Development of Microstructure during Intermediate- and Final-Stage of Sintering

Takayasu IKEGAMI and Yusuke MORIYOSHI

(National Institute for Research in Inorganic Materials
1-1, Namiki, Sakura-mura, Niihari-gun, Ibaraki 305)
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焼結の中期及び後期段階の微構造変化

池上 隆康・守吉 佑介

(無機材質研究所)
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1. Introduction

An actual development of a microstructure during the intermediate and final stages of sintering may be characterized with the concurrent progresses of densification, grain growth and pore migration in general. The present study was made to derive equations describing such a development.

2. Theory

2.1 Final stage of sintering

Figure 1 shows the schematic development of a microstructure, in which μ_1 and μ_2 are the chemical potentials of atoms at the surface and interface of a smaller grain, and that μ_3 and μ_4 are those of the larger grain, respectively. Six diffusion paths may be available in this structure. We assume that μ_1 is elevated to $\mu_1 = \mu_2$ (assumption (1)) by grain growth. According to the Shewmon's estimation¹⁾, $F_{a14} = k_{14}F_{b14}/r_p^3$, $F_{a23} = k_{23}F_{b23}/Wl^2$ and $F_{a34} = k_{34}F_{b34}/r_p^3$ for the final stage of sintering, where F_{bij} is the difference between the total forces acting on places i and j , F_{aij} is the net force per atom, and k_{14} , k_{23} and k_{34} are constants, r_p is the radius of a pore, and W and l are the thickness and radius of a grain boundary, respectively. When γ is the surface energy, γ_i is the interfacial energy, S_p is a pore surface area and S_i is a grain boundary area,

the total energy Fdr used during migration of a grain boundary, dr , is equal to $\gamma dS_p + \gamma_i dS_i$, and

$$Fdr = (nF_{b14} + F_{b23} + nF_{b34})dr \quad (1)$$

where n is a number of pores at the grain boundary. $\mu_i - \mu_j$ must be proportional to the product of F_{aij} and the distance between places i and j , and

$$\frac{K_s F_{b14}}{r_p^2} = \frac{K_g F_{b23}}{2l^2} + \frac{K_b F_{b34}}{r_p^2} \quad (2)$$

where K_s , K_g and K_b are constants dependent on the geometry of the microstructure. The migration of a pore must be caused by the mass transfers from the surface of a smaller grain to that of the larger one by evaporation-condensation (path I), by surface diffusion (path II) and by bulk diffusion (path III). This migration rate, dX_p/dt , must be proportional to $(k_{pv}/r_p^2 + k_{pb}\delta_b/r_p^4 + k_{ps}\delta_s/r_p^4)F_{b14}$, where δ_b is the effective thickness of bulk diffusion, δ_s is the thickness of the region of enhanced diffusion at the surface, and k_{pv} , k_{pb} and k_{ps} are constants which contain a diffusion coefficient or vapor pressure as well as a shape factor, respectively. The displacement of the center of the pore is caused not only by the mass transfer from the interface of a smaller grain to the surface of the larger one (path VI) across the grain boundary (path IV) but also by that through a grain boundary (path V)

and surface layer (path III). This displacement rate is correlated to the migration rate, dX_d/dt , of a grain boundary, which is proportional to the sum of $S_{TI}k_{ab}F_{b34}/(1/(1-r_p))/r_p^3$ and $S_{TI}\delta_g k_{dg}(F_{b23}+F_{b34})/(r_p^4 \ln(1/r_p))$, where δ_g is the thickness of the region of enhanced diffusion at the grain boundary, S_{TI} is a ratio between the total area S_T and grain boundary area S_I . The total migration rate of the grain boundary, dX_i , is proportional to $k_g F_{b23}/Wl^2$, and then

$$\frac{k_g F_{b23}}{Wl^2} = \left(\frac{k_{pv}}{r_p^2} + \frac{k_{pb}\delta_b}{r_p^4} + \frac{k_{ps}\delta_s}{r_p^4} \right) F_{b14} + \frac{S_{TI}l k_{ab} F_{b34}}{r_p^3(1-r_p)} + \frac{S_{TI}\delta_g k_{dg}(F_{b23}+F_{b34})}{r_p^4 \ln(1/r_p)} \quad (3)$$

is obtained.

If all of the constants, e.g., n , K_s , ..., and the initial conditions, e.g., l and r_p (or a relative density ρ) are given, these equations can be solved. Therefore, one can obtain the dX_i , dX_p and dX_d values from Eq. (3) by using the calculated F_{b14} , F_{b23} , and F_{b34} values. It is obvious that a net increase of a grain size dR ($=\sum dX_i/\sum S_{TI}$) is equal to the sum of $dR_p = \sum dX_p/\sum S_{TI}$ and $dR_d = \sum dX_d/\sum S_{TI}$. From an equation

$$\frac{dR_d}{R} = \frac{K_c(1-\rho)d\rho}{\rho} \quad (4)$$

derived in our previous paper²⁾, the increase of a relative density $d\rho$ or the decrease of a pore size $-dr_p$ can be calculated by using the dR_d value. Repeatedly calculating Eqs. (1) to (4) describes the development of microstructure in the final stage of sintering.

2.2 Intermediate stage of sintering

Similar equations are easily derived for the development of microstructure during the intermediate stage of sintering.

$$F = nF_{b14} + F_{b23} + nF_{b34} \quad (5)$$

$$\frac{K_s F_{b14}}{r_p} = \frac{K_g F_{b23}}{2l} + \frac{K_b F_{b34}}{r_p} \quad (6)$$

$$\frac{k_g F_{b23}}{Wl} = \left(\frac{k_{pv}}{r_p} + \frac{k_{pb}\delta_b}{r_p^3} + \frac{k_{ps}\delta_s}{r_p^3} \right) F_{b14} + \frac{S_{TI}k_{ab}F_{b34}}{l r_p \ln(1/r_p)} + \frac{S_{TI}\delta_g k_{dg}(F_{b23}+F_{b34})}{l r_p^2 \ln(1/r_p)} \quad (7)$$

3. Discussion

A number of authors³⁻⁵⁾ have proposed the

Fig. 1. Diffusion paths and the chemical potentials of atoms during intermediate- and final- stage sintering.

theories of grain growth in a porous compact, in which migration of a grain boundary with pores is controlled by the mass transfer through paths I to III or by that through path IV. The contribution of the mass transfer through paths V and VI to the migration, however, is neglected in these studies, and appreciable grain growth results in less densification. Densification with simultaneous grain growth was, on the other hand, reported in many papers⁶⁻⁸⁾ about the initial and intermediate stage of sintering, but no reasonable model for this phenomenon was proposed in them. Recently, we explained the phenomenon on a densification model⁹⁾, in which the mass transfer through paths IV to VI is predominant.

In the present model, all of the diffusion paths in Fig. 1 is taken into consideration, and the applicability of the present equations is more extensive than that based on the reported grain growth models³⁻⁵⁾, or on our densification model⁹⁾.

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