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Densification of Ceramics Containing Entrapped Gases

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Abstract

Limits to the shrinkage of isolated pores and to the densification of powder compacts have been calculated for various sintering conditions The impeding effect of an entrapped gas diminishes with lower gas pressure in the sintering atmosphere, with higher solid–gas interfacial tension, with smaller initial pore size, and with higher dihedral angle Over 99 5% relative density can be achieved under conventional conditions when sintering fine powders with a pore size of less than a few micrometres In contrast, the final density can be much reduced in coarse powder compacts and under high initial atmospheric pressures The effect of entrapped gas on the driving force and on the rate of densification during sintering is also calculated The effect of pore coalescence due to grain growth on the bloating of compacts is discussed

Die Grenzen der Schwindung von isolierten Poren und die der Verdichtung von Pulverpreßkörpern wurden für verschiedene Sinterbedingungen berechnet Der behindernde Effekt eines eingeschlossenen Gases verringert sich mit geringerem Gasdruck der Sinteratmosphäre, mit höherer Feststoff–Gas–Grenzflächenspannung, mit kleinerer Ausgangsporengröße und mit einem höheren Dihedralwinkel Eine größere relative Dichte als 99 5% kann unter konventionellen Sinterbedingungen nur erreicht werden, wenn Grünkörper mit Porengrößen von weniger als einigen µm verwendet werden Im Gegensatz dazu wird beim Sintern von Grünkörpern mit großen Formgebungsfehlern (Poren, Dichtegradienten) die Sinterdichte stark reduziert, speziell, wenn die Gasdrücke der Sinteratmosphäre hoch sind Der Einfluß eingeschlossener Gase auf die Triebkräfte und die Sinterrate wird berechnet Die Auswirkungen des Porenwachstums während des Kornwachstums auf das Aufblähen von Sinterproben wird diskutiert

On a calculé, pour différentes conditions de frittage, les limites à la réduction de volume des pores isolés et à la densification de compacts de poudre L'effet d'un gaz occlus est moins gênant lorsque la pression de l'atmosphère de frittage ou la taille initiale des pores diminue, et lorsque l'angle dihèdre ou la tension de l'interface solide–gaz augmente On peut obtenir une densité relative supérieure à 99 5% dans des conditions classiques en frittant des poudres fines dont la taille des pores est inférieure à quelques µm Au contraire, on peut réduire notablement la densité finale d'un compact en utilisant des poudres grossières et des pressions atmosphériques initiales élevées On a également calculé l'effet du gaz occlus sur la vitesse de densification et la force motrice du frittage On discute l'effet de la coalescence des pores due à la croissance des grains sur l'apparition de bulles à la surface des compacts

1 Introduction

The densification of powder compacts during sintering is often limited by gases entrapped in isolated pores[1–3] In the solid state sintering of alumina, Coble[1] demonstrated that nearly full densification of compacts could be achieved after a sintering treatment of a few tens of hours in either H_2 or O_2 but not in N_2 or Ar The limited final density of only 98 2% of the theoretical value found in N_2 and Ar was attributed to difficulties in outward diffusion of inert gas entrapped in isolated pores By contrast, Paek *et al*[3] have recently

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observed that, for MgO doped Al_2O_3, the sintered density and grain size in N_2 atmosphere were approximately equal to those in O_2 atmosphere up to 99% theoretical density and densified further to about 99 5% These results, as typical examples, suggest that the effect of gases entrapped in pores can vary considerably with sintering conditions

The effect of entrapped gas on pore shrinkage has been analyzed theoretically by several authors [4] [5] In particular, Kiparisov and Levinskii[5] have presented a kinetic analysis which involves numerical calculations of the change in pore size with sintering time for various sintering mechanisms In assessing the entrapped gas effect, it can be more helpful to calculate the limiting density of compacts, this allows evaluation of the implications related to powder processing

In the present study, the limiting density of a sintered body has been calculated for various sintering conditions the initial size of isolated pores, the pressure of sintering atmosphere, the solid–gas interfacial tension, the extent of pore coalescence due to grain growth, and the dihedral angle The driving force for, and the rate of densification of, a compact with an entrapped gas have also been computed

2 Calculation and Discussion

2.1 Sintering model

For simplicity, the size of the isolated pores is assumed to be uniform and their total number constant, as in Coble's final stage sintering model [6] Also, no evolution of gases during sintering is assumed to occur Since pore coalescence by grain growth can lead to porosity increase,[7] the limiting porosity calculated here may correspond to the minimum value attainable in a non-diffusing or a slowly diffusing gas atmosphere within reasonable sintering time span Pores are presumed to be present at grain boundaries for fast densification Unless the dihedral angle at the pore–grain boundary junction is 180°, the radius of curvature of the pore increases, resulting in lower driving force for densification The effect of dihedral angle on densification will be treated separately.

