Rev. Adv. Mater. Sci. 55 (2018) 78-81

COPPER PENTAGONAL MICROPYRAMIDS GROWN BY MECHANICALLY ACTIVATED ELECTRODEPOSITION

A.A. Vikarchuk[1], N.N. Gryzunova[1], M.Yu. Gutkin[2,3,4] and A.E. Romanov[4]

[1]Togliatti State University, Belorusskaya 14, Togliatti, 445667, Russia
[2]Institute of Problems of Mechanical Engineering, Russian Academy of Sciences, Bolshoj 61, Vasil. Ostrov, St. Petersburg, 199178, Russia
[3]Department of Mechanics and Control Processes, Peter the Great St. Petersburg Polytechnic University, Polytechnicheskaya 29, St. Petersburg, 195251, Russia
[4]ITMO University, Kronverskyi 49, St. Petersburg 197101, Russia

Received: December 22, 2018

Abstract. The formation of copper pentagonal micropyramids (PMPs) with high (multiatomic) spiral growth steps, which are grown by electrocrystallization with mechanical activation of the cathode, is studied experimentally. A new spiral-layer growth mechanism for the formation of such PMP is proposed. It is shown that PMPs grow on flat pentagonal microcrystals (PMCs) formed initially and containing fivefold twins with one of the twin boundaries being inclined by the angle of 35°16′ to the {110}-type substrate crystallographic plane. Such crystal geometry causes an inclined growth step on the PMC surface. The preferential deposition of metal atoms on this step leads to the spiral-layer PMC growth and the formation of PMPs with a structure inherited from the PMCs.

1. INTRODUCTION

Metal particles with five-fold symmetry axes (in other words, pentagonal microcrystals (PMCs)) possess unique properties and are of great scientific interest [1,2]. One of the most convenient methods of growing PMCs is the electrodeposition of metals from electrolyte solution [3-6]. Varying the electrolysis conditions (overvoltage at the cathode, current density, pH, temperature and composition of the electrolyte), it is possible to vary the size of PMCs by 3-4 orders of magnitude and to control their structure, texture and surface morphology. In particular, it is possible to grow PMCs of different morphology [5,6].

Using our own technique [7,8] of metal electrodeposition with simultaneous mechanical activation of the crystals growing on the cathode with abrasive microparticles moving in the electrolyte, we fabricated copper layers and coatings composed of pentagonal micropyramids (PMPs). The PMPs had a five-fold symmetry axis and the developed surface in the form of multiatomic steps of growth (Fig. 1). Such coatings are of great practical interest, for example, in application to low-temperature catalysis [7,8].

In the present work, we report experimental data on the crystallography of the PMPs and discuss a possible mechanism of their formation.

2. EXPERIMENTAL

The coatings composed of PMPs were prepared by electrodeposition of copper on the surface of stainless steel microgrids in a sulphate electrolyte in the potentiostatic regime. Electrodeposition was carried out with the use, at the initial stages of electrocrystallization, of mechanical activation of the

Corresponding author: M.Yu. Gutkin, e-mail: m.y.gutkin@gmail.com

© 2018 Advanced Study Center Co. Ltd.

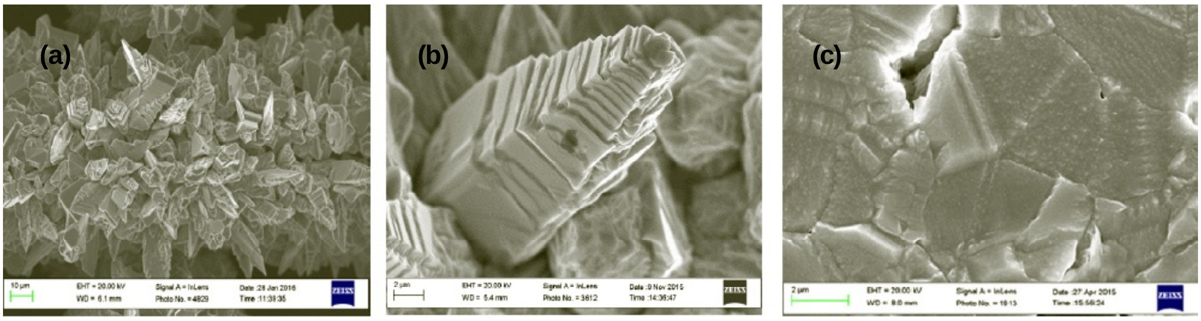

Fig. 1. SEM images of the surface of a copper coating obtained by electrodeposition with mechanical activation of the cathode. (a) General view. (b) A PMP with high growth steps. (c) A flat PMC, which is a possible place of PMP origin.

