Research paper

Oxidation of metal nanoparticles with the grain growth in the oxide

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ABSTRACT

Oxidation of metals can be influenced by the presence of electric field, lattice strain, rearrangement of the oxide structure, and formation of cracks in an oxide. The understanding of the interplay of these factors is still incomplete. We focus on the scenario including the oxide-grain growth. The model used implies that the whole process is limited by diffusion of metal or oxygen atoms along the grain boundaries as it was originally proposed by Fehlner and Mott for macroscopic samples. For nanoparticles, the model predicts a transition from the power-law oxide growth at low conversion to slower growth at high conversion.

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1. Introduction

In the presence of oxygen, metals are usually covered by an oxide film. The understanding of the mechanisms of formation of such films is obviously of high interest from various perspectives, and the corresponding experimental and theoretical studies can be tracked for many decades [1,2]. Nowadays, this area is still open for research [3–5], because the oxide growth occurring via diffusion of metal and oxygen atoms via a film depends on numerous factors including the electric field generated between the metal-oxide and oxide-gas interfaces, appreciable strain in an oxide and metal, and rearrangement of the metal and oxide structures resulting in formation and growth of grains and cracks in an oxide. The role of each of these factors is not trivial, and their interplay is far from simple. Just for one recent example, one can look through interesting results of experimental studies of oxidation of the (111), (100) and (110) Cu surfaces at temperatures between 313 and 453 K by using spectroscopic ellipsometry [6]. With increasing temperature, in the end of the corresponding oxidation runs, the oxide-film thickness was observed to increase from a few nm to about 100 nm, and the oxide growth was logarithmic for thicknesses under 5 nm and of the power-law type with the exponents of 1/3 and 1/2 in the range of 5–25 nm and above 25 nm, respectively.

During the past decade, many experimental studies were focused on oxidation of metal nanoparticles (see, e.g., recent arti-cles [7–13] are references therein). Such particles can often be fully converted into the oxide state. The first theoretical model suitable for this case and focused on the diffusion-limited formation of the oxide shell in metal spherules was long ago proposed by Valensi [14] and Carter [15]. Recent related theoretical treatments scrutinize the role of the embedded electric field in the Cabrera-Mott limit [16–18] and the details of the void formation (Kirkendall effect) in the metal core [19–22].

To extend the conceptual basis for the understanding of oxidation of metal nanoparticles, we present here a kinetic model focused on the effect of growth of grains in the oxide on diffusion of metal or oxygen atoms via the oxide. Basically, this model implying that the oxidation rate is limited by diffusion can be considered as a combination of the Valensi-Carter model for oxidation of spherically-shaped metal particles [14,15] and the model proposed by Fehlner and Mott for bulk metals and taking the grain growth into account (Eqs. (26)–(30) in Ref. [1]; see also Ref. [23]).

In the Fehlner-Mott model, the diffusion of metal or oxygen atoms in the flat oxide film of thickness L is assumed to occur along the grain boundaries. If l is the average grain size, the number of grains per unit area of the cross section along the oxide-metal interface is proportional to $1/l^2$, while the average length of the boundary of the cross section of a single grain is about πl. The diffusion coefficient is proportional to the product of these values, i.e.,

$$D = \eta/l, \tag{1}$$

where η is the corresponding parameter. The diffusion flux calculated per unit area and per unit time in the direction perpendicular

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to the metal-oxide (or gas-oxide) interface is proportional to D and inversely proportional to L, and accordingly the kinetic equation for the diffusion-limited increase of the oxide thickness is represented as

$$\frac{dL}{dt} = \frac{\kappa}{lL}, \tag{2}$$

where κ is the constant related to the representation of the diffusion coefficient and also to the drop of the concentration of diffusing species along the film.

Originally, Fehlner and Mott assumed that the grain growth is linear [1], $l = \mu(t + t_\circ)$, and accordingly $L = A[\ln(t + t_\circ)]^{1/2}$, where $t_\circ$, μ, and $A = (2\kappa/\mu)^{1/2}$ are constants. In reality, the grain growth is usually described by employing the power law,

$$l = \mu t^m, \tag{3}$$

where $m < 1$ is the exponent, and accordingly one has [23]

$$L = At^{(1-m)/2}, \tag{4}$$

where $A = \{2\kappa/[(1-m)\mu]\}^{1/2}$.

Concerning the power law for the grain growth (Eq. (3)), the conventional Lifshitz-Cahn-Allen analysis of domain coarsening yields $m = 1/2$ [24]. More recent and detailed studies show that the grain growth appears to include dislocation-mediated grain-boundary migration and grain rotation, so that m may be smaller than $1/2$ and asymptotically the growth may be infeasible (for the theory and experiment, see, e.g., Refs. [25–27] and [5,28,29], respectively). Despite the advances in this area, the understanding of the details of the growth of grains in metals is still incomplete. The details of the growth of grains in oxide during metal oxidation are, basically, lacking and open for debate.

