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A model of Kirkendall hollowing of core–shell nanowires and nanoparticles controlled by short-circuit diffusion

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Abstract—We propose a model for the hollowing of the core–shell nanowires caused by the Kirkendall effect during chemical reaction (oxidation) on the nanowire surface. We consider the self-diffusion of the atoms of the core along the grain boundaries in the shell, on the exposed surface of the core, and along the core–shell interface as the main factors controlling the hollowing kinetics. The model relies on the variational method of calculating the chemical potential of the metal atoms diffusing along the core–shell interphase boundary. A comparison of model predictions with the results of hollowing studies of Ni–NiO core–shell nanoparticles [J.G. Railsback et al., ACS Nano 4 (2010) 1913–1920] gave a value for the self-diffusion coefficient of Ni along the grain boundaries in NiO at 573 K of 3×10^{-20} m^2 s^{-1}, in good agreement with the literature data. We demonstrate that high values of the contact angle of the core on the shell promote pore instability and formation of secondary side pores (pores multiplication).

Keywords: Nanowire; Nanovoid; Nanoparticles; Surface diffusion; Interface diffusion

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1.Introduction

Hollow nanoparticles and inorganic nanotubes have attracted a great deal of interest because of their unique functional properties and possible applications in various fields of nanotechnology [1]. The nanoscale Kirkendall effect offers a unique synthesis tool for producing of variety of hollow nanostructures [2]. It was first reported by Yin et al. during their studies of the interaction of Co nanoparticles with sulfur, oxygen and selenium in a fluid environment [3]. The interaction between metal nanoparticle and reactive environment produces a shell of reaction product (i.e. sulfide or oxide) that fully covers the metal core. When the outward diffusion of cations through this shell is faster than the inward diffusion of anions, a supersaturation of vacancies is created in the metal core (Kirkendall effect). These vacancies eventually coalesce into single or multiple pores that consume the core material. During the last decade this nanoscale Kirkendall effect has been reported in a number of systems, most notably in metal–oxide couples [4–6]. Several analytic [7,8] and atomistic [9,10] models of nanoparticle hollowing have been proposed, but all of these rely on bulk diffusion processes in the metal core and treat symmetrical pores nucleating in, or close to, the center of nanoparticles. At the same time, in a number of experimental studies it was observed that the pores nucleate at the metal–reaction product (i.e. oxide) interface. This is understandable since the interfaces between dissimilar materials often represent efficient sinks for vacancies, and as such they are the preferential sites for pore nucleation. At the temperatures at which solid-state diffusion is active the shape and growth kinetics of interface pores should be strongly affected by surface and interface diffusion, which are significantly faster than bulk diffusion [11]. Although an important role of these short-circuit diffusion paths in Kirkendall hollowing has been acknowledged [6,12], no quantitative treatment of the problem is available in the literature. In this work we aim to fill this gap by proposing a quantitative model for the nanoscale Kirkendall effect controlled by surface, grain boundary (GB) and interface diffusion. Our goal is to study the effect of various diffusivities on the morphology of partly hollowed nanoparticles and on the kinetics of hollowing.

2. The model

We will consider the following model for the hollowing of a cylindrical core–shell (metal–oxide) nanowire (see Fig. 1): metal atoms of the core diffuse along the grain boundaries (GBs) of the shell and react with gas (oxygen) on the shell surface. The size and shape evolution of the metal core is

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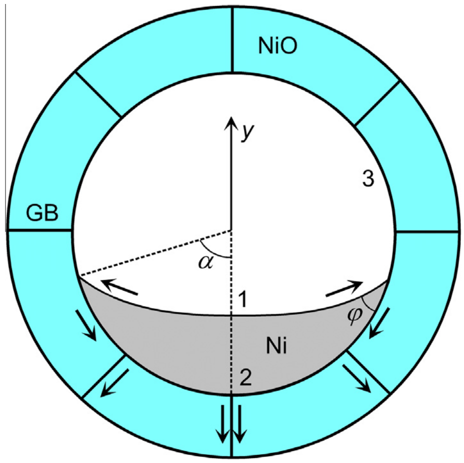

Fig. 1. Schematic illustration of the model. The hollowing of the core (Ni)–shell (NiO) nanowire during annealing is controlled by a combination of metal atom self-diffusion on the surface of the core (1), along the core–shell interface (2), and along the GBs in the shell. We assumed either slow or fast diffusion of metal atoms on the inner surface of the shell (3).

