

Structural study of Ag layers deposited from solution of silver sulphite complexes

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When silver coating deposition proceeds via the discharge of silver sulphite complexes, this coating is of a rather good quality. The application of cathodic current pulses was found to increase the degree of microcrystallinity of Ag layers. This fact can be illustrated, particularly, by a decrease of the dimensions of Ag crystallites from 0.7–5 μm at a constant current to 0.1–0.5 μm at a pulse current, i. e. approximately tenfold. Unfortunately, the problem of porosity of Ag coatings electrodeposited from sulphite solutions remains unsolved. The porosity of these coatings makes 1–3% of its surface.

Key words: silver, sulphite solutions, SEM, X-ray microanalyzer, porosity

INTRODUCTION

Silver is one of the commonly used functional metals for various engineering applications due to its excellent electrical and thermal conductivity and good ductility. However, the use of mainly cyanide solutions for the deposition of silver coatings on various substrates essentially limits its scope of application. Therefore, from the practical point of view, it is important to replace the high-toxic cyanide solutions by less or nontoxic solutions. Among these, sulphite-containing solutions offer serious advantages.

There are some reports in the literature on silver plating from solutions of this kind [1–5]. Most publications on this subject are related with applicability. The results of electrochemical study have recently been presented in our publications [3–5]. Particularly, dependence of the exchange current densities of silver on the concentration of free sulphite ions in a series of isopotential solutions and a reasonable mechanism of electrode reaction have already been studied.

It is well known that knowledge of the structure and composition of the electrode surface and the electrodeposited

layers is of great importance for explaining the mechanism of electrode reactions under study and the most important properties of these overlayers. It is obvious that insights into the structural properties of silver deposits may allow not only improving the technological parameters of the silver plating process from sulphite solutions, but also expanding the area of its applicability.

The purpose of the present communication is to establish the main structural characteristics of silver coatings electrodeposited from sulphite solutions. Having in mind that, in some cases, silver coatings can be somewhat porous, a correlation between the results obtained with different substrates – silver and copper – will be made as well.

EXPERIMENTAL

The solutions were prepared from distilled water, p.a. qualification salts Na₂SO₃ and Ag₂SO₄. The electrolytes were prepared freshly before every new experimental series because of the rapid sulphite ion oxidation by air oxygen. All experiments were performed at a temperature of 20 °C.

The deposition of silver was performed galvanostatically or with a pulse current at 5 mA/cm² on copper and silver

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plates using the AUTOLAB 302 system and the control device program GPS for a computer. The mode of the pulse current was as follows: duration of each current pulse was 0.1 s, followed by a 0.5 s break. The total duration of electrolysis in both cases was 30 min. Surface morphology was investigated with the LEO 435VP and Philips XL 30 ft. 6 scanning electron microscopes.

The calculated thickness of the silver layer was close to 10 μm .

RESULTS AND DISCUSSION

Figure 1 shows representative SEM images of the morphology of silver layers electrodeposited at a constant current (5 mA/cm²) (a) or using a pulse current (b). As one can see, when a pulse current was used, the linear dimensions of crystallites were smaller and ranged from 0.7 to 5 μm (a) and from 0.1 to 0.5 μm (b).

A closer examination of the SEM images obtained from the surface of a silver sample deposited with a pulse current showed that, even in this case, the surface of the electrode had some regions where the deposits seemed to be rather inhomogeneous (Fig. 2). It is quite possible that the coating consisted of pure silver, but this inhomogeneity was due to the different orientation of Ag crystallites. For a more detailed analysis, different magnification of SEM images was applied. Part of the obtained results is presented in Fig. 2a, b. It should

be noted that in these cases silver was electrodeposited on a copper substrate.

Then, using SEM with an X-ray microanalyzer, we found that in the sampled regions, as shown in Fig. 2b, indications of the presence of copper were revealed (Fig. 3). Bearing in mind that copper ions are absent in the working solution and that copper deposition from sulphite solutions is rather difficult, it can be concluded that the X-ray microanalyzer fixed the copper phase from the copper substrate. In some cases, a signal indicating the presence of Na in the pore was identified (Fig. 3b). On the basis of our experimental data, this fact cannot be reasonably explained.

As for the contents of copper in silver coating pores, it can be rather roughly supposed that their values can be approximately correlated with the total area of these pores.

