ELSEVIER

Ceramics International 25 (1999) 723–726

CERAMICS
INTERNATIONAL

Sintering kinetics of α-Al_2O_3 powder

Wenming Zeng, Lian Gao*, Linhua Gui, Jinkun Guo

State Key Lab on High Performance Ceramics and Superfine Microstructure Studies, Shanghai Institute of Ceramics,
Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

Received 21 July 1998; received in revised form 8 October 1998; accepted 7 December 1998

Abstract

The sintering kinetics of α-Al_2O_3 powder are reviewed in this paper. The initial sintering of α-Al_2O_3 micropowder and α-Al_2O_3 nanopowder is all controlled by grain boundary diffusion. The sintering kinetics dominate up to a relative density of 0.77, where the coarsening kinetics dominate during further densification. Herring's scaling law can be used to predict the approximate sintering temperature of α-Al_2O_3 powder and demonstrates that if the particle size can be reduced to <20 nm, sintering below 1000°C may be possible. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Powder; A. Sintering; D. α-Al_2O_3; Kinetics

1. Introduction

Alumina is one of the more widely used and studied advanced ceramic materials. The relative abundance and low cost of the material resource is advantageous for commercial applications, while the availability of the material in highly purified grade makes it well suited to fundamental studies in material research. Among its desirable features, alumina shares with other advanced ceramics the characteristics of high-temperature stability and the retention of strength at high temperatures. These features are related to sintering technology of alumina powder, while the investigation of the sintering kinetics of alumina powder is very important for the improvement of sintering technology.

The determinations of the kinetics of sintering have been successfully made using the relationship between linear shrinkage rate and mechanism [1–6]. The initial sintering kinetics of alumina micropowders have been investigated since 1963 according to the relationship [2–4]. Recently, the sintering kinetics of nanocrystalline α-Al_2O_3 powder have been also studied [7]. This present paper reviews the sintering kinetics of α-Al_2O_3 powder.

2. Initial stage sintering kinetics of α-Al_2O_3 powder

The successful determinations of the kinetics of sintering have been made using the relationship between linear shrinkage rate and mechanism [1–6]. If the densification of the green body is controlled by lattice diffusion or grain boundary diffusion at the initial stage of sintering, the relationship between linear shrinkage rate ($\Delta L/L_0$) of the green body and time (t) can be expressed as [4]

$$\Delta L/L_0 = (K\gamma a^3 D/kTr^p)^m t^m \tag{1}$$

where $\Delta L/L_0$ is linear shrinkage rate, K, p, and m are all constants, D is self-diffusion coefficient, γ is surface energy, r is particle radius, a^3 is vacancy volume, k is Boltzmann's constant, T is absolute temperature and t is time. The values of K, p, and m are determined by different mechanisms and conditions, whose results are shown in Table 1 [4]. In Table 1, a is vacancy size and b is grain boundary thickness.

Comparing the experimental data with Eq. (1) and Table 1, the sintering mechanics at the initial stage can be determined.

Johnson and Cutler (1963) [3] obtained the activation energies of an agglomerated α-Al_2O_3 powder with an average diameter of 0.2–0.5 μm and a dispersed α-Al_2O_3 powder with a mean diameter of 3–5 μm as 627 and 593 kJ mol^{-1}, respectively. The initial stage sintering of both powders was found to be controlled by grain boundary diffusion. Young and Cultler (1970) [2] studied the sintering of a dispersed α-Al_2O_3 powder with a mean diameter of 1–2 μm and determined activation energy of the grain boundary diffusion of α-Al_2O_3 powder as 481 ± 41.8 kJ mol^{-1}.

In 1998, Li et al. [7] investigated the initial stage sintering of a soft and a hard agglomerated α-Al_2O_3 powders

---

* Corresponding author. Tel: +86-21-6251-2990; fax: +86-21-6251-3903.
E-mail address: liangaoc@online.sh.cn (Lian Gao).

0272-8842/99/$ - see front matter
PII: S0272-8842(99)00008-5

Table 1
Values of constants for Eq. (1) under different diffusion mechanism and conditions

Diffusion path	Initial contact	K	m	p
Bulk	Spherical	$31/\pi^2$	0.46	3
Bulk	Paraboloid	$20/\pi$	0.46	2
Bulk	160° cone on a plane	$180\ \tan^2 10°/\pi^2$	0.33	3
Bulk	Spherical, grooved neck	$23/\pi^2$	0.46	3
Bulk	Spherical	$20/2^{1/2}$	0.40	3
Bulk	Spherical	2	0.50	3
Grain boundary	Spherical	$50b/7\pi$	0.31	4
Grain boundary	Paraboloid	$10b/7\pi$	0.31	3
Grain boundary	160° cone on a plane	$55b\ \tan^2 10°$	0.25	4
Grain boundary	Spherical, grooved neck	$3b/2$	0.31	4
Grain boundary	Spherical	$15a$	0.33	4

with a diameter of 10 nm. For both powders the initial stage sintering was found to be controlled by grain boundary diffusion, and activation energies of both powders were determined to be 354 and 481 kJ mol^{-1}, separately. The diffusion coefficient of the soft agglomerated α-Al_2O_3 powder from 900 to 1200°C was estimated as $D_B \approx 10^{-5} \exp(-354000/R_s)$ (m^2 s^{-1}).

All the above results are summarized in Table 2.

3. Sintering of α-Al_2O_3 powder at a constant heating rate

The relationship between relative density ρ of the specimen and relative density ρ_g of the green body and linear shrinkage rate $\Delta L/L_0$ of the specimen can be expressed as [8]

$$\rho = \rho_g/(1 - \Delta L/L_0)^3 \tag{2}$$

Table 2
Sintering activation energy of different α-Al_2O_3 powders

Diameter (μm)	State of agglomerate	Initial stage activation energy (Q,kJ mol^{-1})
0.2–0.5	Agglomerated	627 [3]
1–2	Dispersed	481 ± 41.8 [2]
3–5	Dispersed	593 [3]
0.01	Soft agglomerated	354 [7]
0.01	Hard agglomerated	481 [7]

Young and Cutler (1970) [2] studied the initial sintering of α-Al_2O_3 powder with a mean particle diameter of 1–2 μm with constant rate of heating (4°C/min). In their experiments, nonlinear initial effects were observed in several aluminas. This is probably caused by particle size distributions or by changes in mechanism, e.g. volume to grain boundary or surface to grain boundary diffusion.

Li et al. (1998) [9] investigated the sintering kinetics of α-Al_2O_3 powder with a mean particle diameter of 10 nm by sintering at a constant rate (10°C/min), whose results are shown in Fig. 1. It can be seen from Fig. 1 that the densification of the green body mainly occurred between 1200 and 1450°C, and maximum shrinkage rate (3.42×10^{-4} s^{-1}) occurred at about 1350°C and decreased after 1350°C. From Eq. (1), the relative density of the specimen at the maximum linear shrinkage rate can be calculated as 77.58%, which is in very good agreement with the result of Lange [10]. The data strongly suggest that the sintering kinetics dominate up to a relative density of 0.77, where the coarsening kinetics dominate during further densification [10].

4. Conventional sintering of α-Al_2O_3 powder

The effect of the particle size on sintering temperature can be predicted by Herring's Scaling Law [11]. For

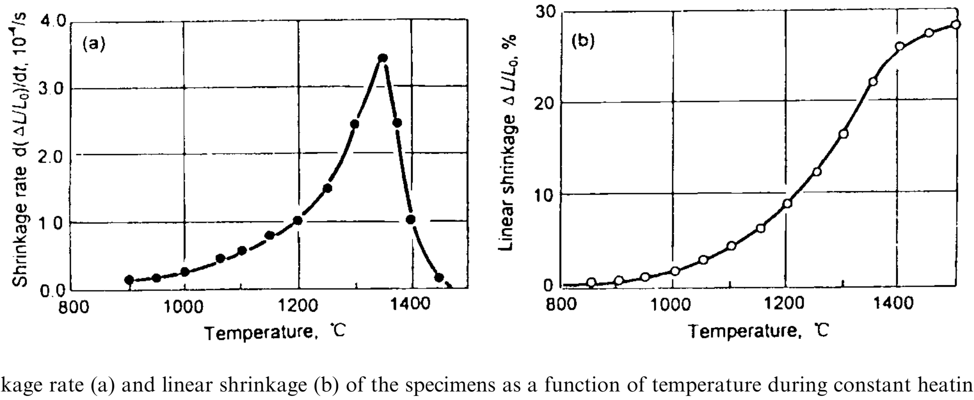

Fig. 1. Linear shrinkage rate (a) and linear shrinkage (b) of the specimens as a function of temperature during constant heating rate sintering [7].

both powders with diameters of r_1 and r_2, there is the following relationship for sintering time (Δt) at the equal sintering extent at the same temperature (T)

$$\Delta t_2(T) = \lambda^n \Delta t_1(T) \tag{3}$$

where $\lambda = r_2/r_1$. If the sintering process is controlled by lattice diffusion, $n = 3$; if by grain boundary diffusion, $n = 4$.

Suppose that the temperatures of the specimens at the equal sintering extent at same sintering time are T_1 and T_2, respectively, then

$$\Delta t_1(T_1) = \Delta t_2(T_2) = \lambda^n \Delta t_1(T_2) \tag{4}$$

Since the sintering rate is inversely proportional to Δt_1, if the sintering rate obeys Arrhenius's Law, then

$$\lambda^n = \exp[Q_1/R(1/T_1 - 1/T_2)] \tag{5}$$

where Q_1 is the sintering diffusion activation energy of powder with a diameter of r_1.

According to Eq. (5), the sintering densification temperature of powders with different particle diameters could be estimated. Assuming that 0.6-μm-diameter α-Al_2O_3 powder is sintered to 95% theoretical density at 1500°C and activation energies are 418 and 543 kJ mol^{-1} as obtained from the sintering Mg-doped and pure α-Al_2O_3 respectively [12], the calculated results are shown in Table 3.

Peeleen (1979) [13] used many large agglomerate α-Al_2O_3 Powder with 0.3 μm to sinter to a relative density of 99.9% at 1850°C for 10 h. This temperature is more than 450°C higher than the predicted result of Table 3.

Li et al. [9] determined the relationships between relative density and linear shrinkage of the specimen and sintering temperature under the conventional sintering condition, whose result are shown in Fig. 2. It can be seen from Fig. 2 that the specimen is mainly densified at the temperature range 1000–1350°C, and its relative density is up to 98.85% after conventional sintering at 1400°C for 2 h.

Table 3
Predicted sintering temperatures of α-Al_2O_3 powders with different particle diameters

Particle diameter (μm)	Sintering temperature (°C)	
	Lattice diffusion	Grain boundary diffusion
	$Q_1 = 543$ kJ mol^{-1}	
0.30	1407	1378
0.10	1278	1216
0.08	1255	1187
0.06	1225	1151
0.04	1185	1104
0.03	1158	1072
0.02	1122	1029
0.01	1064	963
0.005	1011	902
	$Q_1 = 418$ kJ mol^{-1}	
0.30	1381	1345
0.10	1223	1148
0.08	1194	1114
0.06	1159	1072
0.04	1112	1018
0.03	1080	982
0.02	1038	934
0.01	972	860
0.005	913	795

Obviously, although the sintering temperature of α-Al_2O_3 nanopowder with a mean particle diameter of 10 nm was decreased by 300–400°C as compared to that of α-Al_2O_3 micropowder, there is a very large difference between the actual sintering temperature from Li et al. [9] and the predicted value of Table 3. This is probably caused by low relative density of the green body (36.62%) through dry pressing.

Yeh and Sacks (1988) [14] used an agglomerate-free α-Al_2O_3 dispersion with a 0.06-μm diameter to prepare homogeneous green bodies with ~69% relative density and ~10 nm median pore radius by using slip casting technique. The specimens were sintered to a relative density of >99.5% at 1150°C and an average grain size of

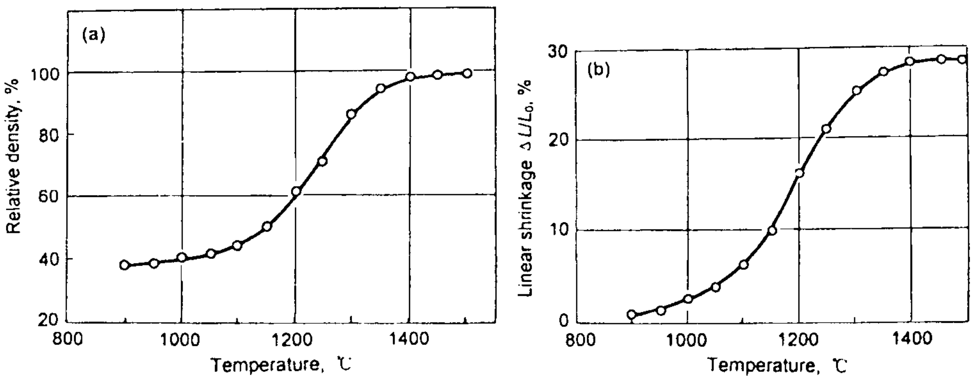

Fig. 2. Relative density (a) and linear shrinkage (b) as a function of sintering temperature at conventional sintering [9].

0.25 μm. This densification temperature is very consistent with the predicted result of Table 3.

Therefore, once agglomerates are eliminated, the most important criterion for lower sintering temperature is the use of smaller particles and attainment of a uniform high green density. Herring ± s scaling law can be used to predict the approximate sintering temperature and demonstrates that, if the particle size can be reduced to < 20 nm, sintering below 1000°C maybe possible. Thus, α-Al_2O_3 nanoceramics with a grain size of < 100 nm may be also fabricated.

5. Summary

As reviewed above, the initial sintering of α-Al_2O_3 micropowder and α-Al_2O_3 nanopowder is found to be controlled by grain boundary diffusion. The sintering kinetics dominate up to a relative density of 0.77, where the coarsening kinetics dominate during further densification. Herring's scaling law can be used to predict the approximate sintering temperature of α-Al_2O_3 powder and demonstrates that if the particle size can be reduced to < 20 nm, sintering below 1000°C may be possible. α-Al_2O_3 nanoceramics with a grain size of < 100 nm may be also fabricated.

Acknowledgements

The authors acknowledge the financial support provided by the Natural Science Foundation of China and the Foundation of this Laboratory.

References

[1] D.L. Johnson, J. Appl. Phys., 40 (1) (1969) 192–200.
[2] W.S. Young, I.B. Cutler, J. Am. Ceram. Soc., 53 (12) (1970) 659–663.
[3] D.L. Johnson, I.B. Cutler, J. Am. Ceram. Soc., 46 (11) (1963) 545–550.
[4] D.L. Johnson, I.B. Cutler, J. Am. Ceram. Soc., 46 (11) (1963) 541–545.
[5] W.D. Kingery, M. Berg, J. Appl. Phys., 26 (10) (1955) 1205–1212.
[6] R.L. Coble, J. Am. Ceram. Soc., 41 (2) (1958) 55–62.
[7] J.G. Li, X.D. Sun, Y.R. Wang, W.X. Dong, H.Q. Ru, S.M. Hao, Acta Metallurgica Sinca, 34 (2) (1998) 189–194.
[8] C. Greskovich, K.H. Lay, J. Am. Ceram. Soc., 55 (1972) 142–148.
[9] J.G. Li, X.D. Sun, Y.R. Wang, W.X. Dong, H.Q. Ru, S.M. Hao, Acta Metallurgica Sinca, 34 (2) (1998) 195–199.
[10] F.F. Lange, J. Am. Ceram. Soc., 72 (1) (1989) 3–15.
[11] C. Herring, J Appl. Phys., 21 (1950) 301–303.
[12] G.L. Messing, M. Kumagai, Am. Ceram. Soc. Bull., 73 (10) (1994) 84–91.
[13] J.G.J. Peelen, Ceram. Int., 5 (2) (1979) 70–75.
[14] T.-S. Yeh, M.D. Sacks, J. Am. Ceram. Soc., 71 (10) (1988) 841–844.