ISSN 1063-7850, Technical Physics Letters, 2014, Vol. 40, No. 2, pp. 174–176. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © A.E. Romanov, L.M. Dorogin, A.L. Kolesnikova, I. Kink, I.S. Yasnikov, A.A. Vikarchuk, 2014, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2014, Vol. 40, No. 4, pp. 72–78.

A Model of Whisker Crystal Growth from a Pentagonal Small Particle

A. E. Romanov*, L. M. Dorogin, A. L. Kolesnikova, I. Kink,
I. S. Yasnikov, and A. A. Vikarchuk
Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia
Institute of Physics, Tartu University, 51014, Tartu, Estonia
Togliatti State University, Togliatti, 3445667 Russia
Institute for Problems of Mechanical Engineering, Russian Academy of Sciences, St. Petersburg, 199178 Russia
**e-mail: aer@mail.ioffe.ru*

Received August 27, 2013

Abstract—We present a physical model of growth of whisker crystals from metal pentagonal small particles (PSPs). The model is based upon the notions of nucleation and slippage of prismatic dislocation loops in the elastic field of disclination defects that are inherent in PSPs. In the framework of this model, the escape of interstitial dislocation loops at the PSP surface leads to an increase in the whisker length relative to the base, while incorporation of the vacancy-type loops is accompanied by their accumulation on the internal surface. The model is illustrated by calculations that show a gain in the total PSP energy as a result of the formation of a pair of prismatic dislocation loops with opposite signs.

DOI: 10.1134/S1063785014020266

It is well known that nano- and micron-sized metal particles (with a fcc crystalline structure) can possess fivefold symmetry axes [1]. This is confirmed by the synthesis of particles with specific shapes (habits) including dodecahedron, icosahedron, pentagonal prism, etc. The unusual shape of pentagonal small particles (PSPs) and the mechanical stresses present in these species are related to a specific internal defect structure with multiple twins [2]. In order to describe this defect structure and internal stresses in PSPs, a model was developed that employed the concept of wedge disclinations and was called the disclination model [3]. According to this model, the elastic energy of a PSP increases in proportion to its volume and the squared power of characteristic disclination defects (see formula (2) below). A reset of the energy accumulated in growing PSPs proceeds via various relaxation mechanisms, including the PSP surface modification (see, e.g., [4–6]).

Possible PSP surface modifications include the experimentally observed formation of prismatic and cone-shaped whisker crystals, which have been situated in most cases in the sites of pentagonal symmetry axis emergence at the PSP surface [7]. Figure 1a shows a scanning electron microscope (SEM) image of the typical electrodeposited PSP of copper with modified surface morphology, where an icosahedral particle exhibits a prismatic whisker protrusion. The present

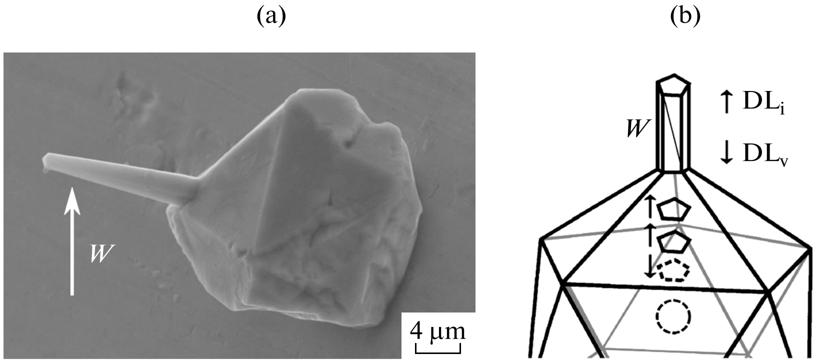

Fig. 1. (a) SEM image of a pentagonal copper particle with protruding whisker crystal and (b) physical model of a whisker growing from an icosahedral particle with an internal cavity by means of prismatic dislocation loops.