The oxide-film-formation model defined by Eqs. (2)–(4) is generic and, as many other models of metal oxidation, does not take various complicating factors into account. In particular, it ignores the lattice strain related to the mismatch of the metal and oxide lattices. Although in general this strain is expected to be important, it can be appreciably relaxed if the oxidation process is accompanied by grain growth. Thus, the model is more or less self-consistent from this perspective. In addition, the model operates with the average grain size. In reality, the grain size is expected to change along the coordinate perpendicular to the metal-oxide (or gas-oxide) interface because at any given time the formation of oxide takes place primarily near one of these interfaces. From the latter perspective, it is instructive to take this feature of the oxidation process into account in order to confirm that Eq. (4) holds in this case. This was a complementary goal of our work. The corresponding analysis is of interest only for theoreticians, and accordingly it is outlined in Appendix so that one may avoid its reading. Our main goal was to generalize Eqs. (2) and (4) for the case of spherically shaped metal nanoparticles. The corresponding results are presented in Section 2.

To motivate the main nanoscience-related part of our work, we may e.g. notice that the interpretation of the already mentioned kinetics of oxidation of the Cu single-crystal surfaces implies that the grain growth takes place in the films with thicknesses of 5–25 nm and the whole process can be described by using Eq. (4) with $m = 1/3$ [6]. Direct observation of structural evolution of 5–10-nm-sized grains during magnesium oxide growth was recently reported in Ref. [5]. In addition, we may refer to recent high-resolution study [10] explicitly showing that the oxidized aluminum nanoparticles may exhibit appreciable surface roughness. Taken together, these studies indicate that the oxide shell in metal nanoparticles can be heterogeneous, i.e., the relaxation of the oxide structure in general and oxide grains in particular may occur in such particles on the time scales comparable or longer than the

time scale of oxidation, and accordingly the grain growth may be relevant for the interpretation of the corresponding oxidation kinetics.

2. Nanoparticles with grains in the oxide shell

For oxidation of metal nanoparticles, we use a spherically symmetric core-shell model (Fig. 1) so that the oxide shell is located at $\rho \leqslant r \leqslant R$, where r is the radial coordinate, and R and ρ are the particle and metal-core radii. The process is considered to be limited by diffusion of metal or oxygen atoms via the oxide shell. At any given r inside this shell, the total diffusion flux is represented as

$$J = -4\pi r^2 D \frac{\partial c}{\partial r}, \tag{5}$$

where $4\pi r^2$ is the surface area of the corresponding sphere, c is the concentration of the species controlling the oxidation rate, and D is the diffusion coefficient. In the Valensi-Carter model [14,15], this coefficient is considered to be constant. Here, however, we operate with the diffusion coefficient expressed via the average grain size (Eqs. (1) and (3)).

Assuming as usual that the time scale of the formation of the steady-state concentration profile is short, one can integrate Eq. (5) in the steady-state approximation,

$$c(r) = c(R) + \frac{J}{4\pi D}\left(\frac{1}{r} - \frac{1}{R}\right). \tag{6}$$

The absolute value of the concentration drop, $\Delta c \equiv |c(\rho) - c(R)|$, is accordingly given by

$$\Delta c = \frac{|J|}{4\pi D}\left(\frac{1}{\rho} - \frac{1}{R}\right). \tag{7}$$

The values of $c(\rho)$ and $c(R)$ are determined by thermodynamics. Thus, Δc is determined by thermodynamics as well, i.e., it is independent of ρ and R (if the oxide growth is controlled by diffusion of metal atoms, Δc is nearly independent of oxygen pressure, while for diffusion of metal atoms it depends on oxygen pressure), and Eq. (7) can be used to describe the dependence of the diffusion flux on ρ and R,

$$|J| = 4\pi D \Delta c \left/ \left(\frac{1}{\rho} - \frac{1}{R}\right)\right. . \tag{8}$$

The mass-balance equation at the metal-oxide interface is

$$c_m 4\pi \rho^2 \frac{d\rho}{dt} = -\zeta |J|, \tag{9}$$

where c_m is the concentration of metal atoms in the core, and ζ is the coefficient related to the stoichiometry of oxidation. Using Eq. (8) for J in combination with Eqs. (1) and (3) for D and l, this equation can be rewritten as

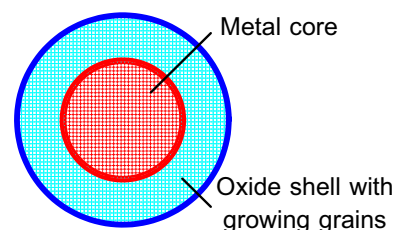$$\left(\rho - \frac{\rho^2}{R}\right)\frac{d\rho}{dt} = -\frac{A}{t^m}, \tag{10}$$

Fig. 1. Core-shell model for oxidation of metal nanoparticles.