Sintering of spherical particles of two immiscible phases controlled by surface and interphase boundary diffusion

L. Klinger, E. Rabkin *

Department of Materials Science and Engineering, Technion—Israel Institute of Technology, 32000 Haifa, Israel

Abstract

We propose a model of sintering of axisymmetrical particles of two immiscible, non-reacting phases controlled by self-diffusion along the particle surfaces and along the interphase boundary (IB) separating the particles. The model relies on a variational method of calculating the chemical potentials of the species diffusing along the IB, and on the explicit scheme of treating the displacements of the triple line where two surfaces and the IB meet. Our numerical results demonstrate that mutual wettability and relative size of the particles do not affect the shrinkage rate during the initial stages of sintering. At the final stages, better mutual wettability results in larger shrinkage. A large difference between the surface and IB diffusivities of two species results in transient morphologies of sintered particles which are very different both from the initial and the final configurations. Based on published data on the kinetics of sintering of three-particle W–Cu–W agglomerates [J.-S. Lee et al., Acta Mater. 60 (2012) 123–130], the self-diffusion coefficient of Cu along the Cu–W interface at 1000 °C was estimated at $(3.3 \pm 0.8) \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, which is comparable to the surface self-diffusion coefficient of Cu at the same temperature.

Keywords: Sintering; Surface diffusion; Interface diffusion; Theory

1. Introduction

A classical model of neck growth between two identical spherical particles is the cornerstone of the theory of sintering [1]. The fundamental parameters determining the sintering behavior of two spherical particles are the neck radius, r, and the linear shrinkage, Δy, defined as a mutual approach of the crystalline lattices of two particles normalized by their initial separation [1]. For the shrinkage to occur during sintering of crystalline particles, the grain boundary between them should be capable of absorbing and emitting vacancies. Several mechanisms controlling the sintering kinetics are usually discussed in the context of two-particle sintering model, namely surface diffusion, lattice diffusion and grain boundary diffusion. Of these, only the latter two can result in densification. For example,

when grain boundary diffusion is the only mechanism controlling the sintering kinetics, the following kinetic laws are obtained: $r \sim t^{1/6}$, and $\Delta y \sim t^{1/3}$, where t is the sintering time [1,2]. It should be noted that parameter Δy is different from the relative mutual approach of the centers of mass of two particles, Δy_m, which is non-zero even for the non-densifying sintering mechanisms, merely leading to the overall shape change of the particles without mutual drift of their lattices [1]. Treating the problem of sintering of two spheres assuming that surface and grain boundary diffusion proceed with comparable rates presents a formidable challenge, and rigorous treatments have only become available over the last two decades [3,4]. Relaxing the assumption of equal particle radii introduces an additional complication of curvature-driven grain boundary migration, which is described by an independent kinetic constant (grain boundary mobility). The corresponding analyses rely on various approximations (i.e. flat grain boundaries) [4–6] or on numerical methods [7], and rigorous treatment

* Corresponding author. Tel.: +972 4 829 4579; fax: +972 4 829 5677.
 E-mail address: erabkin@tx.technion.ac.il (E. Rabkin).

of the non-steady-state, coupled surface diffusion and grain boundary migration problem appeared only recently [8].

In spite of its importance in the sintering of heterogeneous powder mixtures, the problem of sintering of spherical particles of two different immiscible phases has received very little attention in the literature. This is because treating the chemical interdiffusion along the interphase boundary (IB) coupled with its migration is even more complicated than in the case of grain boundaries. To the best of our knowledge, the work of Wakai et al. [9] is the only one dedicated to this problem. They assumed that the surfaces of two particles evolve by an evaporation–condensation mechanism, so that the normal velocity of the element of the surface scales with the deviation of local surface curvature from its average value. By analogy, they considered a similar kinetic law for the IB, though physical justification for this type of dependence in the case of IBs is lacking.

In the present work we analyze the sintering behavior of spherical particles of two different immiscible phases separated by an IB. Keeping possible applications in nanotechnology in mind, we will limit ourselves to the sintering process controlled by self-diffusion along the particle surfaces, and by chemical interdiffusion along the IB (lattice diffusion usually contributes to sintering for the particles larger than several micrometers in size, or at very high temperatures [1]). We will base our analysis on the method of treating the capillary-driven interdiffusion along the IBs formulated in our recent work for the two-dimensional case [10], and extend it to axisymmetrical three-dimensional solids.

