Sintering forces in equilibrium and non-equilibrium states during sintering of two particles

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Abstract

The sintering force was originally defined for an equilibrium state, in which the sintering contraction is balanced by an external force. The concept of sintering force can be expanded to non-equilibrium process of sintering by using Beere’s definition of sintering force. The sintering of two spherical particles was simulated by using the Surface Evolver program. The shrinkage rate was approximately proportional to the sintering force in a non-equilibrium process. The sintering force in a non-equilibrium process was smaller than the force necessary to stop the shrinkage at equilibrium.

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1. Introduction

Nanocrystalline particles are thermodynamically unstable at elevated temperatures. Two particles make a bond by sharing the interface, and form an energetically stable particle pair. This phenomenon of bonding of particles with the application of heat is called sintering [1–3], which is one of methods to fabricate nanocrystalline materials. Sintering accompanies the motion of mass centers of particles. The densification and shrinkage take place as the centers of particles approach one another. The position of particles and their morphology change as a result of mass transport involving multiple diffusion paths: evaporation–condensation, surface diffusion, grain boundary diffusion and lattice diffusion [2–8].

Gregg and Rhines [9] defined sintering force, as a force which is necessary to just stop the sintering contraction along one axis of the sinter body. Their definition of sintering force is based on an equilibrium state under external force, in which the sintering contraction is balanced with the external force. However, sintering is actually a non-equilibrium process, in which surfaces and grain boundaries of bonded particles evolve toward an equilibrium minimizing the sum of surface energy and grain boundary energy. In the macroscopic continuum theory of sintering, the shrinkage rate is expressed as a response to the driving force of sintering [10–12]. But, no comprehensive treatment of the comparison between the driving force in non-equilibrium process and the sintering force at equilibrium is available.

The aim of this work is to find fundamental principles for controlling the complicated microstructural evolution of nanocrystalline materials during sintering. In this paper we have studied the driving force in non-equilibrium process of sintering by computer simulation, and compared it with the sintering force at equilibrium under the external force.

2. Numerical methods

2.1. Modeling of non-equilibrium process of sintering

Although several mechanisms contribute simultaneously in sintering, it is helpful to analyze a model in which a single given mechanism contributes in an important way. Kuczynski [2], Kingery and Berg [4], and Coblenz et al. [5] analyzed the kinetics of sintering by evaporation–condensation. It is the simplest model for analyzing the problem of non-equilibrium process of sintering, because...
the surface motion in the sintering by evaporation–condensation is expressed by \[13,14\]

\[ v = M \gamma_s (\kappa - \kappa_{av}) , \]  

(1)

where \( v \) is the normal velocity, \( M \) is the mobility, and \( \gamma_s \) is the surface energy. The mean curvature \( \kappa_{av} \) is defined by two principal curvatures. The average of mean curvature \( \kappa_{av} \) is given by

\[ \kappa_{av} = \frac{1}{S} \int_S \kappa \, dS , \]  

(2)

where \( S \) is the surface area. Eq. (1) describes the surface motion by difference in mean curvature.

2.2. Surface evolver program

The non-equilibrium process of sintering was investigated by using Brakke’s Surface Evolver program \[15\]. The outline of Surface Evolver program is briefly described here. The surface of a grain, including both the grain boundary and the surface, is represented as a set of triangular finite elements, or facets as shown in Fig. 1. Each facet consists of three edges and three vertices. The surface and the grain boundary have energies proportional to their area. The Surface Evolver program evolves the surface toward minimal energy by a gradient descent method under any constraint. The gradient of energy at a vertex is a force, which must be converted to a velocity vector for the motion. This conversion involves what may be called the mobility factor; how a vertex responds to the force on it. The resistance to motion of a vertex is proportional to the area associated with the vertex. The actual motion is found by multiplying the velocity by time step. The motion by the difference in curvature (Eq. (1)) can be approximated by enforcing the constraint on conservation of the total volume of particles \[13,14\].

The sintering process of two identical spheres, as shown in Fig. (1), was investigated by assuming that the surface energy \( \gamma_s = 1 \), the grain boundary energy \( \gamma_{gb} \), and the mobility \( M = 1 \) are isotropic. In equilibrium the dihedral angle \( \phi \) between the grain boundary and the surface are given by \( \gamma_{gb} = 2 \gamma_s \cos(\phi/2) \). The dihedral angles for \( \gamma_{gb}/\gamma_s = 1, 0.5 \) and 0 are 120, 151, and 180\(^\circ\), respectively. The black dot inside a particle in Fig. 1 indicates the mass center. The distance \( R \) between two particles is defined as a distance between mass centers of particles.

3. Numerical computation results

3.1. Densification by motion of mass center of particles

When two identical particles with radius \( r \) touch, they form a common circular interface, i.e. the neck area increases. The densification and shrinkage require that the mass centers of particles approach one another. The normalized distance between particles \( R_p = R/2r \) is shown in Fig. 2 as a function of dimensionless time \( t^* = \gamma_s M t/r^2 \). The distance between two particles is unchanged until \( t^* = 0.02 \). The evaporation–condensation mechanism gives neck growth but no shrinkage at initial stage of sintering, so it is often referred to as ‘non-densifying mechanism’ \[7\].

If the grain boundary acts as a source/sink of vacancy, for example, in the sintering by grain boundary diffusion and lattice diffusion, the lattice sites at the boundary is created or destructed, which in turn, causes the relative motion of crystalline particles. When we have only the vaporization–condensation process active, the crystalline

![Fig. 1. Geometry of the two-particle model in three dimensions. (\( x = \) neck radius). The black dot inside a particle indicates the mass center. The example of triangular mesh is shown for a particle on the right-hand side.](image-url)
lattice of the particle does not move relative to the grain boundary. Although, the crystalline lattice does not move, the mass center of the particle still shifts due to the mass transport toward the neck. After $t^* = 0.1$, the distance between the mass centers decreases gradually to the final equilibrium value.

3.2. Relation between the sintering force and shrinkage rate

The sintering force is originally defined for equilibrium states in which the external force just stops the sintering contraction along one axis of the sinter body [9]. Alternatively Beere [16] expressed the sintering force as the sum of the surface tension acting between two particles and the force acting through the grain boundary area [16,17]

$$F = \int c \gamma_s \sin \frac{\psi}{2} ds - \gamma_s k_{av} A_{gb},$$

(3)

The first term in the right side of Eq. (3) is an integration of surface tension along the periphery of the neck. The second term arises from the average of mean curvature $k_{av}$ (Eq. (2)). By substituting $\cos \alpha$ for $\sin (\psi/2)$ into Eq. (3), the idea of sintering force carries over to non-equilibrium states during sintering

$$F = \int c \gamma_s \cos \alpha ds - \gamma_s k_{av} A_{gb},$$

(4)

where $\alpha$ is the angle between the tangent of the surface and the unit normal to the grain boundary. Fig. 3 shows the sintering force for various dihedral angles as a function of time. The sintering force peaks at $t^* = 0.06$, and reaches zero at equilibrium. As the dihedral angle increases, the maximum sintering force increases, and the time needed to reach equilibrium becomes slightly shorter.

The sintering force is the driving force for shrinkage in sintering. We define a relative measure of the linear shrinkage along the axis connecting the mass centers,

$$\Delta R/2r = 1 - R^*.$$  

(5)

The shrinkage rate, or strain rate, is

$$\dot{\varepsilon} = -\frac{dR^*}{dr} = -\frac{\gamma_s M}{r^2} \frac{dR^*}{dr},$$  

(6)

The shrinkage rate was calculated from Fig. 2, and plotted as a function of the sintering force in Fig. 4. Although, the shrinkage rate–sintering force curves showed slight non-linearity, the shrinkage rate was approximately proportional to the sintering force,

$$\dot{\varepsilon} = -\frac{F}{K},$$  

(7)

$$K = k' \frac{r^3}{M},$$  

(8)

where $K$ is the effective viscosity and $k'$ is a coefficient. The values of $k'$ varied with dihedral angle, $k' = 2.3, 2.9, \text{and} 3.4$ for $\psi = 180, 151 \text{and} 120^\circ$, respectively.

3.3. Comparison with sintering force in equilibrium states

When there is no constraint, two touching particles reach the final equilibrium shape with the minimal energy, which is determined by the sum of the surface energy and the grain
boundary energy. If the motion of a particle is constrained by an external force, the equilibrium shape of a particle will be different from that of an unconstrained one [18]. The energy of a pair is the sum of energies associated with particles’ surface area $A_s$ and the grain boundary area $A_{gb}$:

$$E = \gamma_s A_s + \gamma_{gb} A_{gb}. \quad (9)$$

When $\gamma_{gb} < 2 \gamma_s$, the total energy of a bonded particle pair decreases from the energy of two separated spherical particles $2E_0$ as the common interface grows and the surface area decreases,

$$\Delta E = E - 2E_0, \quad (10)$$

where the energy of one spherical particle with radius $r$ is $E_0 = 4\pi r^2 \gamma_s$.

Here we consider the equilibrium shape of two identical particles for constrained situation, in which the distance $R$ between mass centers of two particles is fixed. The normalized reduction of energy $\Delta E^* = \Delta E/2E_0$ is plotted as a function of the normalized distance $R^*$ in Fig. 5. The energy–potential curve has a minimum at the equilibrium distance. The depth of the energy–displacement curve is the bond energy of the particle pair. The lower the $\gamma_{gb}/\gamma_s$, the more strongly the particles are bonded together.

The sintering force $F$ is the external force necessary to constrain the position of particles. The work done by the external force for virtual displacement is equivalent to the change of total energy,

$$F \, dR = dE. \quad (11)$$

The slope of the energy-potential curve in Fig. 5 gives the sintering force in equilibrium state [18].

The sintering force is plotted as a function of $R^*$ in Fig. 6. The sintering force in equilibrium state (dashed lines) is different from that of the non-equilibrium process of sintering (solid lines). Let us consider that the external force $F_A$ is applied at $R_A^*$ in Fig. 6. The external force changes the vacancy concentration at the boundary, and the difference in vacancy concentration vanishes. The crystalline lattice of the particle will not move under $F_A$ even if the grain boundary acts as a sink of vacancy. However, the external force...
force cannot stop the shift of position of mass centers by evaporation–condensation process, because there is a gradient of curvature on the surface. The surface of the particle pair continues to evolve until the mass centers stop at $R^*$, which is the equilibrium position under the external force $F_A$. The sintering force $F_A$ in non-equilibrium process is not a force which just stops the shrinkage at $R^*$.

Fig. 7 shows the average of mean curvature $\kappa_{av}$, which is defined by Eq. (3), as a function of the distance between particles (solid lines), $\kappa_{av}$ decreases from the initial value of a sphere $2/r$, and reaches to the equilibrium as the distance between particles decreases. On the other hand, $\kappa_{av}$ of equilibrium states under constraint (dashed lines) is much smaller than that of non-equilibrium process of sintering (solid lines). Some shapes of particle pair are shown in Fig. 7. At $R^* = 2$ the particle pair in equilibrium under constraint is elongated, while the particles in non-equilibrium process are spheres. The difference of $\kappa_{av}$ between the equilibrium state and non-equilibrium state is understood, because the elongated shape has lower $\kappa_{av}$ than a sphere. From Eq. (4), the lower $\kappa_{av}$ in equilibrium under constraint gives higher sintering force. The elongated shape of particles is the origin of large sintering force in equilibrium under constraint.

### 4. Conclusion

We analyzed sintering force and motion of particles during sintering of two spherical particles by using Brakke’s Surface Evolver program. The concept of sintering force could be expanded to non-equilibrium process of sintering. The linear relationship between the shrinkage rate and sintering force was observed. It was necessary to distinguish between the sintering force in non-equilibrium process and that in equilibrium under external force. While the sintering force is the external force necessary to constrain the position of particles in equilibrium, the sintering force in non-equilibrium process of sintering was associated with shrinkage rate. The sintering force in non-equilibrium process was smaller than the force necessary to stop the shrinkage. The low $\kappa_{av}$ of elongated particles under constraint was the origin of large sintering force to stop the shrinkage.

### References

[1] J. Frenkel, Viscous flow of crystalline bodies under the action of surface tension, J. Phys. USSR 9 (1945) 385–391.
[2] G.C. Kuczynski, Self-diffusion in sintering of metallic particles, Trans. A Inst. Mining Met. Engrs 185 (1949) 169–178.
[3] H.E. Exner, E. Arzt, Sintering processes, in: R.W. Cahn, P. Haasen (Eds.), Physical Metallurgy, Elsevier, Amsterdam, 1996, pp. 2628–2662.
[4] W.D. Kingery, M. Berg, Study of the initial stages of sintering solids by viscous flow, evaporation–condensation, and self-diffusion, J. Appl. Phys. 26 (1955) 1205–1212.
[5] W.S. Coblenz, J.M. Dynys, R.M. Cannon, R.L. Coble, Initial stage solid state sintering models. A critical analysis and assessment, in: G.C. Kuczynski (Ed.), Materials Science Research, vol. 13, Plenum Press, New York, 1980, pp. 141–157.
[6] M.F. Ashby, A first report on sintering diagrams, Acta Metall. 22 (1974) 275–289.
[7] F.B. Swinkels, M.F. Ashby, A second report on sintering diagrams, Acta Metall. 29 (1981) 259–281.
[8] H.E. Exner, Principles of single phase sintering, Rev. Powder Metall. Phys. Ceram. 1 (1979) 7–251.
[9] R.A. Gregg, F.N. Rhines, Surface tension and the sintering force in copper, Metall. Trans. 4 (1973) 1365–1374.
[10] R.K. Bordia, G.W. Scherer, On constrained sintering-I. constitutive model for a sintering body, Acta Metall. 36 (1988) 2393–2397.
[11] A. Jagota, P.R. Dawson, Micromechanical modeling of powder compacts—Part I: unit problems for sintering and traction induced deformation, Acta Metall. 36 (1988) 2551–2561.
[12] R.M. McMeeking, L.T. Kuhn, A diffusional creep law for powder compacts, Acta Metall. Mater. 40 (1992) 961–969.
[13] J.W. Cahn, J.E. Taylor, Surface motion by surface diffusion, Acta Metall. 42 (1994) 1045–1063.
[14] F. Wakai, F. Aldinger, Sintering through surface motion by the difference in mean curvature, Acta Mater. 51 (2003) 4013–4024.
[15] K.A. Brakke, The surface evolver, Exp. Math. 1 (1992) 141–165.
[16] W. Beere, The second stage sintering kinetics of powder compacts, Acta Metall. 23 (1975) 139–145.
[17] J. Svoboda, H. Riedel, H. Zipse, Equilibrium pore surfaces, sintering stresses and constitutive equations for the intermediate and late stages of sintering-I. computation of equilibrium surfaces, Acta Metall. Mater. 42 (1994) 435–443.
[18] F. Wakai, F. Aldinger, Equilibrium configuration of particles in sintering under constraint, Acta Mater. 51 (2003) 641–652.