To check additionally whether the determination of Cu signals in the pores of Ag deposits was not caused by the contamination of reagents with Cu salts, separate experiments were carried out with a pure silver substrate. In this case, electrolytical silver was also porous (Fig. 4). However, with the use of an X-ray microanalyzer, it was shown that the elemental composition of the incorporated particles in the pores differed from data on Ag coatings on the Cu substrate. One can see in Fig. 5 that a signal characteristic of sulphur was revealed in this case. Such a finding may be due to Na₂SO₃ or its degradation compounds. Of course, that such a supposition should be strongly verified in future. The possibility of

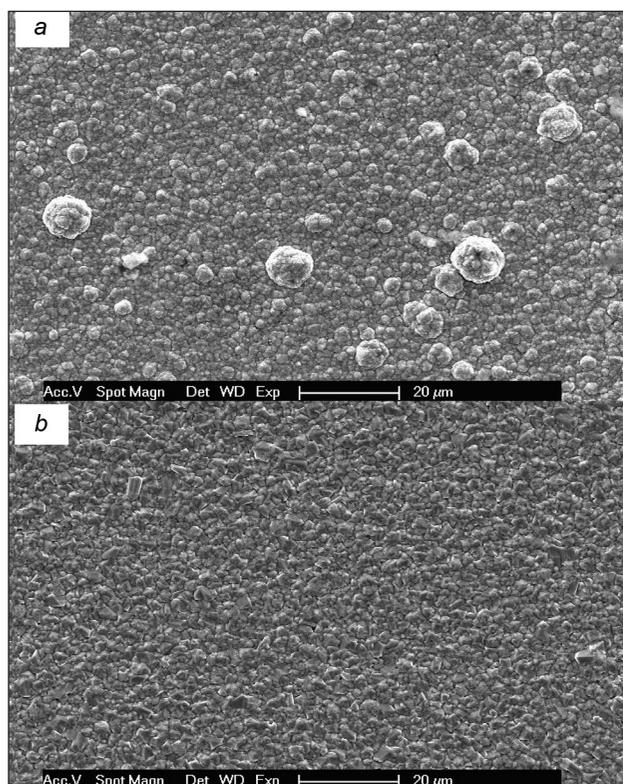


Fig. 1. SEM images of the morphology of silver coatings. Cathodic current density: 5 mA/cm². The current mode: constant (a) or pulse (b)

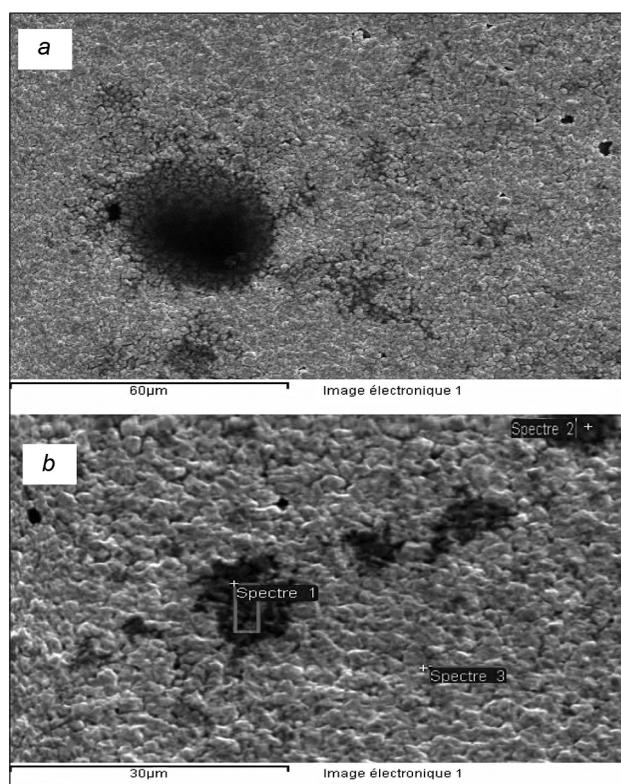


Fig. 2. SEM images of the morphology of silver coatings obtained with the pulse current at different magnification

