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Densification of Ceramics Containing Entrapped Gases During Pressure Sintering

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Abstract

The effect of external pressure on the final densification of ceramics containing entrapped insoluble gases has been calculated. The increase of attainable density is considerable even for medium-pressure sintering of the order of 10–100 atm. High external pressure has its justification in faster densification. The effect of pore coalescence due to grain growth on the attainable density is also assessed.

Der Einfluß äußeren Drucks auf die Endphase der Verdichtung keramischer Werkstoffe mit eingeschlossenen unlöslichen Gasen wurde berechnet. Die erreichbare Erhöhung der Dichte ist selbst für das Sintern bei mittleren Drücken in der Größenordnung von 10–100 atm beträchtlich. Hoher äußerer Druck hat für schnelleres Verdichten seine Berechtigung. Auf den Einfluß des durch Kornwachstum verursachten Zusammenwachsens von Poren auf die erreichbare Dichte wird ebenfalls eingegangen.

On a calculé l'effet d'une pression externe sur le stade final de densification dans le cas de céramiques content des gaz occlus insolubles. Une augmentation considérable de la densité finale est observée même dans le cas de pressions relativement peu élevées, de l'ordre de 10–100 atm. L'emploi de pressions élevées permet une densification plus rapide. On a également estimé l'effet sur la densité finale de la coalescence des pores causée par la croissance des grains.

In the final stage of sintering, the limit of pore shrinkage is determined by the property of gases entrapped in isolated pores. If the gases are soluble and fast diffusing through the solid, the gas pressure in the pores will be identical to the pressure of the gases in the external atmosphere.[1] If the gases are slowly diffusing, the gas pressure is expected to maintain an equilibrium with the capillary pressure of the pores in shrinkage. For both cases, the maximum attainable density is the theoretical value, in contrast to the case of a practically non-diffusing gas, where the content of gases in pores does not change and complete disappearance of pores is not possible.

A recent calculation,[2] based on a pressure balance between entrapped gases and pore capillary, has revealed that the impeding effect of entrapped gases on densification is significant when the pore size is large (over a few microns) or grain growth is extensive. Poor densification due to entrapped gases can be minimized, however, by applying external pressure. A typical but extreme case is the HIP (hot isostatic pressing) after pore isolation. In this paper, the effect of external pressure on the limiting density is calculated and its implication is discussed.

Figure 1 shows the calculated maximum attainable density of powder compacts with external pressure, B atm, after the isolation of mono-size spherical pores which contain insoluble gases at 1 atm. The density curve for $B = 1$ atm in the figure shows the attainable density for the sintering under 1 atm pressure and with solid–gas interfacial tension of 1 N/m, as in an earlier calculation.[2] The increase of attainable density by excess external pressure is considerable, in particular for powder compacts containing large pores. For instance, 10 atm pressure, which is a typical value for gas pressure sintering, can increase the sintered density from 98·6 to 99·6% for pores of 8-μm radius. For small pores, a less significant increase in attainable density is noticed, unless the excess external pressure is very high. This result arises from the contribution of external pressure relative to the capillary pressure. As the

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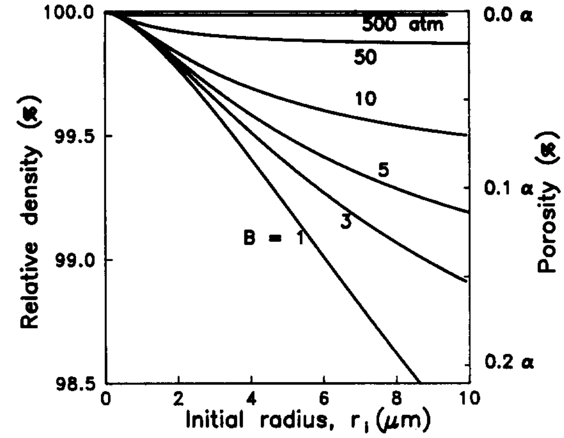

Fig. 1. Maximum attainable density versus initial pore radius, r_i, with initial porosity of α%, for various external pressures, B atm, after the isolation of pores which contain insoluble gases at 1 atm. The ordinate is scaled by assuming initial density of 93% of the theoretical value.

pore size decreases, the capillary pressure of pores increases and the relative contribution of external pressure diminishes. According to Fig. 1, nearly theoretical density can be obtained under less than a few hundred atmospheres pressure for compacts containing any practical size of pores. In the actual HIP process, however, an external pressure of a few thousand atmospheres is applied. For the purpose of pure densification, such high pressure may not be needed, as shown in Fig. 1. Nevertheless, high external pressure can be justified by faster densification and thus minimization of the grain growth.

Figure 2 shows, as an example, calculated densification curves under various external pressures for compacts of 3-μm initial pore radius, surface tension of 1 N/m, initially entrapped gas pressure of 1 atm, and initial relative density of 93%.

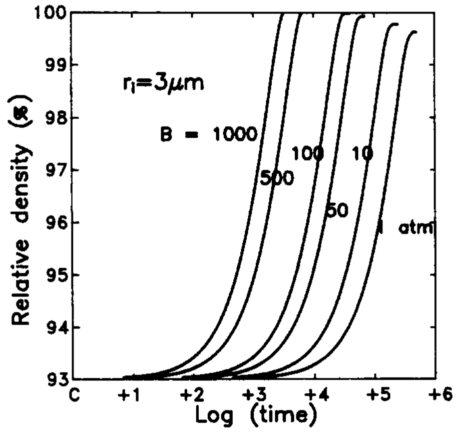

Fig. 2. Calculated densification curves with external pressure, B atm, for compacts of 3-μm initial pore radius and surface tension of 1 N/m. Pressure sintering time is in normalized units (see text).

For the calculation, Coble's concentric sphere model[3] is assumed for compact geometry, and the volume diffusion for the densification mechanism is assumed to be as in the earlier calculation.[2] For final-stage sintering, shrinkage of isolated pores under external pressure of less than a few thousand atmospheres, diffusion is usually the predominant mechanism for ceramics as well as metals.[4] The time is normalized to the kinetic constant, $D\Omega/RT$, where D is diffusivity, and Ω is the molar volume. Figure 2 demonstrates that the increase of external pressure results in considerable increase in densification rate. If the capillary pressure is negligible compared with the external pressure, the densification time can be reduced by the inverse of the factor of pressure increase, as the densification rate is proportional to the sintering pressure.[2] Therefore, in pressure sintering, the value of the external pressure can be selected as a choice of cost and microstructure. Unless grain growth is considerable at the temperature of pressure sintering, high external pressure may not be needed for the sintering of compacts.

Grain growth can cause pore coalescence and this can reduce the limiting density.[5,6] In the case of the coalescence of n pores during final-stage sintering, the replacement of r_i on the abscissa in Fig. 1 by $r_i n^{1/3}$ permits the estimation of the coalescence effect. If Coble's final stage model[3] is accepted, the effect of grain growth by a factor S turns out to be a scaling of r_i in Fig. 1 by $r_i S$. Figure 1 can therefore be used as a general guide for the estimation of maximum attainable density in pressure sintering.

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