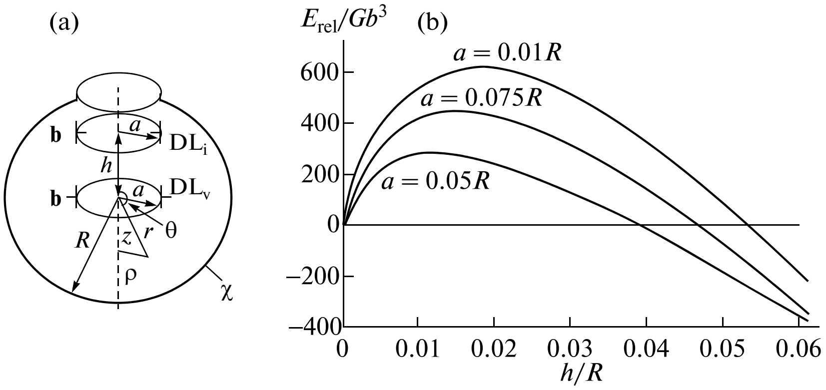

Fig. 2. Model calculations: (a) geometry of the nucleation and separation of prismatic dislocation loops in an icosahedral particle; (b) dependences of stress relaxation energy E_{rel} on position h of interstitial dislocation loop (for an immobile vacancy loop) for the following model parameters: particle radius, $R = 500$ nm; Poisson's ratio, $\nu = 0.3$; and dislocation core radius, $r_{\mathrm{core}} = b = 0.4$ nm.

Letter describes a physical mechanism responsible for the formation of this whisker.

The problem of whisker-crystal growth on galvanic coatings has been actively discussed since the 1940s in the context of failures of electronic devices caused by short-circuit through whiskers formed on electric contacts (see, e.g., review [8]). An important feature of these whiskers is their growth (protrusion) out of a metal (from the base), and the presence of internal stresses has been treated as one of the necessary conditions for the appearance of such micro- and nanoobjects [9]. The proposed model of whisker growth from PSPs is based upon Eshelby's notion [10] that dislocation loops might be involved in the transport of matter from the base to a growing whisker. Internal stresses present in the PSP act as the driving force of the nucleation and propagation of prismatic dislocation loops. Previously, we studied the interaction of dislocation loops with isolated wedge disclinations, including the relaxation of stresses in extended prismatic pentagonal crystals [11] and in the vicinity of disclinations emerging at the half-space surface [12].

First, let us qualitatively describe the mechanism of whisker formation in a PSP (Fig. 1b). It is assumed that a repeated process of nucleation of prismatic dislocation loop pairs consisting of an interstitial dislocation loop (DL$_i$) and vacancy loop (DL$_v$) takes place inside an icosahedral PSP. After nucleation, the loops are spatially separated so that the interstitial loops are transferred toward the particle surface and the vacancy loops are accumulated in the central region. This spatial separation is driven by internal stresses of disclination defects inherent in PSPs. Upon emergence at the particle surface, DL$_i$ contributes to the whisker growth and DL$_v$ can be absorbed by an internal cavity formed in the central region. The possible slippage of dislocation loops, which accounts for the mass transfer, is a collective mode of atomic motion that requires lower energy consumption that does the motion of individual atoms or vacancies.

Now let us consider in more detail the energy balance of the process of nucleation and separation of prismatic dislocation loops with opposite signs in a PSP. The initial icosahedral PSP has a specific internal structure comprising six wedge disclinations with a power of $\omega_D = 2\pi - 10\arcsin(1/\sqrt{3}) \approx 7°21' \approx 0.128$, which pass via the opposite vertices of the icosahedron [3]. In order to simplify calculations, let us replace this icosahedron by a sphere of radius R with an interstitial Marks–Yoffe disclination [13] that is a result of averaging of the wedge disclinations (sphere χ in Fig. 2a). The Marks–Yoffe disclination is determined by eigenstrain components (expressed in spherical coordinates) with the characteristic values $\varepsilon_{\vartheta\vartheta}^{*(\chi)} = \varepsilon_{\varphi\varphi}^{*(\chi)} = \chi = \frac{3}{2\pi}\omega_D \approx 0.0613$, which induce the following mechanical stresses in the particle:

$$\sigma_{rr}^{(\chi)} = \frac{4G\chi}{3}\left(\frac{1+\nu}{1-\nu}\right)\ln\left(\frac{r}{R}\right), \tag{1a}$$

$$\sigma_{\theta\theta}^{(\chi)} = \sigma_{\varphi\varphi}^{(0)} = \frac{4G\chi}{3}\left(\frac{1+\nu}{1-\nu}\right)\left[\ln\left(\frac{r}{R}\right) + \frac{1}{2}\right]. \tag{1b}$$

Here, (r, θ, φ) are spherical coordinates with an origin at the PSP center, R is the PSP radius, G is the shear modulus of the particle material, and ν is the Poisson's ratio. The elastic energy in the PSP (which is taken to be its initial energy) can be expressed as

$$E_\chi = \frac{8\pi\chi^2 G(1+\nu)R^3}{27(1-\nu)}. \tag{2}$$

Figure 2a shows a modified state of the PSP in which two coaxial circular prismatic dislocation loops of opposite signs are formed with the Burgers vectors **b** (for DL$_v$) and –**b** (for DL$_i$). Both loops have the same radius a, but DL$_v$ is situated at the PSP center while DL$_i$ is shifted along the axis by distance h relative to DL$_v$. This configuration of dislocation loops ensures the conservation of matter. The role of DL$_v$ consists in forming a vacancy reservoir (cavity), while DL_i transfers material to the growing whisker upon emergence at the PSP surface.

Total elastic energy E_{total} of the modified PSP state is a sum of several components:

$$E_{total} = E_{\chi} + E_v + E_i + E_{\chi v} + E_{\chi i} + E_{vi}, \tag{3}$$

where E_v and E_i are the energies of DL_v and DL_i, respectively; $E_{\chi v}$ and $E_{\chi i}$ are the energies of interaction of the Marks–Yoffe disclination with DL_v and DL_i, respectively; and E_{vi} is the energy of interaction between the two loops. The difference of PSP energies before and after the nucleation of loops, E_{rel}, can be expressed as follows:

$$E_{rel} = E_{total} - E_{\chi}. \tag{4}$$

In order to determine the various energy contributions in sum (3), let us use the results of recent investigation [14] specially devoted to an analysis of the elastic properties of prismatic dislocation loops in a spherical particle. In particular, for the loop, self-energies E_v and E_i can be determined by directly using [14, Eq. (21)] and loop interaction energy E_{vi} can be calculated using stresses due to a circular prismatic loop in a ball expressed analytically in terms of Legendre polynomials [14]. These relations are not presented here due to being very cumbersome.

Interaction energies $E_{\chi v}$ and $E_{\chi i}$ are conveniently expressed via work spent for the creation of dislocation loops in the elastic field of the Marks–Yoffe disclination:

$$E_{\begin{Bmatrix}\chi v\\ \chi i\end{Bmatrix}} = \{\pm\} b \int_0^a \sigma_{zz}^{(\chi)}\Big|_{\begin{Bmatrix}z = 0\\ z = h\end{Bmatrix}} 2\pi\rho d\rho, \tag{5}$$

where $\sigma_{zz}^{(\chi)}$ is the component of the Marks–Yoffe disclination stress tensor, which can be determined using standard transformations in spherical coordinates for stress components given by formulas (1).

