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Analytical and Kinetic Monte–Carlo Study Shrinkage by Vacancy Diffusion of Hollow Nanospheres and Nanotubes

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1. Introduction

Recently, Sun *et al*. [1] have developed a simple and generic approach to the synthesis of hollow noble metal nanostructures. The key step of this process is the redox reaction between a silver template and the solution of the appropriate salt precursor. A quite different method for synthesizing hollow (binary) nanostructures makes use of the Kirkendall effect of diffusion [2]. Such hollow nanostructures have a wide range of technological applications such as catalysis, vehicles for drug delivery, containment of environmentally sensitive species.

However, it has been noted [3,4] that hollow nanospheres should in fact be unstable in principle and, with time, they will tend to shrink into a solid nanosphere. The mechanism of shrinking can be considered as resulting from the vacancy flux from the inner surface to the external surface.

2. Results and discussion

In this work, shrinking via the vacancy mechanism of a pure element hollow nanosphere and nanotube is described analytically. Using Gibbs-Thomson boundary conditions in quasi steady-state at the linear approximation, we determine the collapse time as a function of geometric size both for hollow nanoshpere (Eq. 1) and nanotube (Eq. 2):

$$\tau(\delta)=\ln\left[\frac{(1-\varepsilon_0)(1+\varepsilon_0)^3}{\left(1-\varepsilon_0^3\right)^{\frac{4}{3}}}\frac{\left(1-\varepsilon_0^3\delta^3\right)^{\frac{4}{3}}}{(1-\varepsilon_0\delta)(1+\varepsilon_0\delta)^3}\right]-2\varepsilon_0\left(\frac{1-\varepsilon_0}{1-\varepsilon_0^3}-\delta\frac{1-\varepsilon_0\delta}{1-\varepsilon_0^3\delta^3}\right), \tag{1}$$

$$\frac{5}{4}\tau(\delta)=\ln\left[\frac{1+\left(1-\varepsilon_0^2\delta^2\right)^{\frac{1}{2}}}{1+\left(1-\varepsilon_0^2\right)^{\frac{1}{2}}}\right]+\arcsin(\varepsilon_0\delta)-\arcsin(\varepsilon_0)+\varphi_1(\varepsilon_0)-\varphi_1(\varepsilon_0\delta)+ \\ +\left[\varphi_2(\varepsilon_0\delta)-1\right]\ln(\delta)+\left[\varphi_2(\varepsilon_0\delta)-\varphi_2(\varepsilon_0)\right]\ln(\varepsilon_0) \tag{2}$$

with

$$\varphi_1(x)=\frac{1+3x+x^2}{2\left(1-x^2\right)^{\frac{1}{2}}(1+x)},\ \varphi_2(x)=\frac{2+2x-3x^2+2x^3+2x^4}{2\left(1-x^2\right)^{\frac{3}{2}}(1+x)}, \tag{3}$$

where $\tau=6c_{\mathrm{V}}^{\mathrm{eq}}D_{\mathrm{V}}t\beta/r_{\mathrm{f}}^3$ ($c_{\mathrm{V}}^{\mathrm{eq}}$ and D_{V} are the equilibrium concentration and the diffusion coefficient of the vacancies, respectively; $\beta=2\gamma\Omega/kT$ and $\beta=\gamma\Omega/kT$ for hollow nanospheres and nanotubes, respectively; γ is the surface energy, Ω is the atomic volume and r_{f} is the radius of a collapsed compact nanosphere or nanorode), $\delta=\varepsilon/\varepsilon_0$ and $\varepsilon=r_{\mathrm{i}}/r_{\mathrm{e}}$ is the ratio of the inner r_{i} and the external r_{e} radii of the hollow nanosphere or nanotube at time t ($\varepsilon=\varepsilon_0$ at $t=0$).

Kinetic Monte Carlo (KMC) simulation by the Metropolis algorithm confirms the predictions of the analytical model (as an example see Figs. 1 and 2).

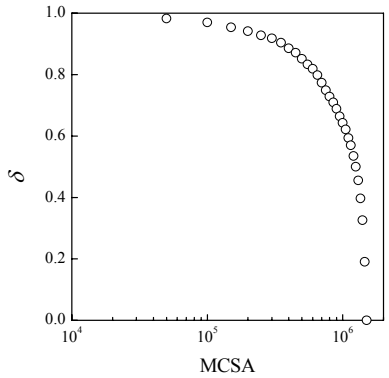

Fig. 1. KMC simulation of the shrinking kinetics of a f.c.c. pure element nanotube with $\varepsilon_0 = 0.5$, $r_f = 8\sqrt{3}a$ (a is the lattice parameter) and the pair interaction energy $\phi/kT = -1.2$.

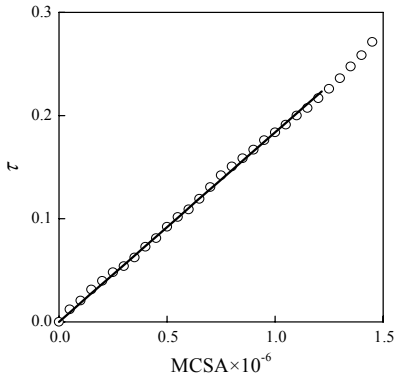

Fig. 2. Test of Eq. 2 on the basis of the results of KMC simulation shrinking kinetics of a f.c.c. pure element nanotube with $\varepsilon_0 = 0.5$, $r_f = 8\sqrt{3}a$ and $\phi/kT = -1.2$ (see Fig. 1).

It was shown on the basis of this simulation that the averaged surface energy per unit area (γ) of the external surface of such nanoobjects during shrinking is at least no lower than γ of the {110} crystallographic surface. It is well-known from both experimental data and molecular dynamics (MD) simulations using the embedded-atom method that the {110} surface inclines to reconstruction with increasing atomic density. Therefore, we can anticipate that the reconstruction processes will occur in areas of high energy facets on the external surface of such nanoobjects both in real experiments and in MD simulations by the embedded-atom method.

3. Conclusion

The shrinkage via the vacancy mechanism of a pure element hollow nanosphere and nanotube has been described. Using Gibbs-Thomson boundary conditions an exact solution has been obtained of the kinetic equation in quasi steady-state at the linear approximation. The collapse time as a function of the geometrical sizes of hollow nanospheres and nanotubes has been determined. KMC simulation of the shrinkage of these nanoobjects was performed: it completely confirmed the predictions of the analytical model. However, it has been shown on the basis of this simulation that under real conditions reconstruction of the external surface can occur. This reconstruction could not be taken into account either in the theoretical analysis or KMC simulation.

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References

[1] Y. Sun, B. Mayers and Y. Xia, Adv. Mater., 15 (2003) 641.
[2] Y. Yin, R.M. Rioux, C.K. Erdonmez *et al*, Science, 304 (2004) 711.
[3] K.N. Tu and U. Gösele, Appl. Phys. Lett., 86 (2005) 093111.
[4] A.M. Gusak, T.V. Zaporozhets, K.N. Tu and U. Gösele, Phil. Mag., 85 (2005) 4445.