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Computer Simulation of the Formation of Hollow Nanocrystals

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Abstract
Experiments on the formation of hollow nanocrystals of cobalt sulphide by way of the Kirkendall effect have been reported recently by Yin *et al*. We perform a set of Monte Carlo simulations of the process to explore the phenomenon.

1. Introduction

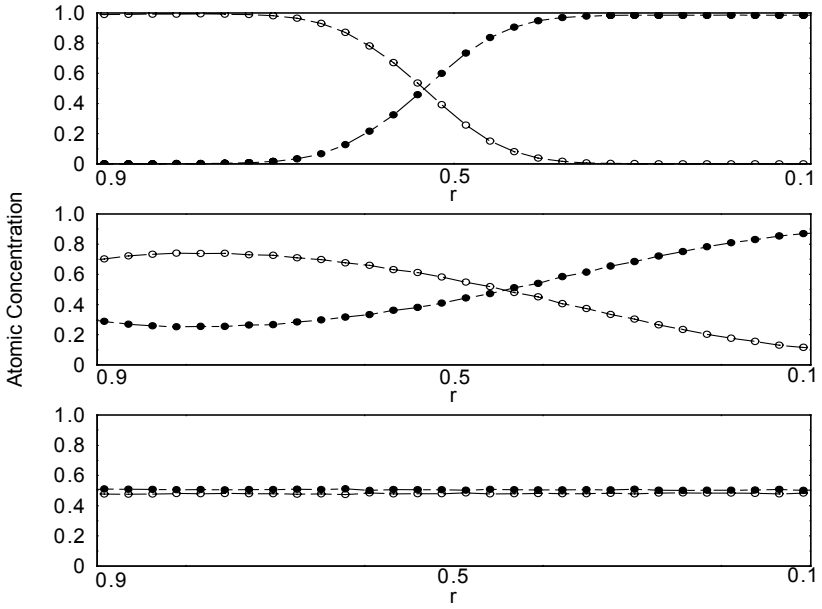
A recent experiment on cobalt nanocrystals heated in sulphur at 180 ºC showed the fascinating formation of hollow nanospheres of cobalt sulphide by the process of interdiffusion with the formation of Kirkendall porosity (at the centre of the original cobalt nanocrystal) [1]. We have undertaken a computer simulation/analytical study to explore this phenomenon.

2. Computer simulation

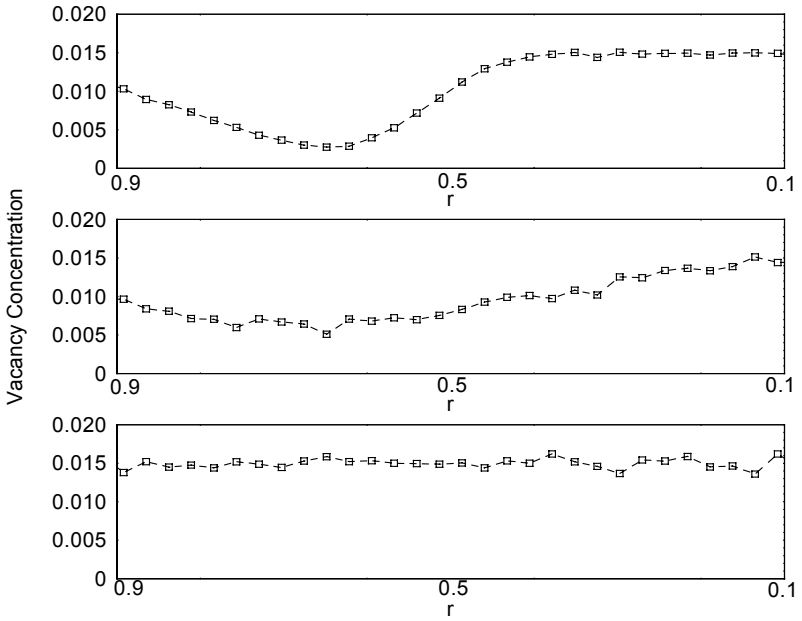
We considered a diffusion couple prepared as two concentric layers or shells with a total width d of about a hundred lattice planes. The internal core ($r_1 \geq r \geq r_0$) consists of A which is a much faster diffuser than the external shell, which is of material B ($r_2 \geq r > r_1$, $r_2 - r_1 = d$). For definiteness, we assume that the ratio of atom-vacancy exchange frequencies $w_A/w_B = 100$. The atomistic simulation employed a new simulation procedure that employed moving boundaries. The experiments were done for the case of a spherical geometry [1]. Assuming that at the initial time there is already a small pore at $r = 0$ the general behaviour of the interdiffusion couple in a spherical geometry can be satisfactorily modeled by a planar geometry. The boundary conditions for the vacancy site fraction were as follows: $c_V(r{=}0.9,t) = c_V(r{=}0.1,t) = \text{constant}$.

3. Results

Profile results are shown in Figure 1a,b for small, intermediate and long times. During interdiffusion the diffusion couple moves some 25% of its length, creating further porosity. Anomalous behaviour (compared with standard interdiffusion couples) of the atomic and vacancy profiles occurs because there are no active vacancy sources and sinks within the diffusion zone. At short times, vacancies are quickly depleted on the slow diffuser side. Continued depletion occurs before the couple starts moving (upper part of Fig.1b). Once the vacancies are taken directly from the left boundary (modeled as an active source of vacancies in the computer simulation) the movement of the couple starts. At the same time, the interdiffusion process proceeds in the usual way (upper part of Fig. 1a shows symmetric atomic concentration profiles). Once movement starts the interdiffusion process is somewhat accelerated (middle parts of Figs 1a,b). At some stage there is no need for vacancy depletion any longer and the active sink (right boundary) stops, but the active source is still in operation until both the vacancy and atomic concentrations become constant throughout the couple (end of interdiffusion process: lower parts of Figs. 1a,b).



(a)



(b)

Figs. 1a,b. Atomic and vacancy profiles at short, intermediate and long diffusion times.

Reference

[1] Y. Yin et al., Science, 304, (2004) 711.