mat zinc coating and of the bright zinc coating of 25 μm thickness are shown in Fig. 4.

Analysis of the bright zinc coatings at even higher magnification led to the morphologies shown in Fig. 5. The analyzed surface was (50×50) nm². As can be seen from Fig. 5, surfaces of the bright zinc coatings are covered with hexagonal zinc crystals. It is shown by the STM software measurements that the roughness of the hexagonal zinc crystals is on the atomic level, *i.e.*, less than the atomic diameter of zinc (0.274 nm).¹⁴

The line sections analysis of these morphologies (*i.e.*, hexagonal zinc crystals) are shown in Fig. 6, from which can be observed that the top surfaces of the hexagonal zinc crystals are relatively flat and mutually parallel.

X-Ray diffraction (XRD) analysis of these coatings showed that the zinc crystallites in the bright zinc coatings are oriented in the (110) plane only. In other words, the zinc crystallites are deposited in a preferred way. This deposit type represents a single-crystal deposit. A typical XRD pattern of a bright zinc coating is presented in Fig. 7b. The X-ray diffraction analysis of the mat zinc coating (Fig. 7a) showed that the orientation of the mat zinc coating is random.

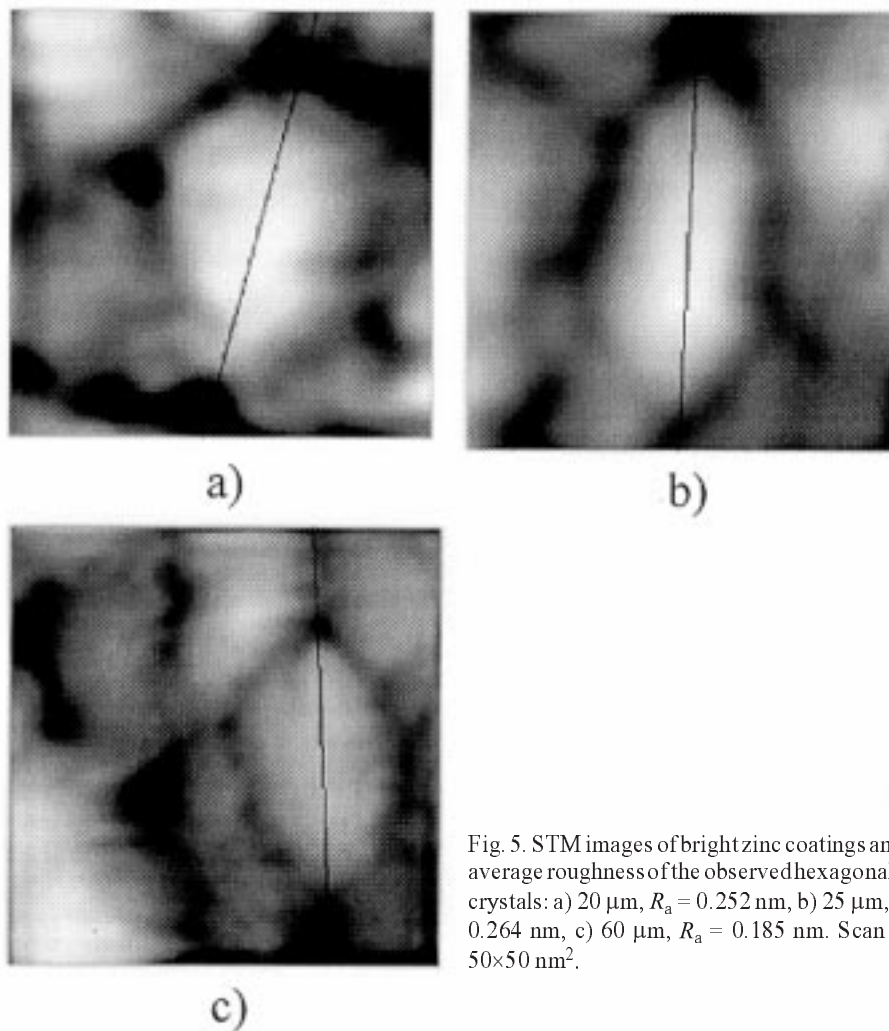


Fig. 5. STM images of bright zinc coatings and the average roughness of the observed hexagonal zinc crystals: a) 20 μm , $R_a = 0.252$ nm, b) 25 μm , $R_a = 0.264$ nm, c) 60 μm , $R_a = 0.185$ nm. Scan size: 50×50 nm².

According to Velinov *et al.*¹⁵ random orientation of a deposit obtained from a pure zinc sulfate solution is the result of autoinhibition of the cathodic process caused by colloidal zinc hydroxide generated within the cathodic layer.

The deposition of bright coatings with a predominance of the preferred (110) orientation can be explained by the theory of Pangarov and Vitkova,¹⁶ who showed theoretically and experimentally that the main cause for a change in the texture type of hexagonally crystallizing metals is crystallization overpotential, and that the texture type requiring the smallest energy will develop.