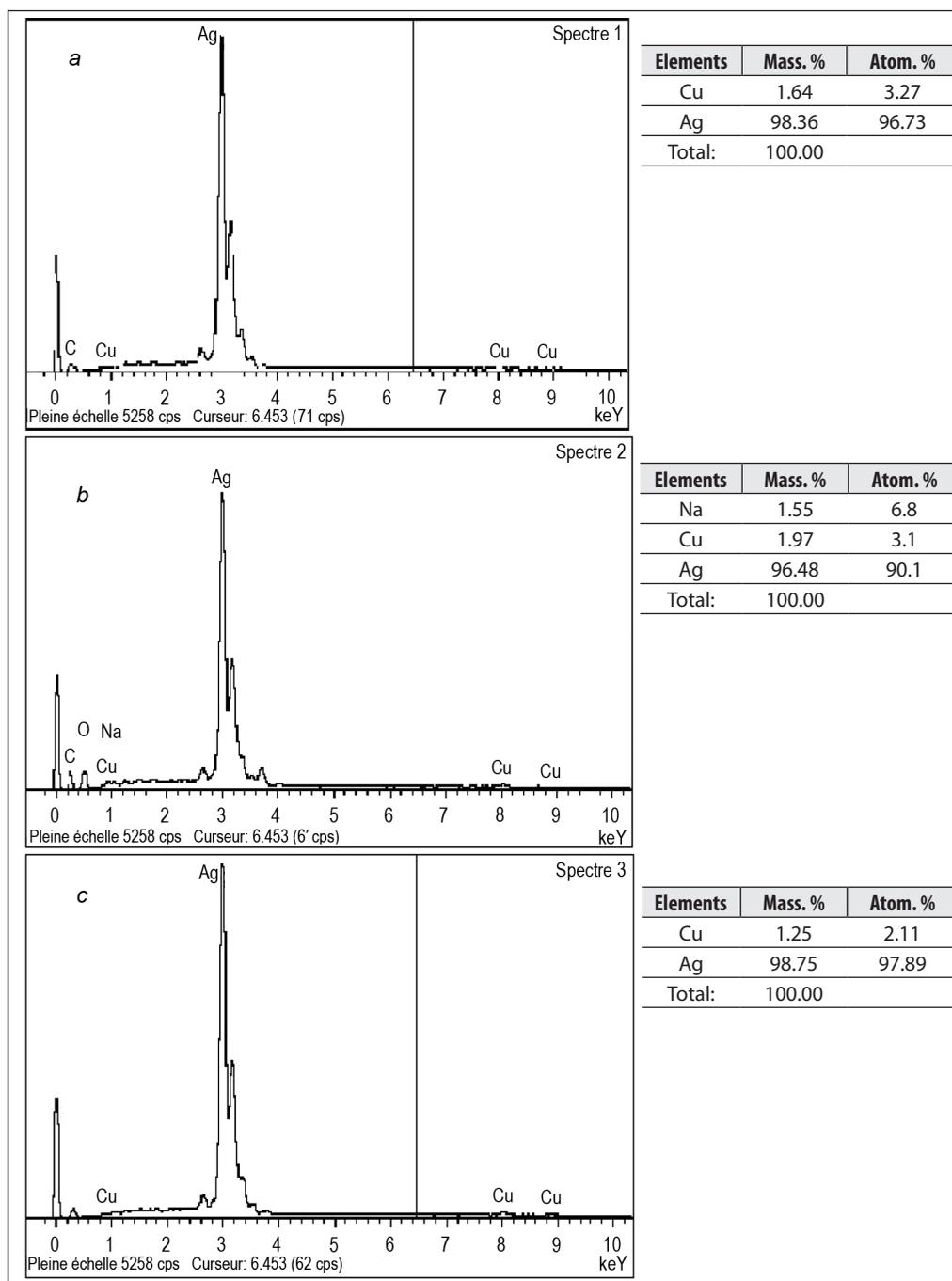


Fig. 3. Elemental composition of silver deposits determined by SEM with X-ray microanalyzer. These spectra were obtained from the sampled separate regions (Fig. 2b)

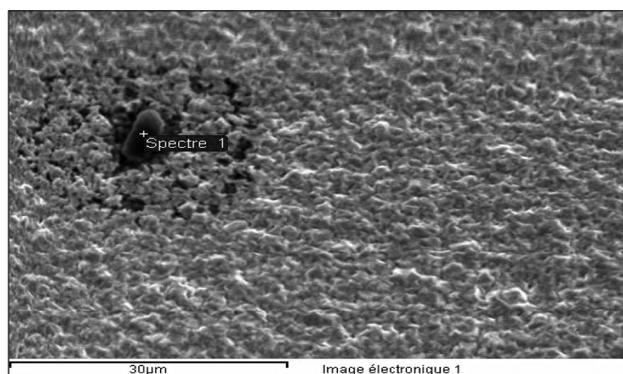


Fig. 4. The same as in Fig. 2, but with the silver substrate

the formation of surface silver sulphide cannot be ruled out, either.

