

Hollowing in Pentagonal Particles: Grain Boundary Diffusion Model

S.A. Krasnitskii^{*} , B.A. Shevchenko, L.A. Sokura , A.M. Smirnov 

ITMO University, Kronverkskiy pr., 49, bldg. A, St. Petersburg, 197198, Russia

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Abstract

An analytical model of pore nucleation via grain-boundary diffusion of vacancies in pentagonal crystals has been proposed. According to this model, the vacancy fluxes along the twin boundaries make the major contribution to the void formation process. The void evolution equation has been derived from the difference in chemical potentials at the inner and outer surfaces determined within the energy approach, taking into account the surface energy of free surfaces and twin boundaries as well as the strain energy of the disclination. The model predicts the existence of critical and optimal void sizes and reveals the conditions under which voids grow, stabilize, or shrink until complete dissolution. In addition, we report on the stress-induced formation of a central pore in initially solid Cu pentagonal particles as a promising way to fabricate hollow structures.

Keywords: Pentagonal crystals; Multiply twinned particles; Pore; Disclination; Grain boundary diffusion

1. INTRODUCTION

Pentagonal crystal (PC) structures such as pentagonal whiskers, decahedral and icosahedral particles are widely employed in photonic, plasmonic and catalytic technologies owing to their $\{111\}$ faceting and cyclic twinning [1–3]. However, the cyclic twinning gives rise to inhomogeneous residual stress-strain state [4–6] that strongly affects functional properties of PCs [7,8]. For example, Huang et al. [7] showed that strained Pd icosahedral nanoparticles exhibit higher catalytic activity towards electrochemical CO_2 reduction than Pd octahedrons of the same size. On the other hand, it is the residual strain that is responsible for the sharp reduction of durability of such catalysts against operational cycles. Zhao et al. [8] demonstrated that after 5000 cycles the mass activity of icosahedral Pt nanocages drops by $\sim 40\%$ in comparison to $\sim 20\%$ for cubic/octahedral counterparts. Such deterioration of the functional performance of icosahedral nanocages can be associated with

structural rearrangements due to relaxation of the residual stress inherent to PCs.

Various stress relaxation channels in PCs including dislocation generation [9–12], formation of the phase inhomogeneities and the misfit layers [13–15] have been examined within disclination concept [16]. The phenomenon of the stress-induced pore nucleation in the PCs [17] has been elucidated in numerous studies as well [18–22]. All these studies consider the pore evolution in PCs in terms of bulk diffusion theory neglecting the fact that in multiply twinned particles the vacancy migration proceeds predominantly along twin boundaries (TBs).

The present work aims at incorporating the effect of grain-boundary diffusion of vacancies along TBs into the analysis of pore evolution kinetics in PCs. In doing so, the main principles of pore evolution in polycrystalline particles given in Refs. [23,24] have been adapted to stress-induced pore formation in multiply twinned particles. In addition, experimental results on the spontaneous formation of pores in Cu and CuO pentagonal particles are demonstrated.

