diffusion-fundamentals

The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Molecular Dynamics Study of Diffusion in Palladium Hollow Nanospheres and Nanotubes

Alexander V. Evteev, Elena V. Levchenko, Irina V. Belova and Graeme E. Murch

Diffusion in Solids Group, Centre for Geotechnical and Materials Modelling,
School of Engineering, The University of Newcastle, NSW 2308 Callaghan, Australia,
E-Mail: Elena.Levchenko@newcastle.edu.au

1. Introduction

The synthesis of nano–scale materials is a rapidly developing field of materials science. Recently, Sun *et al.* [1] have demonstrated the preparation of a number of hollow nanostructures of Au, Pd and Pt by a replacement reaction with Ag starting with solid Ag templates. Such structures have very considerable promise in a wide range of technological applications such as catalysis, precise drug delivery and many others.

However, it has been noted [2,3] that hollow nano-objects should be unstable in principle and, with time, they will tend to shrink. According to [2,3] the mechanism of shrinking can be considered as resulting from the vacancy flux from the inner surface to the external surface. The driving force for this flux is the difference between the vacancy concentrations on the inner and external surfaces. We have described the shrinkage via the vacancy mechanism of a pure element hollow nanosphere and nanotube (see our abstract titled 'Analytical and kinetic Monte–Carlo study shrinkage by vacancy diffusion of hollow nanospheres and nanotubes'). Using Gibbs-Thomson boundary conditions an exact solution was obtained of the kinetic equation. The collapse time as a function of the geometrical sizes of hollow nanospheres and nanotubes was determined. Kinetic Monte-Carlo (KMC) simulation of the shrinkage of these nano-objects was performed: it 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. In the present paper, we study the diffusion in a pure Pd hollow nanosphere and nanotube by performing a molecular dynamics (MD) simulation using the embedded-atom method (EAM).

2. The model

The initial hollow nanosphere and nanotube were cut from a perfect bulk f.c.c. Pd lattice and consisting of 76657 and 51068 atoms in the nanoshells with inner and external radii $r_{i0}\approx 28$ Å and $r_{e0}\approx 65$ Å, respectively. The periodic boundary conditions along the axis of the nanotube, coinciding with the [001] direction (*z*–direction), were imposed. Then, the MD procedure of isothermal annealing was performed.

3. Results and discussion

It was established that the investigated Pd MD models of hollow nano-objects melt at 1500 K. Therefore, our MD study of diffusion in Pd hollow nano-objects was carried out just below the melting temperature at 1450 K. Before the diffusion calculations, a vacancy concentration was permitted to approach equilibrium (this took the first 2.4 ns of our experiment). Then, for different distance intervals in nanoshells, we have calculated the mean square displacement

(MSD) only for those Pd atoms, which during the time of experiment were in the same distance interval (as an example, see the results for hollow nanosphere in Fig. 1). It should be noted that outside the intervals indicated by Fig.1 the MSD is much larger. Therefore, the average diffusion length was confined to less than intervals of 3 Å. Thus, outside these distance intervals it was impossible to determine correctly the diffusion coefficient by the vacancy mechanism. The diffusion coefficient of Pd atoms in different distance intervals in the nanoshell was calculated from the Einstein equation. As can be seen in Fig. 2, the diffusion coefficient in the Pd hollow nanosphere increases with proximity to the surfaces. It is well known that the diffusion coefficient is proportional to the vacancy concentration; therefore, these results demonstrate that the vacancy concentration is larger near the inner and external surfaces compared with the middle part of the nanoshell. Similar results were obtained for nanotubes, with the only difference that an anisotropy of diffusion in the radial direction ($D_\perp$) and along the cylinder axis ($D_\parallel$) is observed $D_\perp/D_\parallel \sim 0.7$. Therefore, the MD results obtained provide quite a strong argument that a pure element hollow nanosphere or nanotube will not shrink readily via the vacancy mechanism.

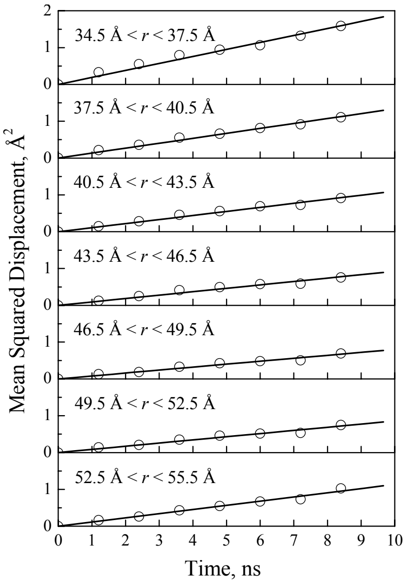

Fig. 1. MSD of Pd atoms by the vacancy mechanism in the hollow nanosphere.

4. Conclusion

MD simulation in combination with the EAM has been used to investigate the diffusion by the vacancy mechanism in a Pd hollow nanosphere and nanotube. We found that the diffusion coefficient in a Pd hollow nanosphere and nanotube is larger near the inner and external surfaces compared with the middle part of a nanoshell. This is quite a strong reason to argue that a pure element hollow nanosphere or nanotube will not shrink readily by the vacancy mechanism.

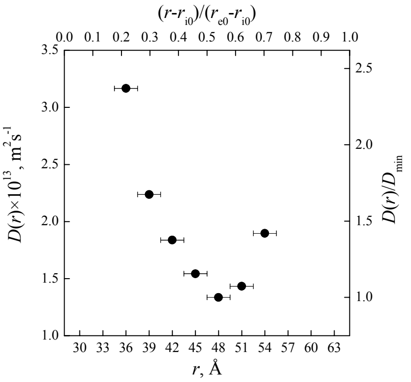

Fig. 2. Diffusion coefficient versus radius.

Acknowledgements: The support of the Australian Research Council is acknowledged.

References

[1] Y. Sun, B. Mayers and Y. Xia, Adv. Mater., 15 (2003) 641.
[2] K.N. Tu and U. Gösele, Appl. Phys. Lett., 86 (2005) 093111.
[3] A.M. Gusak, T.V. Zaporozhets, K.N. Tu and U. Gösele, Phil. Mag., 85 (2005) 4445.