Figure 2b gives a typical example of the dependence of E_{rel} on coordinate h of DL_i (for immobile DL_v). A specific feature of the $E_{rel}(h)$ curves is the presence of a region with $E_{rel} > 0$ for small h and $E_{rel} < 0$ with monotonic decay for large h up to $h = \sqrt{R^2 - d^2}$, at which DL_i emerges at the surface. The region with negative E_{rel} corresponds to the energetically favorable formation of this loop configuration as compared to the initial PSP upon surmounting of the energy barrier with $E_{rel} > 0$. The monotonic decay of E_{rel} with increasing h can be interpreted as being due to the action of a repulsive configuration force on DL_i in the elastic field of the Marks–Yoffe disclination and DL_v, which results in the emergence of DL_i at the PSP surface and the protrusion of growing whisker by distance b. The role of DL_v can be treated as the collective accumulation of vacancies inside the PSP with the subsequent formation and growth of the internal cavity. It is important to note that the formation of dislocation loops in small particles ($R < 10$ nm) is energetically unfavorable.

Thus, the results of our model calculations show that the growth of whisker crystals on PSPs can be treated as a result of relaxation of internal mechanical stresses through multiply repeated events of the nucleation and propagation of prismatic dislocation loops with the emergence of interstitial loops at the PSP surface, which leads to the whisker growth and the simultaneous concentration of vacancy loops inside the PSP with subsequent formation of a cavity. During the analysis of whisker-formation conditions at the developed growth stage, it may be essential to take into account the contribution due to the newly formed whisker surface, as it was demonstrated by Dubrovskii et al [15].

Acknowledgments. We gratefully acknowledge support from the Ministry of Education and Science of the Russian Federation (work under order no. 220 performed at Togliatti State University, project no. 14.B25.31.0011), the project "Mesosystems: Theory and Applications (TK114)"; ENCC (EU29996), ETF (grant nos. 8490, 9007, IUT2-25); and the ERDF projects "TRIBOFILM" (3.2.1101.12-0028), "IRGLASS" (3.2.1101.12-0027), and "NanoCom" (3.2.1101.12-0010).

REFERENCES

1. M. J. Yacaman, J. A. Ascencio, H. B. Liu, and J. Gardea-Torresday, J. Vac. Sci. Technol. B **19**, 1091 (2001).
2. H. Hofmeister, Cryst. Res. Technol. **33**, 3 (1998).
3. V. G. Gryaznov, J. Heidenreich, A. M. Kaprelov, S. A. Nepijko, A. E. Romanov, and J. Urban, Cryst. Res. Technol. **34**, 1091 (1999).
4. V. G. Cryaznov, A. M. Kaprelov, A. E. Romanov, and I. A. Polonskii, Phys. Status Solidi (B) **167**, 441 (1991).
5. A. A. Vikarchuk and I. S. Yasnikov, Phys. Solid State **49**, 1 (2007).
6. I. S. Yasnikov, JETP Lett. **97**, 513 (2013).
7. I. S. Yasnikov and A. A. Vikarchuk, Metal Sci. Heat Treat. **49**, 97 (2007).
8. G. T. Galyon, IEEE Trans. Electron. Packag. Manuf. **28**, 94 (2005).
9. J. Smetana, IEEE Trans. Electron. Packag. Manuf. **30**, 11 (2007).
10. J. D. Eshelby, Phys. Rev. **91**, 755 (1953).
11. A. L. Kolesnikova and A. E. Romanov, Tech. Phys. Lett. **33**, 886 (2007).
12. A. E. Romanov, A. A. Vikarchuk, A. L. Kolesnikova, L. M. Dorogin, I. Kink, and E. C. Aifantis, J. Mater. Res. **27**, 545 (2012).
13. A. Howie and L. D. Marks, Philos. Mag. A **49** (1), 95 (1984).
14. A. L. Kolesnikova, M. Yu. Gutkin, S. A. Krasnitckii, and A. E. Romanov, Int. J. Sol. Struct. **50**, 1839 (2013).
15. V. G. Dubrovskii, V. Consonni, A. Trampert, L. Geelaar, and H. Riechert, Phys. Rev. B **85**, 165317 (2012).

Translated by P. Pozdeev