ISSN 1063-7850, Technical Physics Letters, 2008, Vol. 34, No. 9, pp. 779–781. © Pleiades Publishing, Ltd., 2008.
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Misfit Layer Formation in Icosahedral Nanoparticles

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Received January 22, 2008

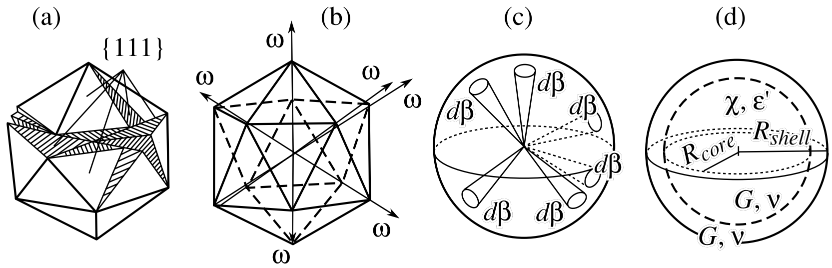
Abstract—We have studied the mechanism of internal stress relaxation in icosahedral pentagonal nanoparticles (PNs), which is related to the formation of a layer accommodating the crystal lattice misfit. The optimum misfit parameter is determined, for which the energy gain as a result of this relaxation is maximum. It is shown that the threshold radii of icosahedral PNs for some fcc metals, at which the formation of a misfit layer becomes energetically favorable, are on the order of ~10 nm.

PACS numbers: 61.46.Hk, 61.72.Lk, 61.50.Ah
DOI: 10.1134/S1063785008090198

As is well known, fine particles (nanoparticles) can possess fivefold symmetry axes (see, e.g., review [1] and experimental reports [2, 3]). The structure of pentagonal nanoparticles (PNs) and the internal mechanical stresses inherent in these objects can be adequately
1 described within the framework of the disclination approach [4, 5]. The internal stresses can relax via the nucleation of various defects [4–5], thus modifying the PN structure. In particular, the relaxation of internal stresses in PNs can proceed via the formation of misfit contact layers, in which the lattice parameters are different from the initial values.

The aim of this study was to elucidate the mecha-
2 nism of formation of a misfit layer in nanodimensional objects, where all three dimensions are of the same order of magnitude, that is, in isocahedral PNs.

It was previously demonstrated (see, e.g., [4, 5]) that PNs of face-centered cubic (fcc) metals can be constructed from several close-packed tetrahedral twinned crystalline regions, which are bounded by planes of the {111} type. In a free state, a gap not filled by the material (a deficit of solid angle β) appears in such a multiply twinned PN. For an icosahedral PN, this deficit is illustrates in Fig. 1a. In the continuum approximation, the deficit of solid angle is eliminated by the introduction of six positive wedge disclinations with a power of 3
$\omega_D = 2\neq - 10\arcsin(1/\sqrt{3}) \approx 7°21'$ so that $\beta = 12\omega_D$ (Fig. 1b) [4]. A simple PN model reduces to substituting a spheroid for the icosahedron and to replacing a discrete ensemble of disclinations by continuously dis- 3
tributed cones with infinitely small solid angle $d\beta$ (Fig. 1c) [9]. The obtained model defect (called distributed Marks–Ioffe disclination [4]) is characterized by 1



3 1 **Fig. 1.** Continuum model of an icosahedral PN with a misfit layer: (1) solid angle deficit in a PN composed of fcc grains bounded by {111} planes; (b) diagram of six wedge disclinations in a compact icosahedral PN (ω is the disclination power); (c) the Marks–
1 Ioffe disclination representing a set of continuously distributed cones with infinitely small solid angle $d\beta$; (d) a spherical particle
1 4 1 with the Marks–Ioffe disclination and a misfit layer (χ denotes the eigenstrain due to the distributed Marks–Ioffe disclination; ε* is the parameter of misfit of the core and shell lattice constants; R_{shell} is the external particle radius; G and ν are the shear modulus and the Poisson ratio of the PN material, respectively).

4 eigenstrain $\varepsilon^{*(\gamma)}_{\theta\theta} = \varepsilon^{*(\gamma)}_{\phi\phi} = \chi = 6\omega_D/4\pi \approx 0.0613$ that induces the following mechanical stresses in the PN [9]:

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

$$\sigma^{(\gamma)}_{\theta\theta} = \sigma^{(\gamma)}_{\phi\phi} = \frac{4G\chi}{3}\left(\frac{1+\nu}{1-\nu}\right)\left[\ln\left(\frac{r}{R_P}\right)+\frac{1}{2}\right], \tag{1b}$$

where (r, θ, ϕ) is the spherical coordinate system related to the PN center, R_P is the PN radius, G is the shear modulus of the particle material, and ν is the Poisson ratio.

