

THE PECULIARITIES OF MORPHOLOGY OF SILVER PENTAGONAL MICROCRYSTALS ELECTRODEPOSITED UNDER POTENTIOSTATIC CONDITIONS

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The interest in silver microcrystals is associated with their numerous practical applications some of which are based on bactericidal properties of this metal. Thus, preparations based on colloidal silver were used in the disinfection and conservation of water and, in concentrations of 0.05–0.1 ppm, demonstrated complete sterilization of even water strongly contaminated with bacteria. These properties can be considerably intensified by increasing the specific surface of particles.

Certain results of studying the morphological peculiarities of the structure of silver pentagonal crystals formed at electrocrystallization under galvanostatic conditions are shown in [1]. However, in this case, the maintenance of a constant current during the electroplating actually led to permanent variations of the true current density of crystal growth due to the changes in their overall surface. The present work shows the results of studying the growth of silver microcrystals under the potentiostatic conditions that ensure a constant growth rate in the major period of crystallization.

Solutions used in silver deposition were prepared with distilled water and contained 35 g/l silver nitrate and 150 g/l ammonium sulfate. The solution pH was brought to 9.8–10.0 by adding 25% aqueous ammonia. Reagents were of the reagent grade of purity. Silver was deposited under potentiostatic conditions at the cathodic overpotential in the range from 100 to 120 mV. The potentiostat Micro Compact PRO was developed in the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences and controlled by a computer with the IPC2000 software. The substrate represented mechanically polished stainless steel and covered with titanium nitride by ion-plasma spraying. The morphology of synthesized silver crystals was studied by scanning electron microscopy (LEO 1455 VP).

The problem of electrochemical methods for synthesizing coarse pentagonal silver crystals with good reproducibility is so far debated. Classical experiments by N. Pangarov on the pulse deposition of silver from a nitrate solution onto a platinum substrate [2] have shown that at overpotentials of 100 mV and higher, crystals of the pentagonal symmetry appeared in the deposits.

Our studies confirmed this result and showed that at the same overpotentials (100...120 mV), pentagonal microcrystals were formed at electroplating on steel covered with titanium nitride and the morphology of synthesized objects was unambiguously determined by the overpotential in the given range.

Thus, at $\eta = 100$ mV, the pentagonal microcrystals grew by the layer-by-layer mechanism (Fig. 1a, 1b). The layer-by-layer growth of such crystals proceeded by the propulsion of the crystallization front formed as “terraces” parallel to the crystal surface. This was accompanied by the macroscopic growth in the direction normal to the substrate and the microscopic growth in the tangential direction.

For $\eta = 110$ mV, pentagonal microcrystals with a void inside were revealed (Fig. 1c). The energetics of the formation of a void in a pentagonal crystal of the electrolytic origin during its evolution was considered in [3], and the mechanism of the void formation was proposed in [4]. According to a model [4], an needle like pentagonal crystal represents an isotropic linear elastic cylinder with the coaxial positive disclination of a strength $\omega = 7^\circ 21'$. This disclination induces axial stresses in the cylinder, i.e., compression stresses near the cyl-

inder axis and tensile stresses near its surface. Internal stresses of such nature make the origination of prismatic dislocation loops of subtraction in the cylinder and their ejection outside to form a void at the cylinder end advantageous as regards the energy [4]. At the lower overpotentials, the stresses are less intense and no void forms.