^{*} Corresponding author: S.A. Krasnitskii, e-mail: krasnitsky@inbox.ru

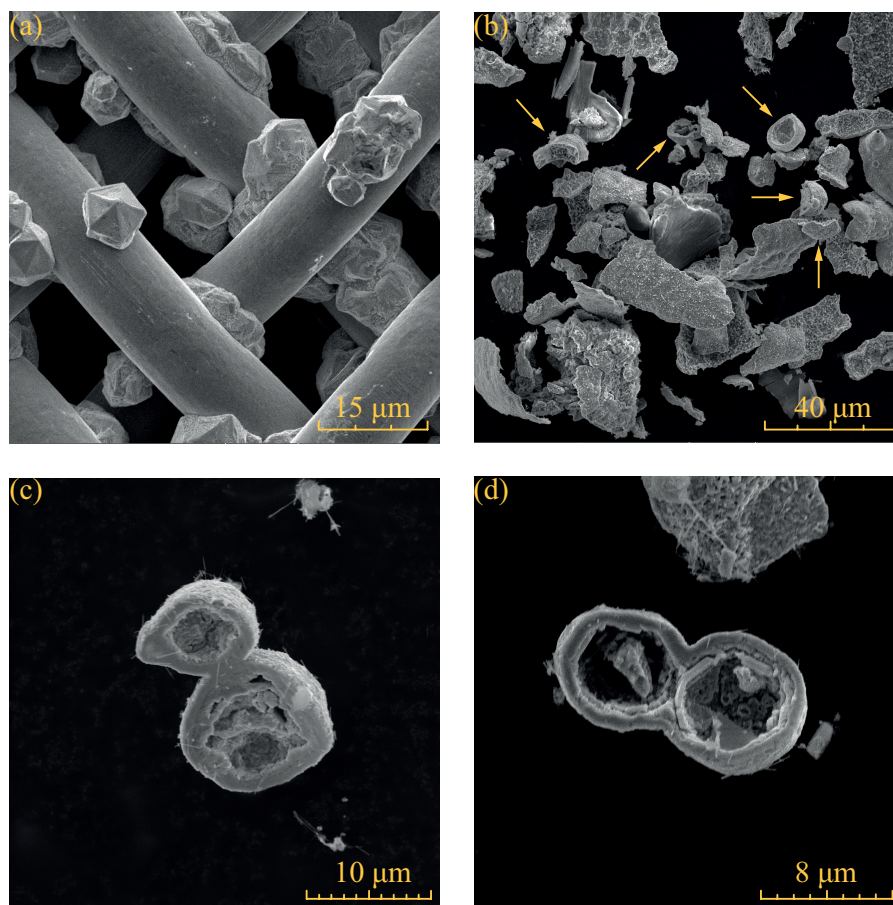


Fig. 1. SEM images of Cu pentagonal particles: (a) pentagonal particles on a steel grid; (b)–(d) spherical hollow particles after annealing. Yellow arrows indicate the particle fragments after mechanical splitting.

2. EXPERIMENT

The PCs were produced in two successive steps. First, Cu pentagonal particles were grown by means of electroplating. Second, these Cu particles were subjected to thermal oxidation in air, which converted them into spherical CuO particles.

The electrolytic deposition was performed in a potentiostatic regime using a P-45X potentiostat-galvanostat. The working electrolyte contained 250 g/l of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 90 g/l of H_2SO_4 , and distilled water. A pure Cu plate served as the anode, and a pure Cu electrode was used as the reference. Prior to deposition, the Cu electrode was etched in HNO_3 . A stainless steel grid was chosen as the substrate for the growth of Cu pentagonal particles. Before use, this substrate was rinsed with $\text{C}_3\text{H}_8\text{O}$ and subsequently cleaned in distilled water using an ultrasonic bath for 15 minutes. The Cu particles were deposited at an overvoltage of 65 mV over a period of 15 minutes.

Upon completion of the deposition, the grids with the grown Cu pentagonal particles were thoroughly rinsed with distilled water and kept in air at room temperature for 1 hour to dry. The dried samples were then annealed in air inside a muffle furnace at 400 °C for 6 hours. As a

result of this heat treatment, the Cu pentagonal particles were converted into spherical CuO particles. Pores in the CuO particles became observable after the particles were mechanically detached from the substrate grids using adhesive tape and split apart.

The geometrical parameters of the microparticles were examined with a MIRA3 TESCAN scanning electron microscope (SEM) operating at an accelerating voltage of 30 kV under high-vacuum conditions.

Figure 1a shows synthesized Cu pentagonal particles on a steel grid. Annealing of particles led to an increase in their size, a change in the shape and faceting, and the appearance of pores (see Figs. 1b–d) in the particles. The presence of flakes around the particles in Fig. 1b can be explained by mechanical splitting required to separate particles from the grid and study their internal structure. Some particles stuck together (Fig. 1c and d), which could occur due to the mechanical impact on the particles during the grid splitting process.

3. MODEL

We consider an elastic cylindrical shell with inner and outer radii a_p and a as a model of a hollow pentagonal

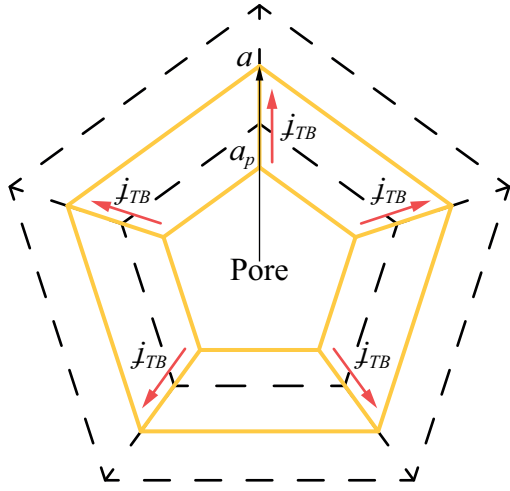


Fig. 2. Model of pore growth in a pentagonal particle due to vacancy diffusion along TBs.