The analysis which will be given below is basically thermodynamic, as in the usual sintering models The limiting density is calculated from a pressure balance between inside and outside the specimen The densification will stop as the capillary pressure at the pore surface is balanced with the difference of gas pressures between pore and atmosphere Hence, the calculation will be reasonably correct On the other hand, the calculated driving force and the rate of densification are based on an additional assumption that the solid grains are easily deformable Hence, the instantaneous driving pressure for densification is given by the pressure difference between that at the specimen surface and at the pore surface under a condition of local equilibrium In real sintering of powder compacts, the assumption may not be exactly correct, since the crystalline material can sustain the shear stress This effect, however, should not be important for the calculation, because we are interested in the relative driving force for the densification of the compacts with and without entrapped gas If the external pressure does not fully affect the local densification surrounding the pore, the relative driving force can be modified accordingly Therefore, the basic ideas and conclusions drawn in this study would be correct and can give a semi-quantitative insight of the entrapped gas effect

2.2 Attainable density with spherical pores

Figure 1 shows, schematically, the shrinkage of a spherical pore (dihedral angle $\phi = 180°$) of radius r_i, in an atmosphere of an insoluble gas at pressure P_i The sealed pore can shrink to r_f until the capillary pressure of pore is balanced with increased gas pressure of $P_f - P_i$ If the entrapped gas behaves like an ideal gas,

$$P_i[(r_i/r_f)^3 - 1] = 2\gamma_s/r_f \qquad (1)$$

This relationship is plotted in Fig 2, which is similar to that obtained in a previous investigation[2] on liquid phase sintering Since, in most sintering processes of fine powders, P_i ranges from 0 to a few atmospheres, $(r_i/2\gamma_s)P_i$ is usually less than 0 5 if γ_s is about 1 N/m, and r_i, a few micrometres Therefore, final pore radius is less than half of the initial value

Under the condition that pores are mono-size and their total number remains constant during isolated

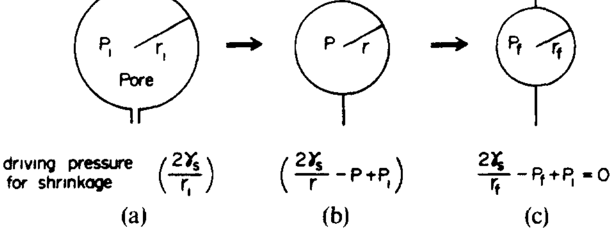

Fig 1. Schematic of pore shrinkage during sintering (a) Just before the isolation of pore, (b) shrinking stage, and (c) final state

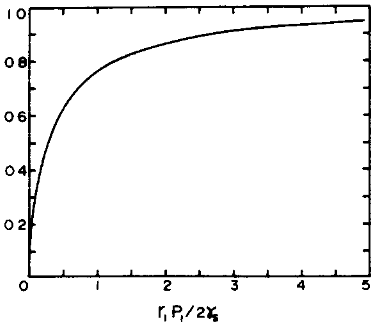

Fig. 2. Variation of final pore radius, r_f, with initial atmosphere pressure in pore, P_i. r_f is normalized to initial pore radius, r_i, and P_i to initial capillary pressure, $2\gamma_s/r_i$.

pore shrinkage, attainable relative density of the powder compact with varying r_i can be calculated and is shown in Fig. 3. Since interconnected pores become isolated when relative density reaches approximately 93%,[8] attainable density can approach the theoretical value, for example, over 99.5%, for pores of less than 3 μm in initial radius, with $P_i = 1$ atm, and $\gamma_s = 1$ N/m ($P_i/2\gamma_s = 0.05\ \mu m^{-1}$), a typical sintering condition. Taking into account the powder size of order 1 μm in typical fine powder processing, a pore of 3 μm radius is extremely large, although pore coalescence by grain growth may occur. Since the interconnected pore size is believed to decrease with decreasing powder size, the final density will increase with finer powder. This result implies that the benefit of fine powder is not only obtaining higher driving force for sintering, but also reducing the effect of entrapped non-diffusing gas on densification.

For sintering of highly decomposable material, such as Si_3N_4, high gas pressure sintering has been proposed in order to suppress the thermal decomposition.[9] Gas pressure sintering, however, has a counter effect on densification, if the gas is slowly diffusing through the matrix. As shown in Fig. 3, increase of gas pressure in the sintering atmosphere can result in very poor densification. If the pressure is increased to 10 atm in the preceding example, the attainable relative density is reduced to about 96%. Therefore, high gas pressure sintering is not recommended before isolation of initially interconnected pores. This conclusion would also apply to the process of sintering plus hipping.