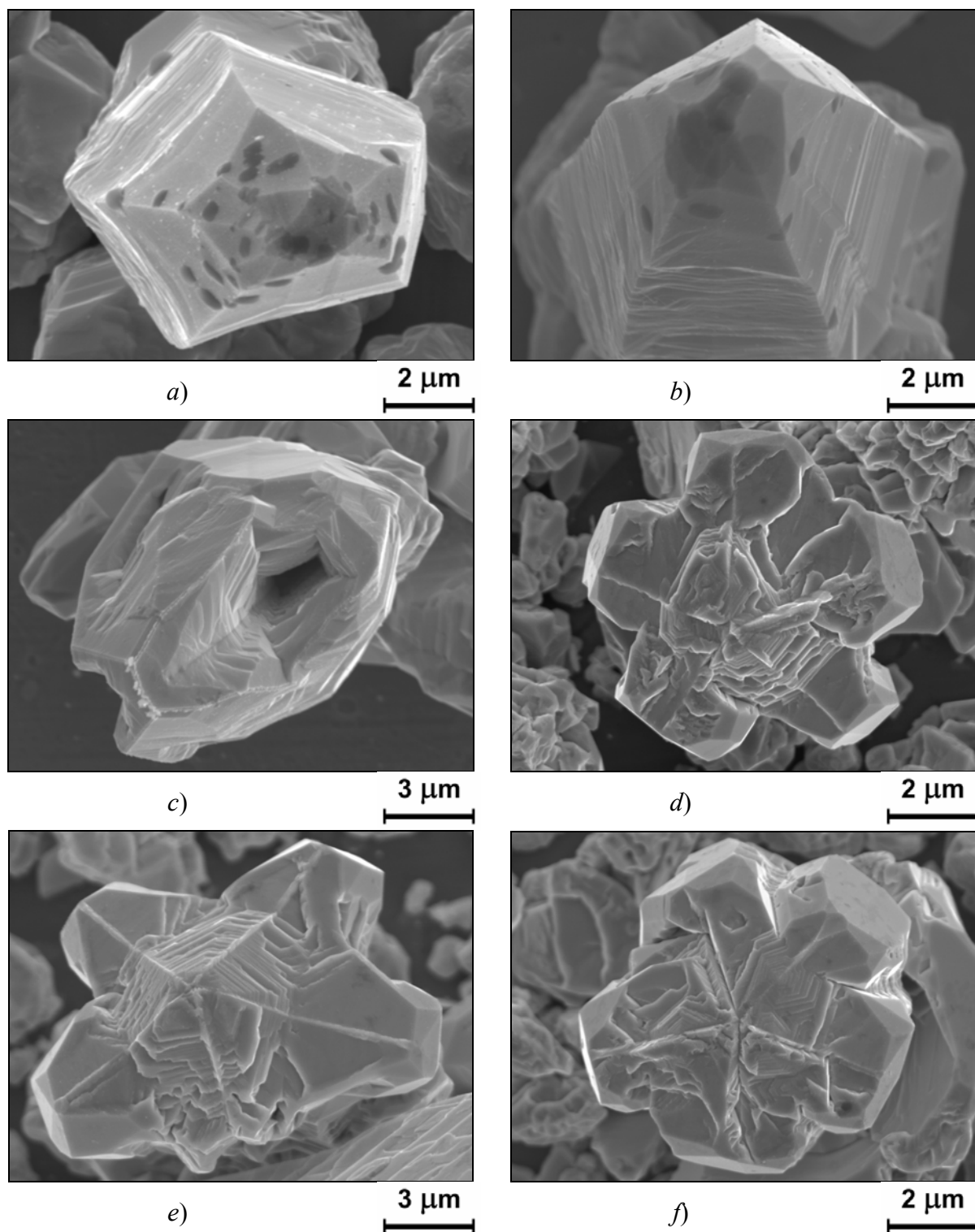


Fig. 1. Pentagonal microcrystals formed at silver electrocrystallization under potentiostatic conditions on an inert substrate: (a – c) pentagonal microcrystals grown by the layer-by-layer mechanism (a, b) without inner void (cathodic overpotential 100 mV) and (c) with a void (cathodic overpotential 110 mV); (d–f) pentagonal “stars” (cathodic overpotential 120 mV).

At $\eta = 120$ mV, the formation of pentagonal “stars” was observed (Fig. 1d-1f). For these objects, the habitus was observed to change due to the active growth by the layer-by-layer mechanism in the sites of maximum concentration of elastic stresses, i.e., near defects of the disclination type (axis of 5-fold symmetry) (Fig. 1d, 1e) and in the vicinity of the twin boundary (Fig. 1f). It deserves mention that in our earlier experiments on copper plating, the above morphology was not revealed and thus is observed here for the first time.

Thus, by varying the cathodic overpotential, it is possible to obtain silver microcrystals with different morphology. The shown experimental results on the dependence of the revealed morphological types on the cathodic overpotential are well reproducible and, hence, allow one to unambiguously determine the technology of their synthesis. Some of the formed morphological types are promising for practical use due to the unique biocide properties of silver.

Acknowledgments

This study was supported by the Analytical Targeted Program «Development of Scientific Potential of Higher Education» of the Ministry of Education and Science of the Russian Federation (project no. 2.1.1/1271); Federal Targeted Program «Scientific and Educational Personnel of Innovative Russia» (state contract no. П2620) and Grant of President of Russia Federation for State Support of Young Russian Scientists – Doctor of Science (project no. МД-902.2010.8)

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THE EXPERIMENTAL PROOF OF THE EVOLUTION OF ELECTROLYTIC SILVER MICROCRYSTALS THROUGH HIGH-TEMPERATURE STATE

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Based on experimental data on the electrodeposition of metals, a model was previously proposed according to which the structure, dimensions, shapes, and scenario of the development of microcrystals during their electrolytic growth are determined by features of the mass and heat transfer in the crystalline islands formed in the initial stages of electrocrystallization [1]. An analysis of the results obtained in [1] shows that, irrespective of the regime of electrodeposition, the temperature in a growing island exhibits a sharp increase in a certain interval of its dimensions and can reach the melting point. After attaining a maximum value, the temperature of the growing microcrystal sharply drops to a substrate temperature level already when the island size is doubled compared to that at the onset of temperature increase. It was pointed out [1] that a maximum temperature in the growing island can be reached by