When a misfit shell with a crystal lattice parameter $a_{\rm shell}$ different from that of the PN core ($a_{\rm core}$) is formed in the PN (Fig. 1d), elastic misfit stress fields arise [10] and the total elastic energy of a new PN of the core–shell type can be written as the sum

$$E_{CP} = E_{\rm misfit} + E_\chi + E_{\rm int}, \tag{2}$$

where $E_{\rm misfit}$ is the misfit energy, E_χ is the Marks–Ioffe
1 disclination energy, and $E_{\rm int}$ is the energy of interaction
1 between the disclination and elastic fields.

The elastic misfit stress fields are determined with allowance for the boundary conditions at core–shell interface and the free PN surface. The interface must obey the condition of continuity for all components of the total displacement and (owing to the symmetry) the condition of continuity for the radial stress component. At the free surface, the radial stress component must vanish. As a result, the misfit stresses are as follows [10]:

$$\sigma^{(1)}_{rr} = \sigma^{(1)}_{\theta\theta} = \sigma^{(1)}_{\phi\phi} = -\frac{4\varepsilon^* G(1+\nu)}{3(1-\nu)}(1-t^3), \tag{3a}$$

$$\sigma^{(2)}_{rr} = -\frac{4\varepsilon^* G(1+\nu)}{3(1-\nu)}t^3\left(\frac{R^3_{\rm shell}}{r^3}-1\right), \tag{3b}$$

$$\sigma^{(2)}_{\theta\theta} = \sigma^{(2)}_{\phi\phi} = \frac{2\varepsilon^* G(1+\nu)}{3(1-\nu)}t^3\left(\frac{R^3_{\rm shell}}{r^3}-1\right); \tag{3c}$$

where superscripts (1) and (2) refer to the core and shell, respectively; $\varepsilon^* = (a_{\rm core} - a_{\rm shell})/a_{\rm core}$ is the misfit parameter of the core and shell crystal lattices; $t = R_{\rm core}/R_{\rm shell}$; $R_{\rm core}$ and $R_{\rm shell}$ are the core and shell radii, respectively, and the other notations are as in Eq. (1). The elastic moduli of the shell are assumed to be the same as those of the particle core.

The misfit energy ($E_{\rm misfit}$) in the proposed model represents the energy of a spheroidal inclusion concentric with the initial spherical particle, which can be described in terms of the general expression for the energy of an inclusion with preset strain level [11]. Using Eqs. (3), this energy can be written as follows:

$$E_{\rm misfit} = -\frac{1}{2}\int\limits_{V_{core}} \varepsilon^*{\rm Tr}\sigma^{(1)}_{ij}dV = \frac{8\pi(1+\nu)F\varepsilon^{*2}}{3(1-\nu)}R^3_{\rm shell}t^3(1-t^3), \tag{4}$$

where $V_{\rm core}$ is the volume of the inclusion (i.e., of the PN core).

The energy of interaction ($E_{\rm int}$) between the discli- 1
nation and elastic stress fields is calculated using a formula for the interaction between two defects [11], that
is, between a distributed disclination and an inclusion: 1

$$E_{\rm int} = -4\pi\int\limits_0^{R_{\rm core}} \varepsilon^*{\rm Tr}\sigma^{(\chi)}_{ij}r^2dr = -\frac{16\pi\varepsilon^*\chi G(1+\nu)}{9(1-\nu)}R^3_{\rm shell}t^3\ln t^3. \tag{5}$$

Now we can determine a difference between the elastic energies of the particle before and after the formation of a shell (assuming that the particle radius remains unchanged):

$$\Delta E_{CP} = E_{CP} - E_\chi = E_{\rm misfit} + E_{\rm int}. \tag{6}$$

Figure 2a shows the plots of ΔE_{CP} versus ratio t of the core and shell radii for various misfit parameters ε^*. As can be seen, the differential energy ΔE_{CP} is negative for $\varepsilon^* < 0$, which implies that the shells with such his misfit parameters are energetically favorable. For a typical value of the Poisson ratio $\nu = 0.3$, the optimum misfit parameter $\varepsilon^*_{\rm opt}$ corresponding to the minimum of ΔE_{CP} amounts approximately to –0.041.