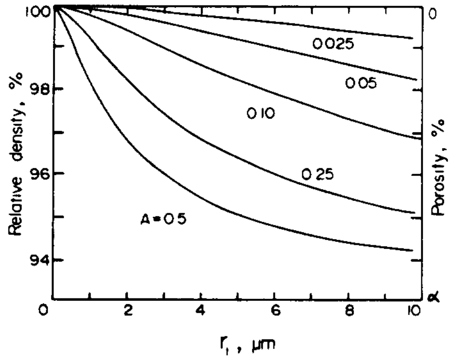

Fig. 3. Maximum attainable density versus r_i, with initial porosity of α% ($A = P_i/2\gamma_s\,\mu m$). The ordinate is scaled by assuming initial density of 93% of the theoretical value.

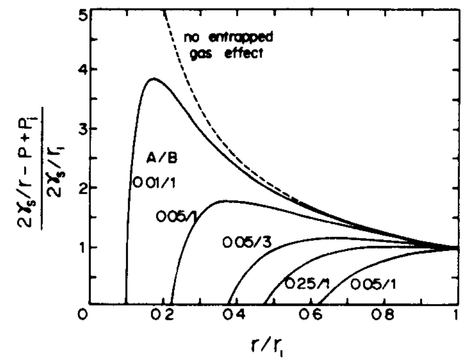

Fig. 4. Variation of relative driving force for densification with pore radius, r, ($A = P_i/2\gamma_s\,\mu m$ and $B = r_i\,\mu m$)

2.3 Sintering rate

The driving force for pore shrinkage should vary with instantaneous pore size because of the increase of capillary pressure as well as gas pressure in the pore. Since the driving force for a shrinking pore of radius, r, and with gas pressure, P, is proportional to $(2\gamma_s/r - P + P_i)$, the driving force relative to initial driving force is $(2\gamma_s/r - P + P_i)/(2\gamma_s/r_i)$. Figure 4 shows the variation of the ratio with pore radius ratio, r/r_i. Compared to the driving force without entrapped gas, the driving force in the presence of a non-diffusive gas is practically unchanged for most of the shrinking range for smaller pores with lower pressure and higher surface tension.

From the relative driving force, the relative densification rate is calculated, as in Fig. 5, using the Coble's final stage sintering model[6] and the equation

$$\frac{dr}{dt} = \frac{D\Omega}{RT}\frac{r_0}{r(r_0 - r)}\Delta\sigma = \text{constant}\,\frac{r_0}{r(r_0 - r)}\Delta\sigma \quad (2)$$

where D is diffusivity, Ω is the molar volume, R is the gas constant, T is absolute temperature, r_0 is the diffusion distance of the material, and $\Delta\sigma$ is the driving pressure for densification. For the calculation, surface tension is taken to be 1 N/m and r_0 is assumed to be 2.43 times the initial pore radius, corresponding to about 93% relative density for a concentric sphere model. From Fig. 5 it is apparent that the densification rate is not significantly lowered by the presence of entrapped insoluble gas for the usual fine powder sintering, except for the range near limiting density. It is, however, noted that high initial

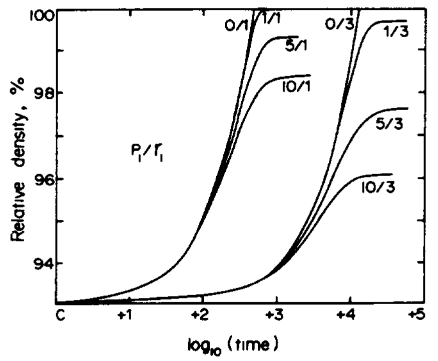

Fig. 5. Calculated densification with sintering time for various P_i (atm) and r_i (μm) Sintering time is in arbitrary units

gas pressure can retard the final densification considerably

2.4 Pore coalescence

No interaction between pores has been assumed in the foregoing When grains grow during sintering, pores at the grain boundaries can coalesce[7] If a pressure balance around coalescent pores is maintained, pore growth and thus density decrease, can result owing to the decrease of capillary pressure around the pores Assuming that an entrapped gas follows the ideal gas behaviour and n pores coalesce, eqn (1) can be modified to

$$P_i[n(r_i/r_f)^3 - 1] = 2\gamma_s/r_f \tag{3}$$

Therefore, Fig 3 can also be used to show the effect of pore coalescence on attainable density, if r_i on the abscissa is replaced by $r_i\ n^{1/3}$