particle. The residual elastic strains in the particle are associated with fivefold twinning of the structure and can be described within the disclination approach by introducing a negative wedge disclination with a strength of $\omega \approx 0.128$. Let us assume that the evolution of the internal pore in the particle is determined primarily by the vacancy migration along TBs (see Fig. 2). Then, for the change in the pore size, one can write

$$\frac{da_p}{dt} = -\Omega j_{TB}, \quad (1)$$

where t is time, Ω is the atomic volume, and j_{TB} is the total vacancy flux along TBs. The vacancy flux can be represented as

$$j_{TB} = -\frac{1}{\Omega} \frac{D_{TB} v_{TB}}{kT} \frac{\mu_2 - \mu_1}{a - a_p}, \quad (2)$$

where D_{TB} is the TB diffusion coefficient, v_{TB} is the number of mobile atoms at the TB, k is the Boltzmann constant, and T is the absolute temperature; μ_1 and μ_2 are the chemical potentials at the inner and outer surfaces of the particle, respectively.

The chemical potentials μ_1 and μ_2 can be determined within the framework of the energy approach [7]:

$$\mu_1 = \Omega \left(\frac{\delta E}{\delta S} \right)_{a = \text{const}}, \quad (3)$$

$$\mu_2 = \Omega \left(\frac{\delta E}{\delta S} \right)_{a_p = \text{const}}, \quad (4)$$

where S is the cross-sectional area of the particles, E is the total energy of the system, defined as the sum of the surface energy

$$E_{surf} = 2\pi\gamma(a + a_p) + 5\gamma_{TB}(a - a_p), \quad (5)$$

and the strain energy of the disclination

$$E_{st} = \frac{G\omega^2}{16\pi(1-\nu)} \left[a^2 - a_p^2 - \frac{4a^2 a_p^2}{a^2 - a_p^2} \ln^2 \frac{a_p}{a} \right], \quad (6)$$

here the following notations are used: γ and γ_{TB} are the specific energies of the free surfaces and TBs, respectively, G is the shear modulus, and ν is the Poisson's ratio. The expressions for the ratio of the variations take the form

$$\left(\frac{\delta E_{sf}}{\delta S} \right)_{a = \text{const}} = -\frac{\gamma}{a_p} + \frac{5\gamma_{TB}}{2\pi a_p}, \quad (7)$$

$$\left(\frac{\delta E_{sf}}{\delta S} \right)_{a_p = \text{const}} = \frac{\gamma}{a} + \frac{5\gamma_{TB}}{2\pi a}, \quad (8)$$

$$\left(\frac{\delta E_{st}}{\delta S} \right)_{a = \text{const}} = \frac{G\omega^2}{16\pi^2(1-\nu)} \frac{a_p^2 - a^2(1 + 2\ln a_p/a)^2}{(a^2 - a_p^2)^2}, \quad (9)$$

$$\left(\frac{\delta E_{st}}{\delta S} \right)_{a_p = \text{const}} = -\frac{G\omega^2}{16\pi^2(1-\nu)} \frac{a^2 + a_p^2(1 - 2\ln a_p/a)^2}{(a^2 - a_p^2)^2}. \quad (10)$$

Substituting Eqs. (2) and (3), with regard to Eqs. (7)–(10), into the expression for the change in the pore radius, we finally obtain the following evolution equation

$$\begin{aligned} \frac{dp}{d\tau} &= \frac{5g}{4\pi^2} \frac{\Delta^6}{p^2} - \frac{(1+p)^2 \Delta^4}{p^2} \\ &+ \varepsilon (p\Delta^2 + p(1+p^2)\ln p) \frac{(1+p)\Delta \ln p}{4\pi^2 p^2}. \end{aligned} \quad (11)$$

Here the following dimensionless notations are introduced:

$$p = \frac{a_p}{a}, \quad (12)$$

$$\Delta = \sqrt{1 - p^2}, \quad (13)$$

$$\tau = \frac{\gamma}{kT} \frac{\Omega}{a_0^3} D_{TB} v_{TB} t, \quad (14)$$

$$g = \frac{\gamma_{TB}}{\gamma}, \quad (15)$$

$$\varepsilon = \frac{a_0}{1-\nu} \frac{G\omega^2}{\gamma}, \quad (16)$$

where a_0 is the radius of initially solid particle.

4. RESULTS

The equilibrium conditions for stable pores can be obtained from the evolution equation if the velocity of the pore surface vanishes, i.e., the left part of Eq. (11) is equal to zero: $dp/d\tau = 0$. Figure 3 illustrates the corresponding surface indicating the equilibrium parameters of stable pore in PCs viz. ratio of pore to particle radii p [Eq. (12)], ratio of TB energy to surface energies g [Eq. (15)] and dimensionless complex ε demonstrating the ratio of volumetric (strain energy of wedge disclination) and surface factors on diffusion process [Eq. (16)].

The dependences $\varepsilon(p)$ determined from condition $dp/d\tau = 0$ [see Eq. (11)] for different values of the ratio of the TB energy to the surface energy g are demonstrated in Fig. 4a. In the region above the curves, $dp/d\tau > 0$, i.e., the pores in the particle will grow until they reach an optimal size at $dp/d\tau = 0$. In the region below the curves, $dp/d\tau < 0$, i.e., the pores in the particle tend to shrink. Of practical interest is ε_{cr} , corresponding to the minimum of the curve $\varepsilon(p)$. If $\varepsilon < \varepsilon_{cr}$, the nucleation of stable pores in the particle fails. Conversely, for $\varepsilon > \varepsilon_{cr}$, a pore in the particle tends to assume an optimal size p_{opt} (stable pores) if the pore size is larger than a certain critical value, $p > p_{cr}$. If $p < p_{cr}$, the pore will shrink until it dissolves completely. In addition, it can be seen that as the contribution of the boundary energy increases ($g \rightarrow 1.0$), the region below the curves reduces and ε_{cr} decreases as well.

The dependences of the ratio of the particle radii p on the dimensionless time τ for different values of the parameters ε and g are shown in Fig. 4b. It can be seen that at relatively low values of the parameters ($\varepsilon = 100$ and $g = 0.1$), the pore radius will decrease until the pore collapses (at time $\tau_f \approx 0.075$). As the contribution of the TBs increases ($\varepsilon = 100$ and $g = 0.5$), an equilibrium position of the pore becomes possible ($p_{opt} \approx 0.15$). Thus, within the framework of the proposed model, the evolution of pores proceeds through grain-boundary diffusion, which in turn is determined by the internal characteristics of the pentagonal particles (the energy of free and TBs, elastic moduli, particle volume, etc.).

5. CONCLUSIONS

In summary, stress-induced pore formation in Cu pentagonal particles has been reported in this study. To accelerate the pore formation, the initially solid Cu PCs were annealed at 400 °C for 6 hours. As a result, the particles were transformed into hollow spherical CuO particles. The pores were observed by scanning electron microscopy after mechanical particles splitting. Evidently these pores are nucleated due to both Kirkendall hollowing accompanied by oxidation and relaxation of residual stress. The latter phenomenon seems to be more predominant to explain the formation of pore nucleus at initial stage of hollowing in pentagonal particles. To support this fact, we proposed a new theoretical model of stress-induced nucleation of pores in PCs focusing on the inward vacancy fluxes along TBs. The model can predict the pore evolution scenarios in PCs (growing or shrinking) with respect to the initial size of particles, material properties (elastic moduli, surface and TB energies) and environment conditions (temperature). In particular, it is demonstrated that with an increasing contribution of TB energy, collapsing pores can switch to a stable scenario. Thus, grain-bound-