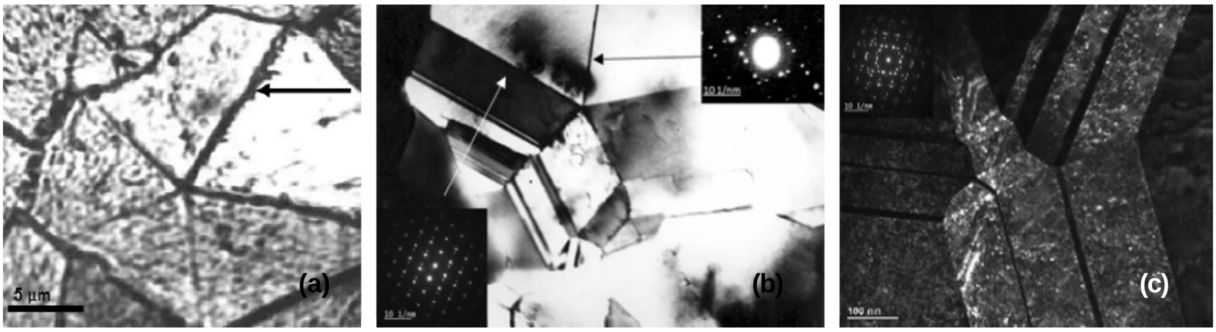

Fig. 2. Similar cyclic five-fold twins on metallographic and TEM images of typical copper PMCs and a central region of a typical PMP. (a) Metallographic image of a typical copper PMC. (b) TEM image of a similar PMC. The top and bottom insets show electron diffraction patterns of regions in the vicinity of the {111}<110>-type growth and {111}<112>-type deformation TBs, respectively; zone axis [110]. (c) TEM image of the PMP central region; zone axis [110].

cathode and the crystals growing on it with moving abrasive particles inert to the electrolyte [7,8].

Changes in the surface morphology of the crystals were observed with electron microscopes Carl Zeiss Sigma and JEOL JCM 6000.

To study the structure of PMPs, cross-section slices and foils were prepared. The foils were studied with transmission electron microscopes TecnaiOsiris and Tecnai G2 F20 at the Belgorod State University (Russia).

3. RESULTS AND DISCUSSION

Experimental observations of the growth process of PMPs (Figs. 1a and 1b) and special experiments on chemical and electrochemical etching to determine the sites of their growth showed that PMPs form and grow on the initially flat PMCs (Fig. 1c). In electrocrystallization, a layer mechanism of crystal growth from 2D embryos is most often realized [5]. These 2D embryos grow laterally and transform to an atomic monolayer. The emergence of each successive layer begins with the appearance of a new 2D embryo. During the growth of such an embryo, a thin adsorption-passivation film is formed on its surface. Mechanical activation of the surface by moving abrasive particles destroys this film and creates favorable conditions for the formation of ragged growth twins separated by twin boundaries (TBs) in the planar crystals. The TBs often form cyclic five-fold twins [1,2] with respect to the <110>-type axis, as is seen in Fig. 2.

In Fig. 2a, the {111} <110>-type TB indicated by the arrow, is of growth origin and is inclined by the angle 35°16′ to the substrate {110}-type plane. Four other TBs are of deformation {111} <112>-origin and perpendicular to this plane. We suggest that deformation twins could be formed due to mechanical activation of the growth surface by abrasive particles and/or stress fields of ragged growth TBs (equivalent to partial wedge disclinations [1,10]). In electron microscopy, TBs of growth and deformation origin differ by contrast (Fig. 2b). Notice that twin domains in PMC in Fig. 2b and the central region of the PMP (Fig. 2c) contain lamellar and multifold deformation twins, which indicates intensive processes of stress relaxation during the microcrystal growth. Similar relaxation mechanisms