2. The model

Let us consider two axisymmetrical particles of immiscible phases A and B joined along an IB (see Fig. 1). Both particles are solids of revolution, which can be obtained by rotating the curves $\{X(s), Y(s)\}$ around the y-axis (see Fig. 1). Here s is the arc length along the curve. The sintering of these particles is determined by four interrelated diffusion processes: self-diffusion of A- and B-atoms along the surfaces of their respective particles (we assume a full immiscibility of the particles, i.e. no diffusion of A-atoms along the surface of B-particle, and vice versa), and interdiffusion of A- and B-atoms along the IB. The diffusion fluxes are driven by the capillary-induced gradients of chemical potentials, and the conditions of continuity for diffusion fluxes and chemical potentials should be fulfilled at the triple line where two surfaces and IB meet. The surface self-diffusion is described by classical Mullins-type equations:

$$j_i^s = -d_i^s \frac{\partial \mu_i^s}{\partial s}; \quad i = A, B, \tag{1}$$

where μ_i^s ($i = A, B$) are the chemical potentials of surface A- and B-atoms normalized by respective atomic volumes Ω_i, and $d_i^s = v_i^s D_i^s \Omega_i^2 / kT$, with v_i^s and D_i^s being the number of mobile i-atoms per unit area of the respective surface and the surface diffusion coefficient, respectively. kT has its usual thermodynamic meaning. In this work, we will assume full isotropy of the surface energies of both phases. In this case, $\mu_i^s = \gamma_i \kappa_i^s$, where γ_i and κ_i^s are the energy and local curvature, respectively, of the surfaces of corresponding phases [11]. Divergence of the surface diffusion fluxes leads the accumulation of atoms on the surface and to its normal displacement, ∂z_i^s:

$$\frac{\partial z_i^s}{\partial t} = -\frac{1}{X} \frac{\partial (j_i^s X)}{\partial s} = d_i^s \gamma_i \frac{1}{X} \frac{\partial}{\partial s} \left(X \frac{\partial \kappa_i^s}{\partial s} \right). \tag{2}$$

A similar set of equations describes the diffusion processes at the IB:

$$j_i = -d_i \frac{\partial \mu_i}{\partial s}; \quad i = A, B \tag{1a}$$

$$\frac{\partial z_i}{\partial t} = -\frac{1}{X} \frac{\partial (j_i X)}{\partial s} = d_i \frac{1}{X} \frac{\partial}{\partial s} \left(X \frac{\partial \mu_i}{\partial s} \right) \tag{2a}$$

with

$$d_i = v_i D_i \Omega_i^2 / kT,$$

where the parameters without superscript "s" describe the IB. For example, μ_i are the normalized chemical potentials of A- and B-atoms at the IB, and D_i are the respective self-diffusion coefficients along the IB. Eqs. (2) and (2a) were first employed by Nichols and Mullins for analysis of the shape evolution of the bodies of revolution controlled by surface diffusion [12].

The combined accretion of A- and B-atoms at the IB during the time interval ∂t leads to the rigid relative translation of crystalline lattices of two particles in the y-direction on ∂y:

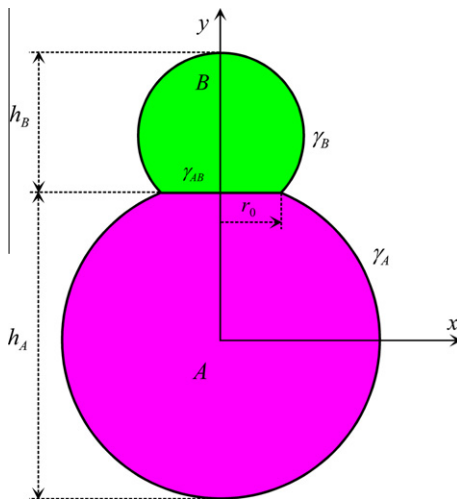$$\partial z_A + \partial z_B = -\partial y X'(s), \tag{3}$$

Fig. 1. The truncated-sphere particles of two immiscible, non-reactive phases A and B, bonded at an initially planar interphase boundary (IB). The IB becomes curved (spherical cap shape) in the final configuration.