At $\eta = 120$ mV, the formation of pentagonal “stars” was observed (Fig. 1*d*-1*f*). 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. 1*d*, 1*e*) and in the vicinity of the twin boundary (Fig. 1*f*). 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.

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References

1. I. S. Yasnikov, I. I. Tsybuskina Morphology of Silver Single Crystals Obtained by Electrodeposition // Technical Physics. – 2008. – Vol. 53, No. 11. – P. 1515 – 1518.
2. N. A. Pangarov Crystal Growth // Moscow: Nauka, 1974 [in Russian].
3. I. S. Yasnikov, A. A. Vikarchuk Evolution of the Formation and Growth of a Cavity in Pentagonal Crystals of Electrolytic Origin // Physics of the Solid State – 2006. – Vol. 48, No. 8. – P. 1433 – 1438.
4. A. L. Kolesnikova, A. E. Romanov Stress relaxation in pentagonal whiskers // Technical Physics Letters – 2007. – Vol. 33, No. 10. – P. 886 – 888.

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 varying the heat transfer conditions, in particular by increasing the local current density and/or decreasing the thermal conductivity of the substrate.

An experimental proof of the local increase and subsequent drop in the temperature during evolution of the growing island was presented in [2], where it was demonstrated that a change in the crystal habit of pentagonal small particles of copper in the course of electrodeposition was determined by the conditions of heat exchange with the substrate. However, that proof was indirect and, hence, an independent experimental proof would allow the aforementioned behavior of the temperature to be considered more reliably substantiated. This work presents such experimental evidence, which was obtained in investigations of the microcrystals of silver grown using the method of electrodeposition.

The electrodeposited silver microcrystals were obtained using an electrolyte based on a silver nitrate solution, which contained 35 g/l $AgNO_3$, 150 g/l ammonium sulfate $(NH_4)_2SO_4$, and 25% aqueous ammonia NH_4OH in an amount corresponding to pH 9.8–10.0. The electrodeposition of silver was carried out in a potentiostatic regime with a cathode overvoltage of $\eta = 80\ldots200$ mV. The substrates were made of polished stainless steel with ion plasma sprayed titanium nitride coating. The morphology of electrolytically grown silver crystals was studied by scanning electron microscopy (SEM) on a LEO 1455 VP instrument.

SEM investigation of the surface of silver microcrystals showed that the variety of morphological forms includes microcrystals with voids (Fig. 1). These microcrystals had the shape of either regular polyhedra (Fig. 1*a*) or pentagonal microcrystals with defects of the disclination type (Fig. 1*b*). In order to obtain contrast images of the surface of voids in microcrystals, it was necessary y to increase the yield of secondary electrons from this surface to the detector. For this purpose, the sample holding table on which a substrate with microcrystals was mounted was oriented at a certain angle relative to the probing electron beam. This angle was experimentally chosen so as to ensure the optimum image contrast. Fairly high contrast was provided when the table surface deviated by ~8°–10° from the horizontal position.

SEM images obtained with good contrast showed that the surface of voids in microcrystals exhibits pronounced dendrite morphology (Fig. 2). The formation of dendrites during electrodeposition is possible as a result of the accelerated crystallization under strongly nonequilibrium conditions [3, 4]. There are two possible mechanisms by which dendrites are formed [3, 4], i.e., (i) due to the excess of adatoms that build into the crystal lattice and (ii) as a result of the heating of a growing microcrystal up to the melting point followed by rapid cooling, that is, under the conditions of accelerated crystallization. Let us consider the probability of each mechanism in more detail.

(i) A crystal with a void is analogous to the Faraday cage or an electrostatic screen [5]. According to the Faraday theorem, the electric field vanishes inside a hollow metal object and, hence, adatoms cannot be supplied to the void, the more so in excess amount. Therefore, the formation of dendrites in the void in a silver microcrystal according to the first mechanism isunlikely.

(ii) As is known, the heating of a metal to the melting point followed by rapid cooling (quenching) can lead to retention of an amorphous state. However, the ability of pure metals to amorphization is only manifested at a very high rate of cooling. For example, inpure nickel this rate is on the order of $\sim10^{10}$ K/s [6].