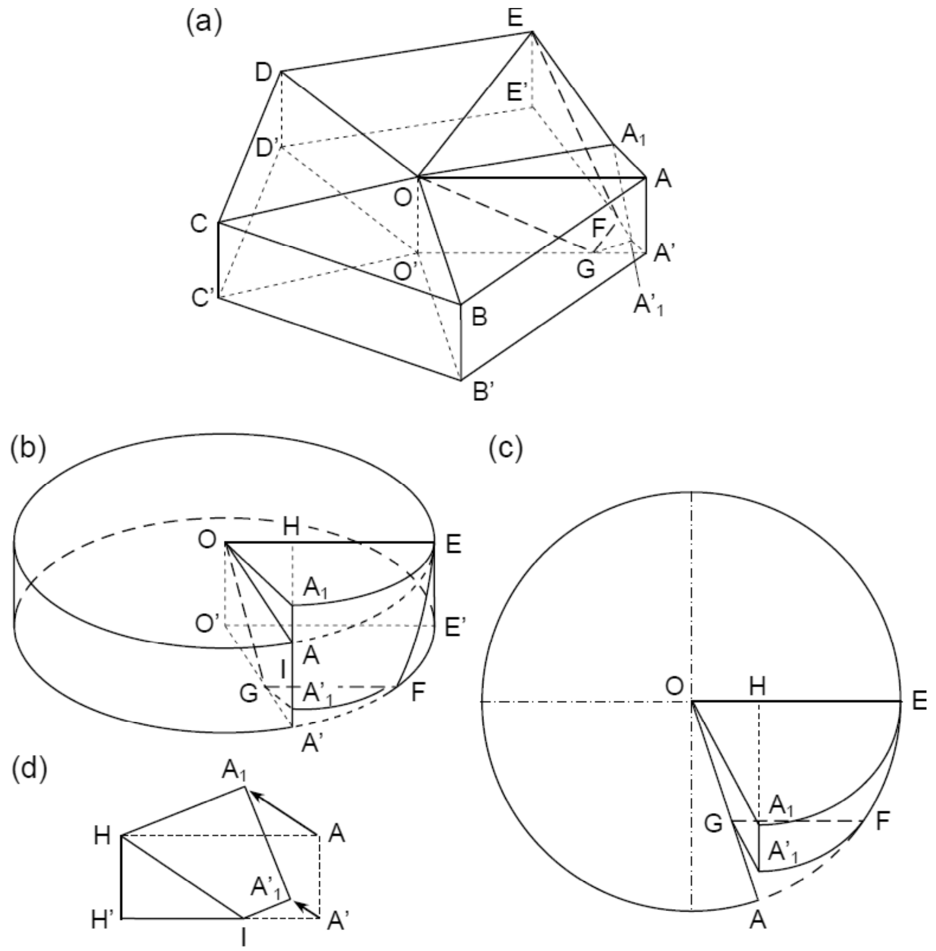

Fig. 3. Sketch of the formation of a high growth step on the surface of a flat PMC. (a) Geometric model of a flat PMC with a surface step formed by faces EA$_1$O and A$_1$AO. (b-d) Sketch of twinning which leads to the step formation on the surface of a flat disk: (b) general view, (c) top view, (d) the plane of twin shear which results in the transformation of region AA'IH to region A$_1$A'$_1$IH; here IH is the crossing line of shear plane AA'H'H and twin plane OEFG (c).

are often observed in PMCs [11]. As is seen from Fig. 2c, the PMC central region does not contain a unite quintuple junction of the TBs forming the five-fold symmetry axis in the PMC, but shows a complex arrangement of crossing twins. Anyway, we conclude that the PMCs formed at the initial stage of electrocrystallization, serve as substrates for the formation of PMPs (Fig. 1b).

Consider a geometric model of the formation of a high growth step on the surface of a flat PMC which consists of five cyclically twinned domains separated by five TBs – AA'O'O, BB'O'O, CC'O'O, DD'O'O, and EFGO (Fig. 3a). Four of these TBs (AA'O'O, BB'O'O, CC'O'O, and DD'O'O) are perpendicular to the substrate plane A'B'C'D'E' and have a common quadruple junction OO', while the fifth TB (EFGO) is inclined to the substrate plane by the angle of 35°16′. The lower face of the PMC is delineated by the broken line A'B'C'D'E'FG, while its upper surface consists of the flat region ABCDEO and the facets EA$_1$O and A$_1$AO that are inclined to it, formed as a result of the twinning of the original region AODEA'O'D'E' along the inclined plane EFGO. The faces EA$_1$O and A$_1$AO form a step on the PMC surface, which, in our opinion, leads to the formation of a PMP in the process of layer-by-layer overgrowth of the stepped surface, in analogy with the whisker growth in the places, where screw dislocations emerge on the substrate surface, by the Frank mechanism.

