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Reactive diffusion and stresses in nanowires or nanorods

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ABSTRACT

Heterostructured nanowires are of prime interest in nowadays technology such as field-effect transistors, field emitters, batteries and solar cells. We consider their aging behavior and developed a model focusing on reactive diffusion in core-shell nanowires. A complete set of analytical equations is presented that takes into account thermodynamic driving forces, vacancy distribution, elastic stress and its plastic relaxation. This complete description of the reactive diffusion can be used in finite element simulations to investigate diffusion processes in various geometries. In order to show clearly the interplay between the cylindrical geometry, the reactive diffusion and the stresses developing in the nanowire, we investigate the formation of an intermetallic reaction product in various core-shell geometries. Emphasis is placed on showing how it is possible to control the kinetics of the reaction by applying an axial stress to the nanowires.

1. Introduction

In Ref. [1] we presented a complete set of analytical equations to describe reactive diffusion in spherical core shell nanostructures. The model takes into account elastic stress, its plastic relaxation, as well as possible non-equilibrium vacancy densities. Furthermore, thermodynamic driving forces are included to model the formation of intermetallic (IM) product phases within an intermediate composition range. Using this model, we studied the reaction in spherical triple core-shell structures *A/B/A* and *B/A/B*, for which Schmitz et al. [2] observed that the growth rate depends on the stacking order. Comparison with the data of atom probe tomography (APT) proved that significant deviations from the vacancy equilibrium concentration develop over time which control stability and reaction rate of the nanometric diffusion couples.

In this paper, we will present a new set of analytical equations, this time to describe reactive diffusion in a *cylindrical* core shell nanostructure. The interest in the cylindrical geometry stems from the ever growing importance of nanowires, nanowhiskers and nanopillars in recent technologies as they are used in new generation of devices or prototypes in numerous fields: field-effect transistors [3,4], battery electrodes [5,6], flexible solar cells … [7]. For such applications, homogeneous nanowires are not sufficient. More elaborate structures, such as core-shell nanowires, are often necessary. If the core shell structure is lost, for example upon heating, the function also deteriorates. Consequently, knowledge about reaction of layers and the developing-relaxing stress field is indispensable to prevent this deterioration and to construct more stable structures.

Basic equations describing the reactive diffusion in cylinders are developed in the following. We will then use computer simulation in order to solve this set of equations. Various examples will help us discuss the interplay between diffusion, elastic stress, plastic relaxation and vacancy concentration. In addition, we will show that applying external forces on the wires allows controlling the reaction: either accelerate or decelerate the process, enhance or hinder the formation of an intermixed phase as desired.

2. Basic equations

In order to keep the analytical formulas transparent, we will refer to isotropic elasticity. As it was pinpointed by Beke et al. in Ref. [8], the creation of a new phase with a different specific volume from the parent phases during reactive diffusion induces a stress-free strain. This stress-free strain, in turns, plays a major role in the kinetics of the process. Therefore, our model needs to describe the stress-free expansion and plastic deformation as it was already discussed in Refs. [1,9]. Stress-free expansion is supposed to be isotropic; accordingly, it has the form $\varepsilon_{ik}^{SF} = \varepsilon^{SF}\delta_{ik}$ (δ_{ik} is the unit tensor). In plastic deformation, volume remains constant, i.e.

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$\mathrm{tr}\widehat{\varepsilon}^P = 0$; i.e. plastic deformation is anisotropic, but it can be supposed that all the non-diagonal elements of the tensor $\widehat{\varepsilon}^P$ are equal to zero, therefore its components can be expressed as $\varepsilon^P_{ik} = \varepsilon^P_{ik}\delta_{ik}$. Thus, the stress induced by the creation of a new phase after plastic relaxation can be written as

$$\sigma_{ik} = \frac{E}{(1+\upsilon)(1-2\upsilon)}\{[(1-2\upsilon)\varepsilon_{ik} + \nu\varepsilon_{ll}\delta_{ik}] - \left[(1+\upsilon)\varepsilon^{SF} + (1-2)\nu\varepsilon^P_{ik}\right]\delta_{ik}\} \quad (1)$$

using the Einstein's summation convention. In terms of displacement ($\vec{u}$), the equation of equilibrium in the case of internal stress-free strain is

$$\frac{1-\nu}{1+\nu}\,\mathrm{grad}\,\mathrm{div}\vec{u} - \frac{1-2\nu}{2(1+\nu)}\mathrm{rot}\,\mathrm{rot}\vec{u} = \mathrm{grad}\varepsilon^{SF} + \frac{1-2\nu}{1+\nu}\mathrm{div}\widehat{\varepsilon}^P \quad (2)$$

where ν is Poisson's ratio, E is Young's modulus.

