Science Bulletin 62 (2017) 818–819

Contents lists available at ScienceDirect

Science Bulletin

journal homepage: www.elsevier.com/locate/scib

Research Highlight

Atomic level understanding of the nanoscale Kirkendall effect

Guozhong Cao

Department of Materials Science and Engineering, University of Washington, Seattle, WA 98195-2120, USA

Exactly 70 years after Kirkendall's revolutionary experiments established the vacancy diffusion mechanism and the resultant Kirkendall effect and Kirkendall pores [1], Sun et al. [2] advanced the understanding of the Kirkendall effect to near atomic level with the real-time tracking three-dimensional (3D) evolution of colloidal nanoparticles under real reaction conditions.

Smigelskas and Kirkendall [1] in 1947 reported an experiment on the interdiffusion between copper and zinc in a copper/brass diffusion couple at high temperatures and found the initial interface or boundary moved toward brass because zinc diffused more quickly than copper, resulting in the establishment of the vacancy diffusion mechanism, still valid till this day. If substantial diffusion takes place at the interface of a binary system, there will be a flux of atoms in one direction and a flux of vacancies in the other, consequently vacancies aggregate to form voids at the interface region of the metal with large diffusivity. Voids and pores grow and coalesce with prolonged heat treatment. Kirkendall effect in the formation of metal alloys was regarded as a serious problem in metallurgical manufacturing because the presence of pores will affect the mechanical, thermal, and electrical properties and cause bonding and adhesion failure, so the major research was focused on suppressing the Kirkendall effect.

Kirkendall effect not only occurs by interdiffusion at the interface of binary metal/alloy systems with substantial difference in diffusion coefficients, but could also take place in solid-gas and solid liquid interactions such as metal oxidation and rusting. When a solid containing element A is brought in contact with a solution or gas containing other element B, elements A and B would react to form a solid coating/shell of AB at the interface. If element A diffuses more rapidly through AB layer than element B, Kirkendall pores would form at the interface between the solid and AB layer. If the solid is small, i.e., at the nanometer scale, the coalescence of the pores will eventually produce a hollow nanostructure.

Hollow nanostructures are promising for applications including catalysis, energy conversion and storage such as solar cells and batteries, ultralight structural materials, thermal and electrical insulators, optics, electronics, and sensors [3–5]. The most popular method to synthesize hollow nanomaterials involves coating of the desired material onto sacrificial templates, however, the subsequent removal of templates is often incomplete, time-consuming, costly, and difficult to scale up [3]. Yin et al. [6] in 2004 first demonstrated the nanoscale Kirkendall effect for the formation of cobalt sulfide, selenide and oxide hollow nanoparticles. Subsequently hollow nanoparticles of various metal sulfides, selenides, tellurides, oxides, nitrides and phosphides were synthesized using such Kirkendall effect [7,8]. Similarly, various nanotubes and yolk-shell nanostructures have been synthesized by Kirkendall effect based mechanism [8,9]. Understanding the detailed evolution of nanoparticles at atomic level will be beneficial for precise control over the two-way materials diffusion in the AB layer, enabling the design and synthesis of nanoparticles with appropriate morphologies and properties.

Sun et al. [2] reported groundbreaking results regarding the real-time tracking 3D evolution of colloidal nanoparticles with a spatial resolution of ca. 5 Å under real reaction conditions (e.g., solution saturated with oxygen) (Fig. 1). By taking oxidation of colloidal iron nanoparticles in solution as an example, Sun et al. [2] reported the simultaneous use of time-resolved small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) for monitoring the oxidation process. The high-resolution X-ray scattering patterns and the high uniformity of the nanoparticles enabled a precise reconstruction of 3D morphologies of the nanoparticles using the ab initio structural calculations. The results revealed the transformational details from the solid iron nanoparticles to hollow iron oxide nanoshells via nanoscale Kirkendall process. In parallel, large-scale reactive molecular dynamics (MD) simulations were consistent with the experiments and elucidated the underlying atomistic mechanism and dynamical evolution of voids during the oxidation of iron nanoparticles. Both simulations and in-situ observations suggest void formation initiates at the metal/oxide interface followed by their coalescence and growth, which are driven by the relatively higher cationic diffusivities compared to anion. The quantitative analysis further reveals that direction of material diffusion (i.e., outward diffusion of iron versus inward diffusion of oxygen) reverses upon oxide crystallization and the stoichiometry of the iron oxide nanoshells can be tuned by controlling the atmosphere. The real-time quantitative results provide the unprecedented knowledge on nanoscale Kirkendall process to complement many intuitive interpretations based on the ex-situ characterizations. Apparently, the 3D structural variation and mass diffusion with such high spatiotemporal resolution are crucial for understanding the nanoscale oxidation mechanism in complex reaction environment (in particular, in liquid solution).

E-mail address: gzcao@u.washington.edu

http://dx.doi.org/10.1016/j.scib.2017.05.006

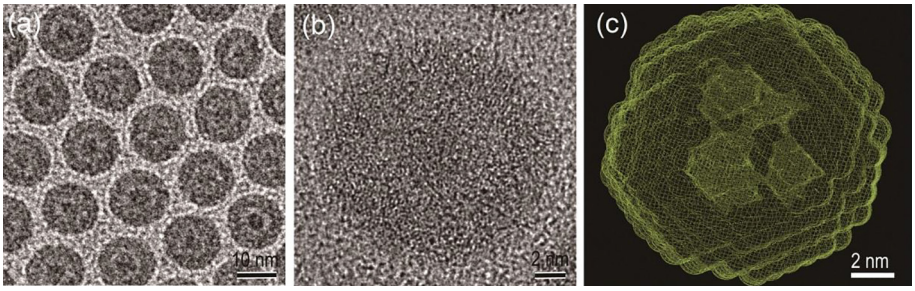

Fig. 1. (Color online) Characterization of products formed from oxidation of iron nanoparticles. (a) Transmission electron microscope (TEM) image of an intermediate oxidation product of iron nanoparticles. (b) High-resolution TEM image of an individual intermediate particle. (c) Image of an intermediate particle constructed from the in-situ synchrotron measurement with ab initio program, highlighting the structural details in the particle. Reprinted with permission from Ref. [2], Copyright © 2017 AAAS.

Conflict of Interest

The author declares that he has no conflict of interest.

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