In Figs. 3b-3d, a sketch of twinning is shown in more detail, resulting in the formation of a surface step created by faces EA$_1$O and A$_1$AO. For simplicity, instead of a planar PMC, a disc with axis OO' and twinning plane OEFG is drawn. Here AA'H'H is the twin shear plane and AA$_1$ (or A'A'$_1$) is the shear direction. As a result of this twinning, the initial segment AOE of the disc upper surface is transformed into the flat region A_1OE inclined to the plane AOE, and the initial region AGF of the disc lower surface into the flat region A'_1GF parallel to the A_1OE. In this case, a wedge-shaped gap formed by the flat region of TB AA'GO and face $A_1A'_1$GO of the emerging twin can open. It is assumed that during the deposition of metal on the disc surface, this gap will overgrow with the formation of three new faces AOA_1, $AA_1A'_1A'$, and $A'GA'_1$.

4. CONCLUSIONS

We have shown that during mechanically activated electrodeposition, copper PMPs (Fig. 1) nucleate on planar PMCs and grow along the <110>-type directions, partially inheriting PMC structure (Fig. 2). A typical PMP contains five main TBs and a set of twin lamellae. The region, where the main TBs meet in the PMC, has a complex defect structure (Fig. 2c) and is the site of active spiral growth of the PMP. According to our geometric model, a step occurs on the PMC surface due to a growth twin formation (Fig. 3). The process of layer-by-layer filling of the {110}-type plane with deposited atoms begins at this step and proceeds along a spiral about the five-fold symmetry axis of the PMC. Such growth leads to the formation of a PMP on the PMC surface (Fig. 1b). The PMP surface is composed of high (multiatomic) steps created by {110}- and {111}-type facets which are perpendicular and inclined to the growth direction <110>, respectively. The complex defect structure of the central region of the PMC, on which the PMP grows, seems to be a reason for splitting of the PMP vertex into two parts that may be one of the channels of strain energy relaxation in PMPs.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation (task No. 16.2314.2017/4.6).

REFERENCES

[1] V.G. Gryaznov, J. Heidenreich, A.M. Kaprelov, S.A. Nepijko, A.E. Romanov and J. Urban // *Cryst. Res. Technol.* **34** (1999) 1091.

[2] L.D. Marks and L. Peng // *J. Phys.: Condens. Matter* **28** (2016) 052001.

[3] A.A. Vikarchuk and A.P. Volenko // *Phys. Solid State* **47** (2005) 352.

[4] C.Z. Yao, B.H. Wei, L.X. Meng, X.H. Hu, J.H. Yao and K.Y. Cui // *J. Electrochem. Soc.* **159** (2012) 425.

[5] I.S. Yasnikov, M.V. Dorogov, M.N. Tyurkov, A.A. Vikarchuk and A.E. Romanov // *Cryst. Res. Technol.* **50** (2015) 289.

[6] A.A. Vikarchuk, N.N. Gryzunova, M.V. Dorogov, A.N. Priezzheva and A.E. Romanov // *Metal Sci. & Heat Treatment* **58** (2016) 12.

[7] N.N. Gryzunova, A.A. Vikarchuk and M.N. Tyur'kov // *Rus. Metall. (Metally)* **10** (2016) 924.

[8] N.N. Gryzunova, A.A. Vikarchuk, V.V. Bekin and A.E. Romanov // *Bull. Rus. Acad. Sci.: Physics* **79** (2015) 1093.

[9] A. Milchev and S. Stoyanov // *J. Electroanal. Chem.* **72** (1976) 33.

[10] R. de Witt // *J. Phys. C: Solid State Physics* **5** (1972) 529.

[11] C.R. Hall and S.A.H. Fawzi // *Philos. Mag. A* **54** (1986) 805.