The pore coalescence can be idealized by assuming the number of pores per grain is constant, as in Coble's final stage model During densification, if the grain size increases S times, scaling of r_i in Fig 3 by $r_i\ S$ should permit an estimate of the effect of grain growth Using powders of 1 μm in size, the grain size and initial pore size at the moment of pore closure may be assumed to be similar to powder size, i e 1 μm Since the grains grow a few times (usually less than 5 times) during final densification of fine powders, for example MgO doped Al_2O_3,[3] the final density can be over 99·6% (near theoretical density), for ambient gas pressure sintering In Coble's observation, however, the final density of the 0 3 μm Al_2O_3 powder compact, sintered in 1 atm N_2, was only about 98·2%, possibly because of extensive pore coalescence and grain growth resulting from a few tens of hours of sintering at high temperatures As indicated in Fig. 3, on the other hand, bloating by pore coalescence due to grain growth can be much more significant for high initial gas pressure sintering

If the entrapped gas is diffusive, the maximum attainable density is, of course, the theoretical one Increase of density during sintering can be faster in a diffusive atmosphere than in a non-diffusive atmosphere, as gas pressure difference between inside the pore and outside the specimen induces the outward diffusion of the gas Nevertheless, this contribution may not be significant, because the densification is not markedly affected by the entrapped gas for most of the densification stage, as shown in Fig 5 Furthermore, since the diffusion distance for elimination of a gas atom is much longer than the diffusion distance of vacancy (which can be eliminated at grain boundaries adjacent to a pore), the outward diffusion of gas should not be important for the densification unless the gas atom is fast diffusing—even for the range near limiting density Therefore, for sintering of fine powder, the gas atmosphere may not have a strong influence if it is not reactive with the materials

Usual ceramic powder compacts may contain impurities, such as graphite and sulphur In these cases, an inert atmosphere can be more beneficial for densification by preventing the formation of slowly diffusing gas than a diffusive and reactive atmosphere with impurities Formation of gases with excess pressure of ΔP after seal-off of interconnected porosities, can seriously impede the densification by reducing the driving force to $2\gamma_s/r - \Delta P(r_i^3/r^3)$

2.5 Non-spherical pores

If the dihedral angle is less than 180°, the equilibrium shape of the pore depends on its location at the grain interface, at a two-grain boundary, three-grain edge and four-grain corner For simplicity the pores are assumed to be present at two-grain boundaries, although a considerable fraction of pores are located at three-grain edges and four-grain corners in a real microstructure Under the condition that surface diffusion is fast enough to maintain a uniform radius of curvature of the pore surface, the pore shape is that of two similar spherical segments in contact at the two-grain boundary Since the capillary pressure of the pore decreases with an increasing number of contacting grains, the calculated limiting porosity corresponds to a minimum porosity

Figure 6 shows calculated equi-density lines for varying ϕ and $P_i r_i/2\gamma_s$ values, where initial pore radius r_i corresponds to the radius of a sphere with equivalent volume of the pore,

$$V = \frac{2\pi}{3}\rho^3\left(1 - \cos\frac{\phi}{2}\right)^2\left(2 + \cos\frac{\phi}{2}\right) \tag{4}$$

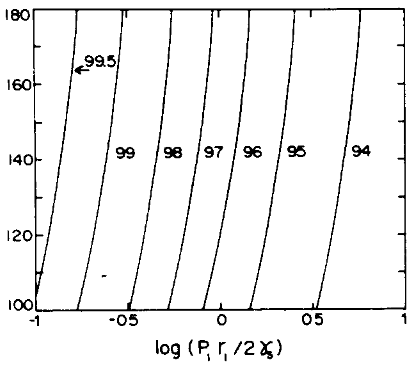

Fig. 6. Final density (%) map as a function of ϕ and $P_i r_i/2\gamma_s$ Initial density is assumed to be 93%

Initial relative density is assumed to be 93%, as in the previous example Under usual sintering conditions ($P \sim 1$ atm, $\gamma_s \sim 1$ N/m and $\phi \sim 150°$), attainable density can still be over 99% for pores less than a few micrometres in radius With decreasing pore size and atmosphere pressure, it is also noticed that the impeding effect of low dihedral angle on densification can be much reduced In contrast, high initial gas pressure (of order 10 atm) or large pore size (a few tens of micrometres) can result in very poor densification

3 Concluding Remarks

Based on a pressure balance calculation, it has been found that, irrespective of sintering atmosphere, near theoretical density can be achieved using fine powder (of order 1 μm) In this sense, fine powder has benefits of lower entrapped gas effect as well as higher driving force for densification In real powder compacts with dihedral angle ϕ less than 180°, the driving force for densification can be considerably reduced Nevertheless, in most of the real powder compacts with ϕ of about 150°, the atmosphere effect can be neglected for fine porosities In contrast, for the densification of coarse powders, selection of atmosphere should be important, since insoluble entrapped gas can significantly limit the densification In the case of high initial gas pressure (e g gas pressure sintering of decomposable material), a poor densification can result even for fine powder compacts, if the gas is slowly diffusing Therefore, gas pressure sintering from the beginning of a heat cycle may not be recommended for normal powder processing

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