When the sampled region was chosen in the area of a homogeneous Ag coating, the same analysis showed a 100% pure silver surface.

From the above experimental data we can conclude that when silver deposition proceeds via the discharge of silver sulphite complexes, the coating is of a rather good quality. Application of cathodic current pulses was found to increase the degree of microcrystallinity of Ag layers. This fact can be illustrated, particularly, by the decrease of the dimensions of Ag crystallites from 0.7–5 µm at the constant current to 0.1–0.5 µm at the pulse current, i. e. approximately tenfold.

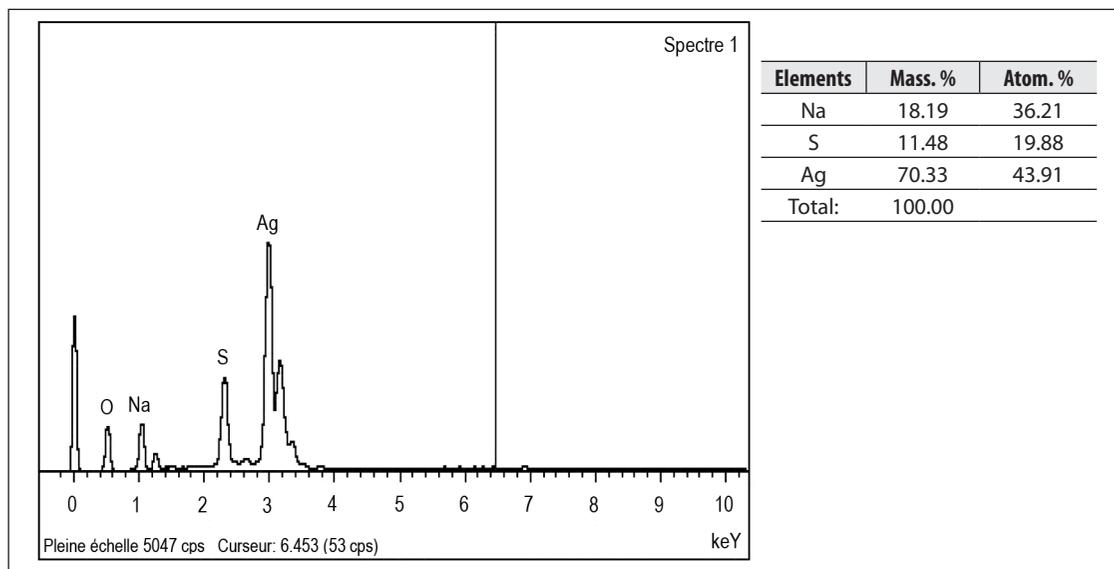


Fig. 5. The same as in Fig. 3, but for the sampled region from Fig. 4

Unfortunately, the problem of porosity of Ag coatings electrodeposited from sulphite solutions remains unsolved. The porosity of these coatings makes 1–3% of their surface.

CONCLUSIONS

1. We succeeded in obtaining microcrystalline galvanic silver layers by reducing silver sulphite complexes. Such layers are of a higher quality when the pulse current is used.

2. However, some porosity (ranging within 1–3% in different regions of the layer) is still present.

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SIDABRO GALVANINIŲ DANGŲ, NUSODINTŲ IŠ KOMPLEKSINIŲ SIDABRO SULFITINIŲ TIRPALŲ, STRUKTŪROS TYRIMAI

Santrauka

Redukuojant sidabro sulfitinius kompleksus, katodo paviršiuje formuojasi gana kokybiška sidabro galvaninė danga. Naudojant impulsinę srovę, sidabro dangos kokybė (smulkiakristališkumas) itin pagerėja. Panaudojus nuolatinę elektros srovę, kai kurių sidabro kristalitių matmenys pakinta nuo 0,7 iki 5 μm , o panaudojus impulsinę – sidabro kristalitių sumažėja beveik 10 kartų (0,1–0,5 μm). Deja, reikėtų pabrėžti, kad iš sulfitinių kompleksų nusodinant sidabro galvanines dangas porėtumo problemos lieka neišspręstos. Šių dangų akytumas skirtingose paviršiaus vietose kinta 1–3 %.