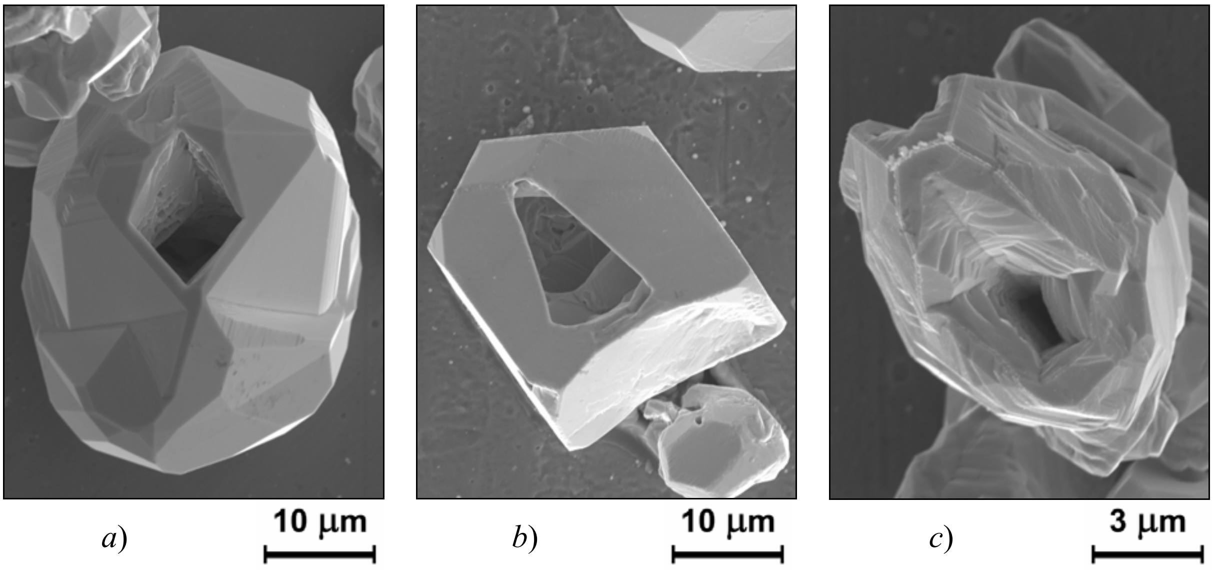

Fig. 1. SEM images of electrodeposited silver microcrystals with voids: (*a, b*) crystals having a polyhedral habit; (c) crystal containing a disclination type defect.

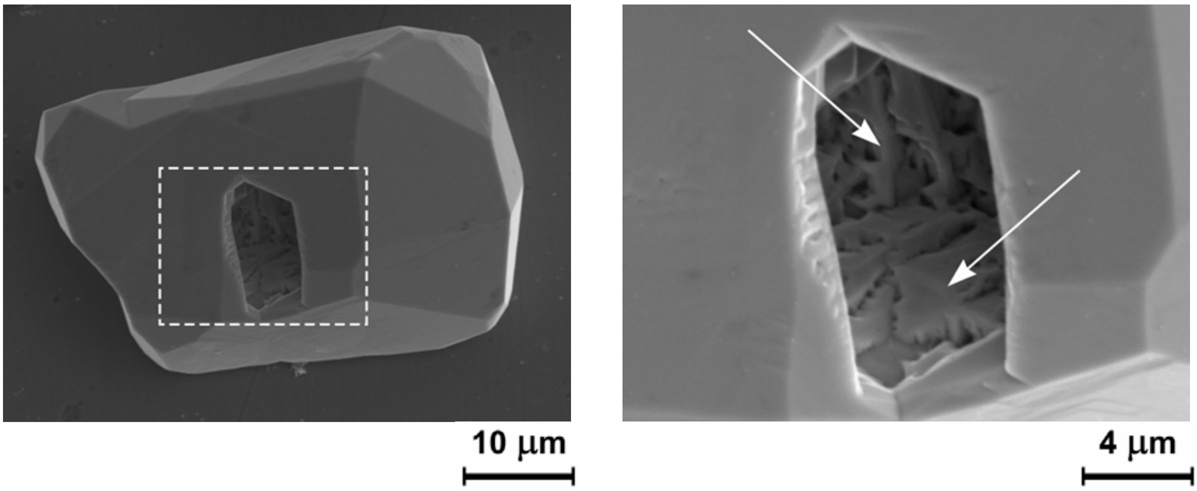

Fig. 2. Dendrite morphology of the void surface revealed by SEM in an electrodeposited silver microcrystal: (*a*) SEM image of a silver microcrystal with a void (dashed square indicates the region presented on a greater scale in micrograph (*b*); (*b*) SEM image with improved contrast, which reveals dendrites (indicated by arrows) in the void.