3. Solution of the equation of equilibrium in the case of a fixed cylinder

In order to mimic the conditions of a core-shell nanowire, we solved the equation of equilibrium assuming a cylindrical symmetry. The wire is also considered fixed at both ends and can be stressed initially in the axial direction (the solution for a free wire is given in Appendix A). This specific geometry implies the following: only the radial component u of the dilatation vector differs from zero (azimuthal and axial components $u_\theta = u_z = 0$). Consequently eq. (2) has the following form in cylindrical coordinates

$$\frac{1-\nu}{1+\nu}\left[\frac{1}{r}\frac{\mathrm{d}(ru)}{\mathrm{d}r}\right] = \frac{\mathrm{d}\varepsilon^{SF}}{\mathrm{d}r} + \frac{1-2\nu}{1+\nu}\left[\frac{\mathrm{d}\varepsilon^P_{rr}}{\mathrm{d}r} + \frac{1}{r}\left(\varepsilon^p_{rr} - \varepsilon^p_{\theta\theta}\right)\right] \quad (3)$$

Here the indices "rr" and "θθ" denote the radial and the azimuthal components of the tensors. Applying axial force to the wire initially and fixing its ends under this stressed state, the solution of the equilibrium equation is

$$u = \frac{1-\nu}{1+\nu}\frac{1}{r}\int_{R_i}^{r} r\left[\varepsilon^{SF} + \frac{1-2\nu}{1+\nu}\left(\varepsilon^P_{rr} + A\right)\right]\mathrm{d}r + C_1 r + \frac{C_2}{r} - \nu\frac{C_3}{E}r \quad (4)$$

where

$$A = 2\int_{R_i}^{r}\frac{\varepsilon^P_{rr}}{r}\mathrm{d}r \quad (5)$$

C_1, C_2 and C_3 are constants of integration to be determined from boundary conditions and R_i is any convenient lower limit for the integral, such as inner radius of a hollow cylinder or $R_i = 0$ for a solid cylinder. Eq. (4) has been obtained using $\mathrm{tr}\widehat{\varepsilon}^P = 0$. Since the wire is fixed at both ends $\varepsilon^P_{zz} = 0$ and $\varepsilon^P_{rr} = -\varepsilon^P_{\theta\theta}$. Note that without any axial initial force, the term $-\nu\frac{C_3}{E}r$ vanishes. Therefore, this term considers that the displacement is affected by the uniform initial stress applied.

Knowing the displacement vector, the components of the total strain tensor in cylindrical coordinates can be determined using $\varepsilon_{rr} = \mathrm{d}u/\mathrm{d}r$, $\varepsilon_{\theta\theta} = u/r$ and $\varepsilon_{zz} = \mathrm{d}u_z/\mathrm{d}z$ [10]. For these we obtain

$$\begin{aligned}
\varepsilon_{rr} &= \frac{1+\nu}{1-\nu}\left\{-\frac{1}{r^2}\int_{R_i}^{r} r\left[\varepsilon^{SF} + \frac{1-2\nu}{1+\nu}\left(\varepsilon^P_{rr} + A\right)\right]\mathrm{d}r + \varepsilon^{SF} + \frac{1-2\nu}{1+\nu}\left(\varepsilon^P_{rr} + A\right)\right\} + C_1 - \frac{C_2}{r^2} - \nu\frac{C_3}{E}\\
\varepsilon_{\theta\theta} &= \frac{1+\nu}{1-\nu}\frac{1}{r^2}\int_{R_i}^{r} r\left[\varepsilon^{SF} + \frac{1-2\nu}{1+\nu}\left(\varepsilon^P_{rr} + A\right)\right]\mathrm{d}r + C_1 + \frac{C_2}{r^2} - \nu\frac{C_3}{E}\\
\varepsilon_{zz} &= C_3/E
\end{aligned} \quad (6)$$

The components of the stress tensors can then be obtained by substituting the strain components in eq. (1):

$$\begin{aligned}
\sigma_{rr} &= -\frac{E}{1-\nu}\frac{1}{r^2}\int_{R_i}^{r} r\left[\varepsilon^{SF} + \frac{1-2\nu}{1+\nu}\left(\varepsilon^P_{rr} + A\right)\right]\mathrm{d}r + \frac{E}{1+\nu}\left(A + \frac{C_1}{1-2\nu} - \frac{C_2}{r^2}\right)\\
\sigma_{\theta\theta} &= \frac{E}{1-\nu}\frac{1}{r^2}\int_{R_i}^{r} r\left[\varepsilon^{SF} + \frac{1-2\nu}{1+\nu}\left(\varepsilon^P_{rr} + A\right)\right]\mathrm{d}r - \frac{E}{1-\nu}\varepsilon^{SF} + \frac{E}{1+\nu}\left(\frac{\varepsilon^P_{rr}}{1-\nu} + \frac{\nu}{1-\nu}A + \frac{C_1}{1-2\upsilon} + \frac{C_2}{r^2}\right)\\
\sigma_{zz} &= -\frac{E}{1-\nu}\varepsilon^{SF} + \frac{\nu E}{1+\nu}\left(\frac{\varepsilon^P_{rr} + A}{1-\nu} + \frac{2}{1-2\nu}C_1\right) + \frac{1-\nu}{(1+\nu)(1-2\nu)}C_3
\end{aligned} \quad (7)$$

The constants of integration can now be determined using the boundary conditions. For instance, in the case of a solid cylinder ($R_i = 0$) with free outer surfaces ($\sigma_{rr}(R_o) = 0$) the displacement at the center of the cylinder is equal to zero: $u(R_i) = 0$. Thus, it follows from eq. (4) that

$$C_2 = 0 \quad (8)$$

By definition C_3 is the uniform axial stress applied initially, so

$$C_3 = \sigma^0_{zz} \quad (9)$$

Moreover, since the cylinder is free to expand in the radial direction, the radial component of the stress tensor vanishes at the