In determining the energy difference (6), we took into account only the volume energy components representing the elastic energy of the particle. However, in addition to the volume energy, there appears the energy of the core–shell interface. This component can be defined as follows:

$$E_\gamma = 4\pi\gamma R^2_{\rm core}, \tag{7}$$

where γ is the specific surface energy of the core–shell interface. Taking into account E_γ, an expression (6) for the energy difference is modified to yield

$$\Delta E^\gamma_{CP} = GR^3_{shell} \times\left(\frac{8\pi(1+\nu)(3\varepsilon^{*2}t^3(1-t^3)-2\varepsilon^*\chi t^3\ln t^3)}{9(1-\nu)}+\frac{4\pi t^2}{\tilde{r}_{shell}}\right), \tag{8}$$

where $\tilde{r}_{\rm shell} = R_{\rm shell}(G/\gamma)$. Figure 2b shows a set of $\Delta E^\gamma_{CP}(t)$ curves constructed for $\varepsilon^* = \varepsilon^*_{\rm opt} \approx -0.041$ and $\nu = 0.3$.

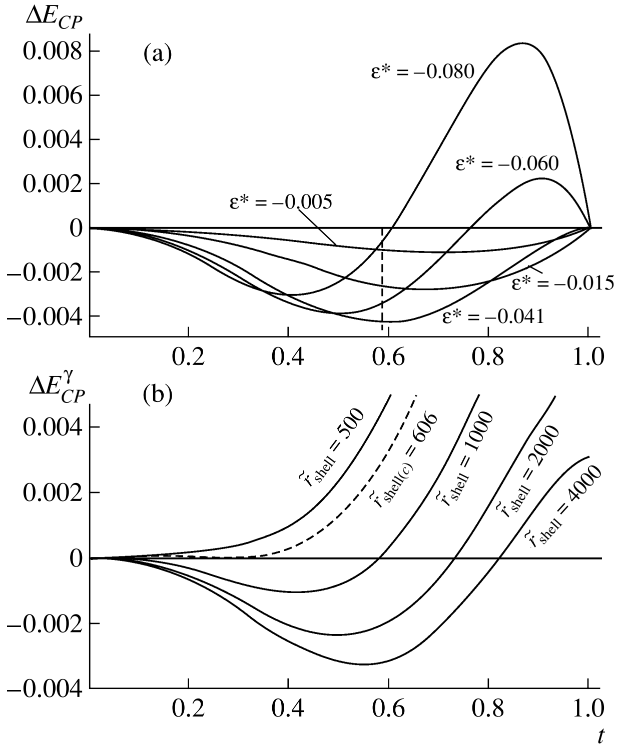


Fig. 2. Plots of the differential energy ΔE_{CP} of icosahedral PNs without and with misfit shells versus ratio t of the core and shell radii: (a) with neglect of the core–shell interface energy for various lattice misfit parameters ε*; (b) with allowance for the core–shell interface energy, for various dimensionless radii $\tilde{r}_{\text{shell}} = R_{\text{shell}}(G/\gamma)$ at ε* = –0.041 (R_{shell} is the external PN radius; γ is the surface energy density). All plots are constructed for the Poisson ratio ν = 0.3; the energy is expressed in units of GR^3_{shell}; G is the shear modulus (same for the core and shell material).

A critical particle radius R_c, above which the formation of a misfit layer is energetically favorable, can be determined from the following criterion:

$$\begin{cases} \Delta E^{\gamma}_{CP} = 0, \\ \dfrac{\partial \Delta E^{\gamma}_{CP}}{\partial t} = 0, \end{cases} \quad t \neq 0. \tag{9}$$

which corresponds to the dashed curve in Fig. 2b with a parameter of $\tilde{r}_{\text{shell}(c)} \approx 0.606$. The results of numerical calculations give the following values of the critical radius for PNs of different materials: $R_c = \tilde{r}_{\text{shell}(c)}(\gamma/G) \approx 7$ nm for Cu ($\gamma = 0.625$ J/m^2, $G = 3.38 \times 10^{10}$ Pa [12]); $R_c \approx 14$ nm for Ag ($\gamma = 0.780$ J/m^2, $G = 3.38 \times 10^{10}$ Pa [12]).

In conclusion, the results of our calculations showed that the formation of a misfit shell (for example, by means of diffusion) on icosahedral PNs is an effective channel of internal stress relaxation in such particles. The optimum misfit parameter $\varepsilon^*_{\text{opt}}$ was determined that provides the maximum energy gain in the case where the core and shell have the same elastic moduli. The critical radii, above which the formation of a layer with lattice parameter misfit is energetically favorable, for typical fcc metals (Cu, Ag) is on the order of ~10 nm.

Acknowledgments. This study was supported in part by the Russian Foundation for Basic Research, project nos. 05-08-655503a and 07-01-00659a. One of the authors (A.E.R.) gratefully acknowledges support from the Meede Program (project no. 1.00101-0337).

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Translated by P. Pozdeev

SPELL: 1. disclination, 2. nanodimensional, 3. disclinations, 4. eigenstrain