Finally, it was shown that the surface of the bright zinc coatings does not consist of small, flat and mutually parallel surface parts, which were characteristic for an elec-

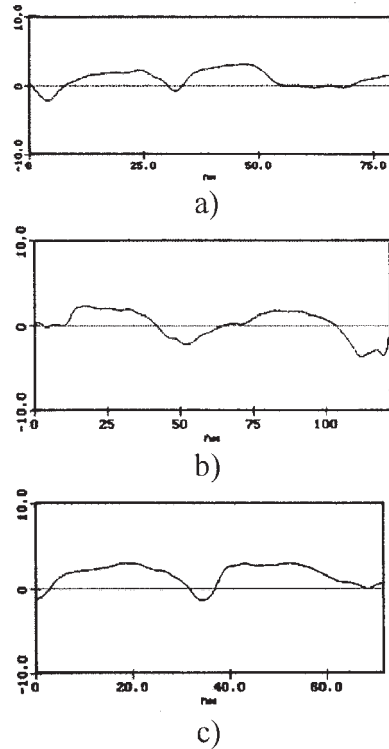
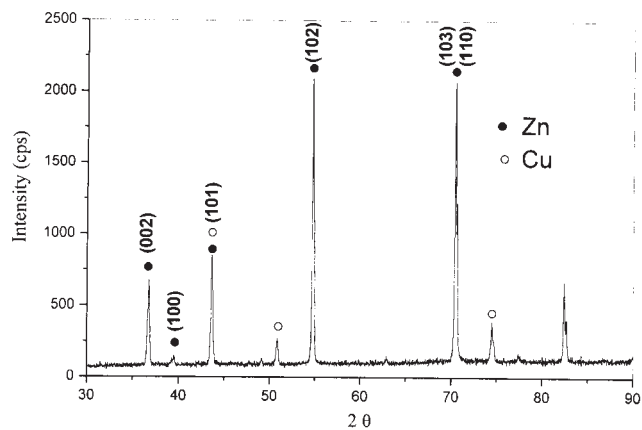


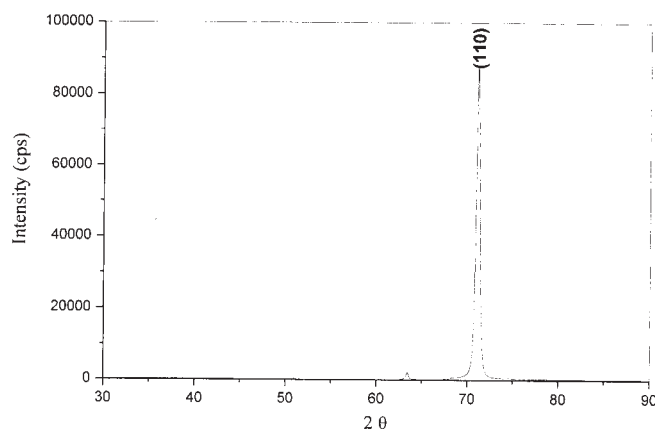
Fig. 6. Typical surface profile of bright zinc coatings from $50 \times 50 \text{ nm}^2$ STM images: a) $20 \mu\text{m}$, b) $25 \mu\text{m}$, c) $60 \mu\text{m}$.

trochemically polished copper surface.¹² Bright zinc coatings are very fine-grained, with hexagonal zinc crystals, the tops of the planes of which are flat and mutually parallel. The roughness of these hexagonal zinc crystals is on the atomic level. Hence, the mirror reflection is obtained from these flat and mutually parallel hexagonal zinc crystals, which exhibit a smoothness on the atomic level. The zinc crystallites in the bright zinc coatings were oriented in the (110) plane only. According to Weil *et al.*,⁹ single-crystal deposits are completely bright. It is known that the reflection of light from the surface of a deposit depends on the state of the base crystal structure (substrate), bath composition, as well as on the nature of the electrodeposited metal. In our case, the mirror reflection from the bright zinc coatings reached 85 %. Hence, a mirror reflection of 85 % is the real value which can be expected for bright zinc coatings electrodeposited from an acid sulfate solution.

Hence, the structural details which determine the brightness of an electrochemically polished metal surfaces are different to those of bright metal coatings obtained by electrodeposition in the presence of brightening agents. In the first case, the brightness of the electropolished metal surface (copper example) is determined by the large areas of flat and parallel to the base structures, which exhibited smoothness on the atomic level. In the second case, the brightness of metal coatings obtained by electrodeposition (zinc example) is determined by the fine-grained deposit, *i.e.*, hexagonal zinc crystals



a)



b)

Fig. 7. XRD patterns of zinc coatings: a) mat coating, b) bright coating. The thicknesses of the observed zinc coatings were 25 μm . The copper peaks on the XRD patterns result from the copper substrate.

the top planes of which are flat and mutually parallel with a smoothness on the atomic level. The differences in structures between the studied bright metal surfaces can be explained, in the first place, by the fact that electropolishing is the opposite process to electrodeposition.

ИЗВОД

СТРУКТУРА СЈАЈНИХ ПРЕВЛАКА ЦИНКА

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Испитана је структура сјајних превлака цинка исталожених из киселог сулфатног електролита са додатком декстрина и салицил алдехида. Показано је да је површина сјајних превлака покривена хексагоналним кристалима цинка, чији врхови су равни и међусобно паралелни, и који су глатки на атомском нивоу. Рендгенско-дифракциона анализа сјајних превлака цинка је показала да су кристали цинка оријентисани само у (110) равни.

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