controlled by metal self-diffusion on the exposed surface (1) and along the core–shell (metal–oxide) interface (2). In the further analysis we will also explore the role of metal diffusion on the internal surface of the shell (3). It should be noted that at the temperatures at which these short-circuit diffusion paths dominate, the atomic mobilities in the oxide are negligible and the shell can be considered as inert. In certain respects, the described problem is similar to the problem of solid-state dewetting of thin metal films on ceramic substrate [13,14], with an important difference that the "substrate" exhibits cylindrical curvature, and the total mass of the metal is decreasing due to chemical reaction (oxidation). As in the case of solid-state dewetting of thin films, the boundary conditions at the triple line (1)–(2)–(3) play an important role in the process and affect its kinetics. It is also important that the hole of the partly hollowed nanowire can grow in size only due to the self-diffusion of metal atoms along the core–shell interface. This diffusion process transports the metal atoms supplied by self-diffusion along the sinking metal surface to the GBs in the shell. The same interface diffusion also causes a drift of the metal lattice toward the shell, which is one of the manifestations of the Kirkendall effect. The lattice drift contributes to the hole growth and should be taken into account in any quantitative model of hollowing. The variational method of treating of such drift was developed in several recent works [15,16] and will be employed in the present study.

The driving force for the surface diffusion is a gradient of the surface curvature κ [17]:

$$V_n = \frac{D_s v_s \Omega^2 \gamma}{kT}\frac{\partial^2 \kappa}{\partial s^2} \tag{1}$$

where V_n is the normal velocity of the metal surface with respect to the lattice of the metal core, D_s is the effective surface diffusion coefficient, v_s is the density of the mobile atoms on the surface, Ω is the atomic volume ($v_s\Omega = \delta_s$, where δ_s is the effective thickness of the surface diffusion layer), s is the coordinate along the surface, γ is the surface energy of the metal core, and kT has its usual thermodynamic meaning.

The flux, j, of the metal atoms along the core–shell interface is driven by the gradient of the chemical potential of the metal atoms, μ, along the interface:

$$j = -\frac{D_i v_i \Omega}{kT}\frac{\partial \mu}{\partial s} \tag{2}$$

where D_i is the effective interface diffusion coefficient and v_i is the density of mobile atoms at the interface ($v_i\Omega = \delta_i$, where δ_i is the effective thickness of the interface diffusion layer). Here, μ is understood as an excess chemical potential associated with the presence of surfaces and interfaces in the system. The divergence of the flux j leads to accumulation of metal atoms at the interface. The condition of matter conservation leads to the following expression for the rate of material accretion at the interface, $\partial h/\partial t$:

$$\frac{\partial h}{\partial t} = \frac{D_i \delta_i}{kT}\frac{\partial^2 \mu}{\partial s^2} - \frac{D_{gb}\delta_{gb}}{kTd}\frac{\mu - \mu_{out}}{w}. \tag{3}$$

The last term on the right-hand side (RHS) of Eq. (3) describes the steady-state GB diffusion of metal atoms through the shell: D_{gb} is the diffusion coefficient of the core component along the GBs in the shell, d is the grain size in the shell, w is the thickness of the shell, and μ_{out} is the chemical potential of metal atoms on the outer surface of the shell. In deriving Eq. (3) we assumed that $d<<2\pi R$, where R is the initial radius of the core. The last term on the RHS of Eq. (3) provides a rigorous description of the GB diffusion flux for the case in which the chemical potential of metal (core) atoms is fixed at μ_{out} in the outside (oxidizing) atmosphere. However, in many cases during the oxidation of metals it is the concentration of metal atoms, rather than their chemical potential, which is fixed on the surface where the oxidation reaction occurs. For example, when all the metal atoms arriving at the surface of the shell swiftly react with oxygen, $c_{out} = 0$ is a good approximation for the respective boundary condition (here c_{out} is the concentration of metal atoms at the intersection of the GBs with the outer surface of the shell). The assumption that the solution of metal atoms in the GBs of the (oxide) shell is ideal yields the following expression replacing the last term on the RHS of Eq. (3):

$$\frac{D_{gb}\delta_{gb}\Omega c_e}{dw}\exp\left(\frac{\mu}{kT}\right) \tag{4}$$

where c_e is the equilibrium concentration of metal atoms in the GBs of planar oxide layer at the metal–oxide interface. We will limit our further consideration by the linear expression in Eq. (3). It also provides a good linear approximation of expression (4) in the relevant range of chemical potential μ for $\mu_{out} \approx -2.75kT$.

For symmetry reasons, the drift of the lattice of the metal core with respect to the shell occurs only in the y-direction (see Fig. 1). In order to calculate the distribution of the chemical potential μ along the core–shell interface we will employ the following obvious geometric relationship between the rate of material accretion at the interface and the drift rate, V_y, of the lattice of metal core toward the shell [16]:

$$\frac{\partial h}{\partial t} = V_y \frac{\partial X}{\partial s}. \tag{5}$$

In this equation V_y is the drift rate of the metal core lattice toward the shell, and $X(s)$ is the x-coordinate of the interface. Substituting Eq. (5) into Eq. (3) yields: