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Rapid Sintering of Alumina in Low Pressure RF Plasma

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Abstract: Three kinds of high-purity Al_2O_3 powders, whose average particle size is 0.1, 0.3 and 3.0 μm respectively, were used as the starting power, and their compacts were fired in the radio-frequency plasma generated at a pressure of 80 Pa using N_2 as the working gas. Experimental results show that the 0.1 and 0.3 μm powder compacts can be sintered to nearly the theoretical density within 60 s and this sintering is almost finished in the heating period. It is concluded that the mechanism of liquid sintering, the electric charge effect of Al_2O_3 powder, and the effect of temperature gradient in the compacts can affect simultaneously on the rapid densification of the compacts in the plasma sintering.

Key words: plasma sintering; alumina; rapid heating

Plasma shows many peculiar properties for specimen heating. Many parameters, such as generating methods, working pressure, and gas species of plasma affect heating characteristics to specimens. The plasma sintering of oxide ceramics was examined to have the characteristics of rapid heating and low temperature sintering [1–4]. Afterwards, it was found that low-pressure (80 Pa) Radio-Frequency (RF) plasma could also be successfully used for the effective rapid heating of materials [5]. Meanwhile, Ar plasma showed the highest heating ability for Al_2O_3 specimens among Ar, H_2, and N_2 plasma, while H_2 plasma revealed higher heating ability for Mo specimens than Ar plasma, owing to the different interaction of ions and electrons and/or dissociated atoms with the specimen surface of different properties [5]. In a word, the special property of plasma heating makes heat transfer and reactivity in sintering much more complicated, compared with a conventional sintering process. A suitable choice of plasma conditions is definitely important depending on the specimen conditions.

On the other hand, the use of fine powder will lower the sintering temperature of materials because of the high surface energy of the fine powder. However, a conventional sintering process heats specimens very slowly, causing particles to coarsen by surface diffusion during the heating. Rapid heating to the sintering temperature of materials could activate the grain boundary and volume diffusions, before the surface diffusion has a chance to substantially coarsen the microstructure and therefore to lower the driving force for shrinkage.

In this study, high-purity Al_2O_3 powder compacts were sintered in RF plasma of N_2 generated at 80 Pa, to examine the densification of the material in the plasma, and to discuss the sintering mechanism under the rapid heating condition.

1 Experimental

The plasma sintering apparatus and plasma generating conditions are the same as described in reference [5]. Three kinds of high-purity α-Al_2O_3 powders, whose average particle size is 0.1, 0.3 and 3.0 μm respectively, were used as the starting powder. **Table 1** shows the characteristics of the powders. The compacts of 5 mm in diameter and about 2 mm in thickness with a green density of about 50% of the theoretical value were formed by a monoaxial press without any sintering additives and binders. The compacts were held on a boron nitride holder at a position of 20 mm below the center of the RF coil, and were fired in N_2 plasma of 80 Pa generated at an input power of 6 kW.

The microstructures of the sintered specimens were observed using a Scanning Electron Microscope (SEM). The density of the compacts was routinely determined by measuring th mass and size, and occasionally by Archimedes method in water.

Table 1 Impure elements in Al_2O_3 powers 10^{-6}

Grain size / μm	Na	K	Mg	Ca	Fe	Si	Ga	Cr
0.1	26	6	1	1	5	10	2	2
0.3	16	7	1	0	3	7	1	—
3.0	148	—	—	—	126	75	—	—

2 Results and Discussion

2.1 Sintering behavior

Figure 1 shows that the shrinkage of the 3.0 µm powder compact took place very slowly compared with that of the others. The densification of the 0.3 µm powder compact, however, was only a few seconds slower than that of the 0.1 µm. The 0.1 and 0.3 µm powder compacts were sintered to the same density of about 96.5% of the theoretical value within 60 s from the generating of the plasma. By comparing the time–temperature dependence [5] and the time–density relation here, it is clear that the densification almost finished in the heating procedure. Moreover, the SEM observation on the fracture surface of the fired specimens showed that abnormal grain growth occurred in the compact of the 0.1 µm grain size after a firing time of 50 s, and then the structure developed very heterogeneous. Grains grew to about 300, 20 and 5 µm in the 0.1, 0.3 and 3 µm powder compacts respectively, after the same firing time for 600 s.

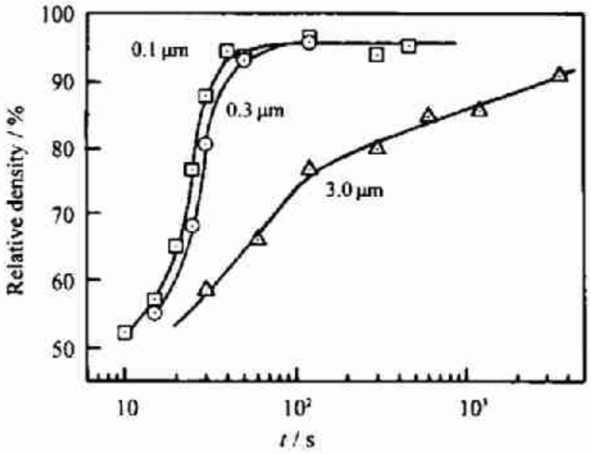

Figure 1 Relative density of sintered Al_2O_3 compacts as a function of firing time in the N_2 plasma.

The density of the 0.1 µm powder compact fired for 50 s in the plasma was determined to be about 95% of the theoretical value by measuring the mass and size. **Figure 2** shows that there are no open pores in the sintered body. Archimedes method can be easily used to determine the density, when the specimen was sintered to this extent. By using Archimedes method the density of the compact was measured to be over 99% of the theoretical value. Generally, the density distribution is quite inhomogeneous in a green compact formed without any additives and lubricants, which would cause heterogeneous shrinkage during the sintering. Moreover, rapid heating of the plasma sintering could also lead to the different densification rate at the surface or center part of the compact. These could introduce macrocracks and/or shape change of the sintered specimens, and cause that the specimen's volume obtained by measuring the size using a micrometer calipers was greater than the real one, thus result in the low measured density value. On the other hand, Archimedes method is not suitable to measure the specimen's density when open pores exist in the specimen, because water can permeate into the pores and make the measured density higher than the real one. For the specimen as shown in figure 2 without open pores in it. Archimedes method can obtain a density value more accurate than that by measuring the size and mass. That is, the pure Al_2O_3 piece of almost the theoretical density could be obtained by plasma sintering.

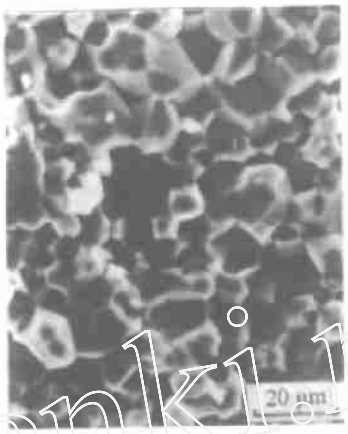

Figure 2 Sectional fracture surface of the 0.1 µm powder compact sintered for 50 s in the plasma.

2.2 Sintering mechanism

The mechanism of mass transport which results in a dense body in the sintering of single-phase crystalline solids has been extensively studied at constant temperatures. The shrinkage rate, effect of powder condition, sintering temperature, and other variables are experimentally found to be in agreement with theoretical predictions. In contrast, the densification during the heating period is little understood, even at a relatively slow heating rate. It is not aimed to give any quantitative investigation here, but only to point out the mechanism which probably acted on the rapid sintering based on the experimental phenomena.

Shown in **figure 3**, the initial portion of fractional shrinkage of the 0.1 µm powder compact can be represented by the relationship $(\Delta V/V_0)$–$t^{1.9}$, and the one of the 3.0 µm powder compact is $(\Delta V/V_0)$–$t^{1.2}$. The value of 1.2 is quite near that of 1.3–1.4 observed by Kingery, *et al.*[6] in the case of liquid phase sintering.

Figure 4 shows the sectional fracture surfaces of the 0.1 and 0.3 µm powder compacts fired for a short time within 30 s. The figure indicates a possibility that trace amount of liquid could exist in the compacts at the early stage of sintering.

Comparing the results shown in **figures 5** and 1, the time when the grain began to grow of the two kinds of compacts corresponds respectively with the time when the compacts were sintered to about 75% of the theoretical density.

The facts above appear to imply that a liquid phase

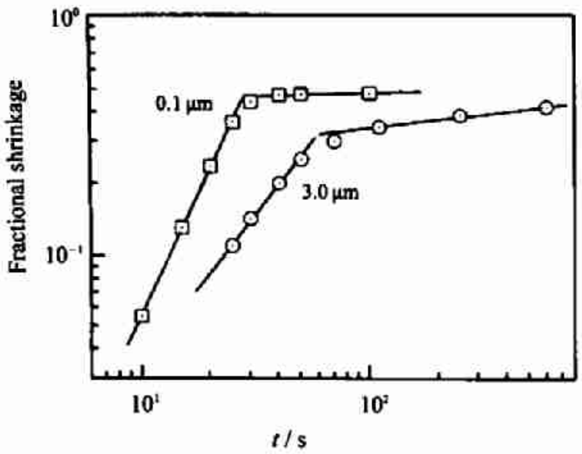

Figure 3 Relation between fractional shrinkage ($\Delta V/V_0$) and sintering time (t) of the compacts in the plasma.

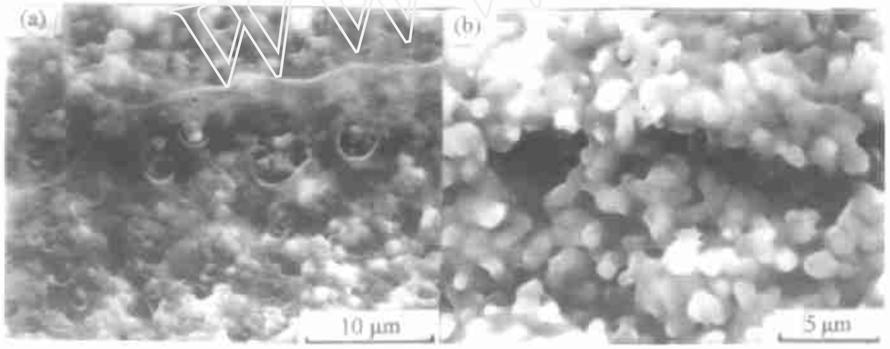

Figure 4 Fracture surfaces of compacts fired in the plasma. (a) The 0.1 μm powder fired for 20 s, and (b) the 0.3 μm for 30 s.

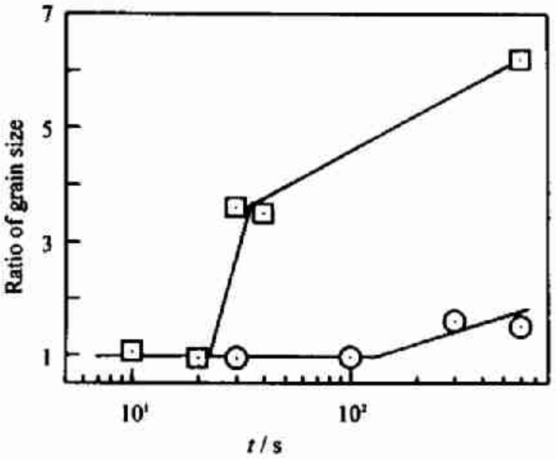

Figure 5 Ratio of grain size in sintered Al_2O_3 compacts to the particle size of starting powder, d/d_0, as a function of firing time.

could play an important role in the early stage of plasma sintering, though it is not clear how the trace amount of liquid phase formed on the particle surface uniformly in tens seconds. Furthermore, it could also be reasonable to consider that the phenomena shown in figures 3 and 5 were partially caused by the electric-charge effect of the Al_2O_3 compacts in the plasma. The electric charge could make the particles easier to move and rearrange, to promote the sintering at the initial stage of firing. On the other hand, Searcy analyzed theoretically the sintering of specimens held in temperature gradients [7]. He pointed out that long-range mass transport by vapor phase or surface diffusion, which cannot cause densification in isothermal systems, could play an important role in the early stage of sintering, when temperature gradients are present. And he referred to that the rapid sintering achieved by Harmer, *et al.* [8] could be considered to be in part driven by temperature gradients during the heating stage of the firing cycle.

Therefore, the high value of 1.9 in $(\Delta V/V_0)$–$t^{1.9}$ for the 0.1 μm powder compact (figure 3), and the fact that the compacts were sintered almost completely during the transit heating period (figure 1), indicate that there could be different mechanisms acted simultaneously on the rapid densification of the fine Al_2O_3 powder compacts in the plasma sintering.

3 Conclusions

(1) The N_2 RF plasma of 80 Pa can heat the Al_2O_3 compacts rapidly to their sintering temperature. The 0.1 and 0.3 μm powder compacts could be sintered to nearly the theoretical density within 60 s, while the 3.0 μm powder compact was sintered relatively slowly.

(2) An important character of the plasma sintering of the fine Al_2O_3 powder is that shrinkage almost occurred in the transit heating duration.

(3) Besides the driving forces affecting a general sintering process,several special mechanisms could also affect the plasma sintering of the fine Al_2O_3 powder.

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References

[1] C. E. G. Bennett, N. A. McKinnon, L. S. Williams: *Nature*, 217(1968). p.1287.

[2] L. G. Cordone, W. E. Martinsen: *Nature Physical Science*, 241(1973). p.86.

[3] D. L. Johnson, R. A. Rizzo: *Am. Ceram. Soc. Bull.*, 59(1980), No.4. p.467.

[4] D. L. Johnson, W. B. Sanderson, E. L. Kemer, J. Knowlton: *Mat. Res. Soc. Symp. Proc.*, 24(1984). p.273.

[5] W. Pan, F. Lü, T. Yoshida: *J. of Univ. of Sci. and Tech. Beijing*, 5(1998). p.31.

[6] W. D. Kingery, M. D. Narasimhan: *J. Appl. Phys.*, 30(1959), No.3. p.307.

[7] A. W. Searcy: *J. Am. Ceram. Soc.*, 70(1987), No.3. p.C-61.

[8] M. Harmer, R. J. Brook: *J. Brit. Ceram. Soc.*, 80(1981). p.147.