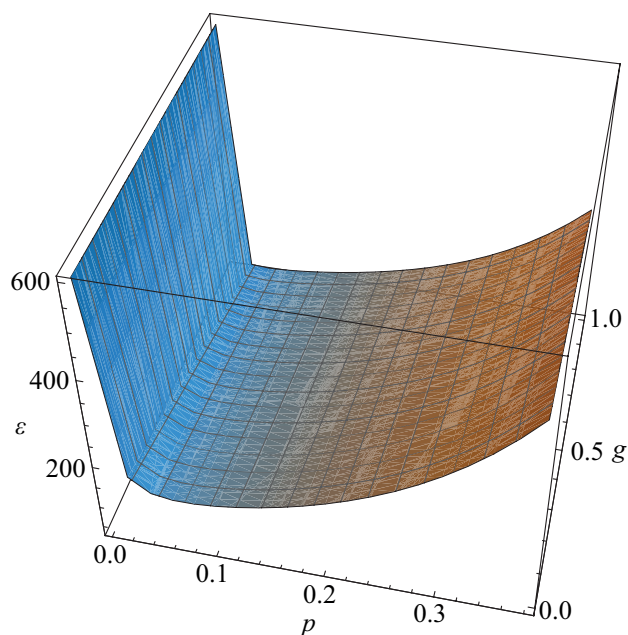


Fig. 3. Map of parameter ε in the space of pore to particle radii ratio p and ratio of TB energies to surface energies g .

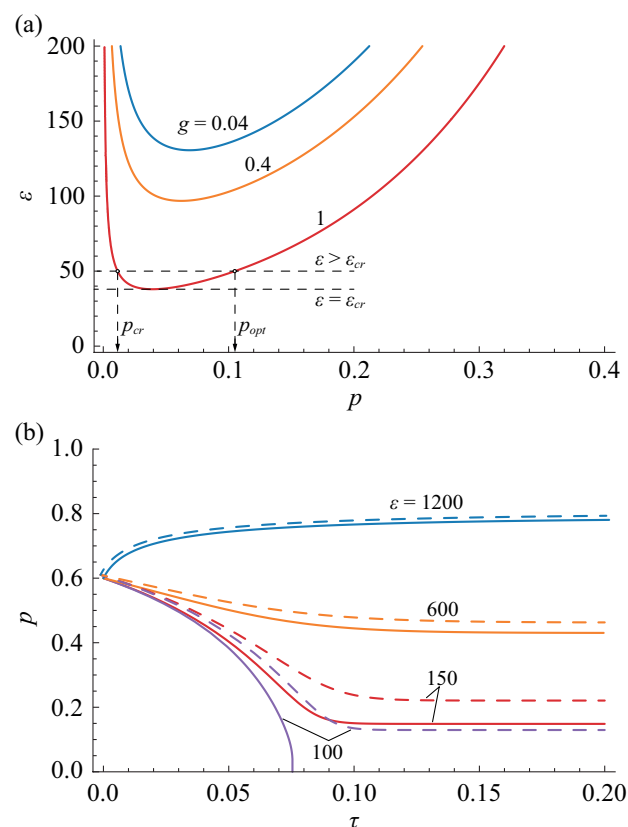


Fig. 4. (a) Stability diagrams of pores in the pentagonal particle as a function of the parameter ε and the normalized pore radius p , constructed for different contributions of the TB energy $g = 0.04$, 0.4 , and 1.0 . (b) Kinetic curves of pore evolution $p(\tau)$, constructed for different values of the parameter $\varepsilon = 100$, 150 , 600 , 1200 and different values of the ratio of the TB energy to the surface energy $g = 0.1$ (solid curves) and $g = 0.5$ (dashed curves). The initial ratio of the pentagonal particle radii is $p_0 = 0.6$.

ary diffusion can be an effective mechanism of pore formation under PC residual stress.

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Образование полостей в пентагональных частицах: модель зернограницной диффузии

С.А. Красницкий, Б.А. Шевченко, Л.А. Сокура, А.М. Смирнов

Университет ИТМО, Кронверкский пр., д. 49, лит. А, Санкт-Петербург, 197198, Россия

Аннотация. Предложена аналитическая модель зарождения пор за счёт зернограницной диффузии вакансий в пентагональных кристаллах. Согласно этой модели, основной вклад в процесс образования пор вносят потоки вакансий вдоль двойниковых границ. Уравнение эволюции поры выведено из разности химических потенциалов на внутренней и внешней поверхностях частицы, определённой в рамках энергетического подхода, с учётом энергии поверхности частицы и энергии двойниковых границ, а также упругой энергии дисклинации. Модель предсказывает существование критических и оптимальных размеров пор и определяет условия, при которых поры растут, стабилизируются или уменьшаются вплоть до полного растворения. Показано, что в изначально сплошных пентагональных частицах Si под действием внутренних напряжений может образовываться центральная пора. Это открывает перспективный способ получения полых структур.

Ключевые слова: пентагональные кристаллы; частицы с многократным циклическим двойникованием; пора; дисклинация; зернограницная диффузия