Estimations based on an analysis of the equations describing the temperature controlled evolution of growing islands according to model [1] show that the period of time during which the island occurs at a high temperature is within $10^{-3}…10^{-1}$ s [7] and, on cooling from the high temperature state at ~ 10^3 K, the cooling rate amounts to ~ $10^4…10^6$ K/s. This cooling rate is by no means sufficient for retaining the amorphous state in a pure metal. Nevertheless, the process of crystallization at these rates possesses a strongly nonequilibrium character, which can result in the formation of dendrites [4]. For example, the formation of fractal structures (dendrites) in some alloys (in particular, of the Fe-B system) was observed in experiments and confirmed by computer simulations at a cooling rate of about 10^6 K/s [8].

Thus, dendrites can form in the voids of electrodeposited microcrystals as a result of the local increase and subsequent drop in the temperature during evolution of the growing islands [9]. SEM images (Fig. 2) provide additional evidence for the validity of a model proposed previously [1], according to which the formation of regular and pentagonal crystals is only possible if the evolution of a growing island passes via a high temperature state.

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References

1. A. A. Vikarchuk, I. S. Yasnikov Specific Features of Mass and Heat Transfer in Microparticles and Nanoparticles Formed upon Electrocrystallization of Copper // Physics of the Solid State – 2006. – Vol. 48, No. 3. – P. 577 – 580.
2. I. S. Yasnikov, A. A. Vikarchuk Effect of Heat Exchange on the Habit of Electrodeposited Pentagonal Microcrystals // Technical Physics Letters. – 2006. – Vol. 32, No. 10. – P. 825 – 826.
3. Yu. D. Gamburg Electrochemical Crystallization of Metals and Alloys // Yanus-K, Moscow, 1997 [in Russian].
4. W. C. Winegard An Introduction to the Solidification of Metals // Institute of Metals, London, 1964.
5. D. V. Sivukhin, General Course of Physics, Vol. 3: Electricity // Fizmatlit, Moscow, 2002, pp. 50–56 [in Russian].
6. K. Suzuki, H. Fujimori and K. Hashimoto Amorphous Metals // Tokyo, 1982.
7. I. S. Yasnikov Mechanism of the Formation of Cavities in Icosahedral Metallic Small Particles of Electrolytic Origin // Physics of the Solid State – 2007. – Vol. 49, No. 7. – P. 1224 – 1228.
8. L. P.Tarabaev, V. O. Esin // Russian Metallurgy (Metally) – 2007. – No. 6. - P. 478.
9. I. S. Yasnikov One Experimental Proof of the Evolution of Electrodeposited Microcrystals via a High-Temperature State // Technical Physics Letters. – 2009. – Vol. 35, No. 12 – P. 1097 – 1099.

THE POSSIBILITY OF THE OPENING OF CAVITIES IN SMALL ICOSAHEDRAL ELECTROLYTIC-METAL PARTICLES BY INCREASING THE TEMPERATURE

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Previous investigations show that a disclination is present at the center of small icosahedral electrolytic copper particles and it can lead to the formation of a cavity in them. On the basis of these investigations, an effective technique was developed for the opening of internal cavities in small icosahedral particles by chemical etching of their surface [1]. This technique underlies a filter that is a metallic mesh microframe with an adsorbing layer consisting of small metal particles with a cavity [2].

However, the chemical etching of the surface of small particles that leads to the opening of the cavity is sometimes inconvenient in applications, because it is impossible to completely remove the etchant components after the opening procedure and the presence of these components changes the adsorption properties of the mesh filter [2].