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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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 $\mu_1$ and $\mu_2$ are the chemical potentials of atoms at the surface and interface of a smaller grain, and that $\mu_3$ and $\mu_4$ are those of the larger grain, respectively. Six diffusion paths may be available in this structure. We assume that $\mu_1$ is elevated to $\mu_2$ (assumption (1)) by grain growth. According to the Shewman’s estimation, $F_{a14} = k_{a14} F_{b14} / \tau_1^2$, $F_{a23} = k_{a23} F_{b23} / Wl^2$ and $F_{a34} = k_{a34} F_{b34} / \tau_2^2$ for the final stage of sintering, where $F_{aij}$ is the difference between the total forces acting on places $i$ and $j$, $F_{b14}$ is the net force per atom, and $k_{a14}$, $k_{a23}$, and $k_{a34}$ are constants, $\tau_p$ is the radius of a pore, and $W$ and $l$ are the thickness and radius of a grain boundary, respectively. When $\gamma$ is the surface energy, $\gamma_1$ is the interfacial energy, $S_p$ is a pore surface area and $S_i$ is a grain boundary area, the total energy $F \, d\tau$ used during migration of a grain boundary, $d\tau$, is equal to $\gamma dS_p + \gamma dS_i$, and

$$F \, d\tau = (n F_{b14} + F_{b23} + n F_{b34}) \, d\tau \quad (1)$$

where $n$ is a number of pores at the grain boundary. $\mu_1 = \mu_2$ must be proportional to the product of $F_{a14}$ and the distance between places $i$ and $j$, and

$$\frac{K_s F_{b14}}{\tau_1^2} = \frac{K_s F_{b23}}{2 l^2} + \frac{K_b F_{b34}}{\tau_2^2} \quad (2)$$

where $K_s$, $K_b$ 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 $(k_{pv} / \tau_1^2 + k_{p\theta} \delta_v / \tau_1^2 + k_{p\theta} \delta_v / \tau_1^2) F_{b14}$, where $\delta_v$ is the effective thickness of bulk diffusion, $\delta_v$ is the thickness of the region of enhanced diffusion at the surface, and $K_pv$, $K_{p\theta}$ and $K_{p\phi}$ 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 IV) 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 \(S_{TT} k_{ab} F_{b34} \left(1/(1 - \tau_p)\right)/\tau_p^2\) and \(S_{TT} \delta_k k_{ab} \left(F_{b23} + F_{b34}\right)/(\tau_p^2 \ln(1/\tau_p))\), where \(\delta_k\) is the thickness of the region of enhanced diffusion at the grain boundary, \(S_{TT}\) is a ratio between the total area \(S_t\) and grain boundary area \(S_b\). The total migration rate of the grain boundary, \(dX_t\), is proportional to \(k_e F_{b23}/Wl^2\), and then

\[
\frac{k_e F_{b23}}{Wl^2} = \left(\frac{k_{PV} + k_{PS} \delta_k + k_{SS} \delta_s}{\tau_p^2} + \frac{k_{PS} \delta_k}{\tau_p^2}\right) F_{b14}
\]

\[
+ \frac{S_{TT} k_{ab} F_{b34}}{\tau_p^2 \ln(1/\tau_p)} + \frac{S_{TT} \delta_k k_{ab} (F_{b23} + F_{b34})}{\tau_p^2 \ln(1/\tau_p)}
\]

is obtained.

If all of the constants, e.g., \(n\), \(K_s\), ..., and the initial conditions, e.g., \(l\) and \(\tau_f\) (or a relative density \(\rho\)) are given, these equations can be solved. Therefore, one can obtain the \(dX_a\), \(dX_p\), 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 \(dR\) (=\(\Sigma dX_a/\Sigma S_{TT}\)) is equal to the sum of \(dR_a = \Sigma dX_a/\Sigma S_{TT}\) and \(dR = \Sigma dX_d/\Sigma S_{TT}\). From an equation

\[
\frac{dR_a}{R} = K_c (1 - \rho) \frac{d\rho}{\rho}
\]

derived in our previous paper\(^2\), the increase of a relative density \(d\rho\) or the decrease of a pore size \(-d\tau_p\) can be calculated by using the \(dR_a\) 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.

\[
F = nF_{b14} + F_{b34} + nF_{b34}
\]

\[
\frac{K_e F_{b14}}{\tau_p} = \frac{K_e F_{b23} + K_e F_{b34}}{2 \tau_p}
\]

\[
\frac{k_e F_{b23}}{Wl} = \left(\frac{k_{PV} + k_{PS} \delta_k + k_{SS} \delta_s}{\tau_p^2} + \frac{k_{PS} \delta_k}{\tau_p^2}\right) F_{b14}
\]

\[
+ \frac{S_{TT} k_{ab} F_{b34}}{\tau_p^2 \ln(1/\tau_p)} + \frac{S_{TT} \delta_k k_{ab} (F_{b23} + F_{b34})}{\tau_p^2 \ln(1/\tau_p)}
\]

3. Discussion

A number of authors\(^3\)\(^-\)\(^5\) have proposed the 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 papers\(^6\)\(^-\)\(^8\) 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 model\(^9\), in which the mass transfer through paths IV to VI is predominant.

In the present model, all of the diffusion paths in Fig.1 are taken into consideration, and the applicability of the present equations is more extensive than that based on the reported grain growth models\(^3\)\(^-\)\(^5\), or on our densification model\(^9\).

References
4) F.A. Nichols, ibid., 51, 468-69 (1968).