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Pressure Filtration and Sintering of Fine Zirconia Powder

T. Uchikoshi,* Y. Sakka, K. Ozawa and K. Hiraga

National Research Institute for Metals, 1-2-1, Sengen, Tsukuba-shi, Ibaraki 305, Japan

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Abstract

Pressure filtration is applied to the consolidation of 3 mol% yttria-doped zirconia fine powder with average particle size of 60 nm over an applied pressure range of 2·5 to 10·0 MPa. Two kinds of aqueous suspension with different rheological behavior, well-dispersed and insufficiently dispersed, respectively, are prepared by changing the amount of dispersant. The kinetics and mechanics of the consolidation of particles are discussed from the dehydration and consolidation rates of the suspensions based on Darcy's law and the Kozeny–Carman equation. The consolidated layer prepared from the well-dispersed suspension shows a good sinterability. Cold isostatic pressing at 400 MPa increases the sintered density of the consolidated layer prepared from the insufficiently dispersed suspension. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Pressure filtration is a useful technique to increase the rate of slip casting of ceramics.[1–4] The advantage is not only the improved productivity but also the reduced segregation. The advantage is greatest in the casting of finer powder, because of the long time needed to cast suspensions of smaller powders without pressure. Many experiments have been reported for the consolidation of submicron or larger-sized powders by pressure filtration.[5–12] Analysis of the dehydration rate of filtrate in a cake has been also attempted.[13–19] However, the consolidation of powders smaller than submicron size by pressure filtration is less common. For the making of good products, the investigation of the rheology of suspensions, of the mechanism of consolidation, of the sintering characteristics of the compact, and of their relationship is very important. Nano-sized particles are very easy to flocculate. Even slight differences in dispersion may influence the mechanism of consolidation or sintering characteristics.[20] In this study, the mechanism of the consolidation of yttria-doped zirconia by pressure filtration is investigated using two kinds of aqueous suspension with different rheological character. The sinterability of the compacts is also investigated and compared with the sinterability of compacts prepared by uniaxial pressing and cold isostatic pressing.

2 Experimental

The experimental work was performed with commercial 3 mol% yttria-doped zirconia powder (Tosoh. Co., TZ3Y; average particle size 60 nm). Different aqueous suspensions with different rheological character were prepared by changing the amount of additional dispersant (ammonium polycarboxylate, Toaghosei Co., ALON A-6114). The suspensions were ultrasonically dispersed for 10 min and stirred by magnetic stirrer for 12 h at room temperature. The rheological behavior of the suspensions was measured by a viscometer (Toki-Sangyo Co., RE500L). The solid content of all the suspensions was 28 vol%. The consolidation of the suspensions was carried out by pressure filtration over an applied pressure range of 2·5 to 10·0 MPa. Before the filtration, the suspensions were evacuated in a vacuum desiccator to eliminate air bubbles. A schematic diagram of the pressure filtration equipment[18] is shown in Fig. 1. A Teflon® membrane filter (0·1 μm average pore size/60 μm thickness) was supported on a stainless steel filter (Nippon Seisen Co. Ltd., NP-Z06; 0·6 mm/1·7 mm) and an acrylic filter (40 μm/10 mm). The heights of the interfaces of piston/suspension and suspension/consolidated layer were measured from the outside of the transparent polycarbonate die during filtration under a constant casting pressure. Cold isostatic pressing (CIP) treatment at 200 or

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*To whom correspondence should be addressed.

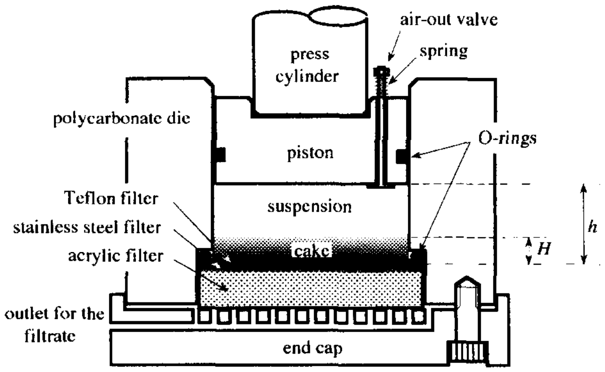

Fig. 1. Schematic diagram of the pressure filtration equipment. The inside diameter of the die is 50 mm.

400 MPa was carried out for some compacts to improve the packing density after the consolidation by pressure filtration. The compacts were dried overnight at 110°C, and sintered in air at fixed temperatures for 2 h. The density of the compacts was measured by the Archimedes' method using kerosene. The microstructure of sintered bodies was observed by SEM using polished and thermally etched surfaces.

3 Results and Discussion

3.1 Rheological behavior

The suspension with the minimum viscosity was obtained at 0·65 wt% of dispersant. This suggested that the suspension with 0·65 wt% of dispersant was well-dispersed. The viscosity of the suspension was increased by reducing the amount of dispersant. When the latter was reduced to 0·35 wt%, the viscosity of the suspension increased rapidly. At 0·30 wt% of dispersant, the suspension became too stiff for slip casting. The relation of shear rate to shear stress is shown in Fig. 2. No suspension behaved as a Newtonian fluid. When the amount of dispersant is 0·65~0·50 wt%, the flow curve shows pseudoplastic behavior. When the amount of dispersant is 0·40 wt%, the flow curve changes to Bingham plastic behavior and some degree of flocculation is presumed. Therefore, the mechanism of consolidation by pressure filtration and the sintering characteristics of the compacts were investigated by using suspensions with 0·65 and 0·40 wt% of dispersant. Hereafter we name these as suspensions A (0·65 wt%) and B (0·40 wt%), respectively.

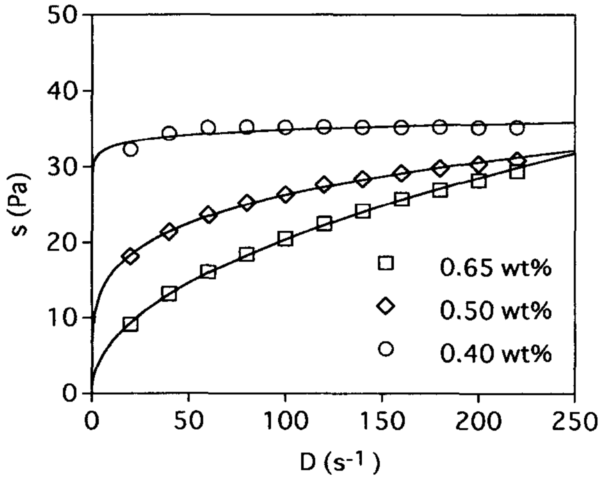

Fig. 2. Shear rate versus shear stress for suspensions with different amounts of dispersant.

3.2 Mechanism of consolidation

The consolidation of a suspension by slip casting proceeds with the filtration and/or the sedimentation of particles.[21] If the contribution of sedimentation is ignored, the rate of consolidation is determined by a simple filtration process. When the flow of filtrate in a consolidated layer is laminar, the flux of filtrate obeys Darcy's law.[22]

$$Q = \frac{kP}{\mu H} \tag{1}$$

where P is the pressure difference across the consolidated layer, μ the viscosity of the filtrate, H the height of the consolidated layer and k the permeability of the layer. The relation between the flux of filtrate, the void fraction of the consolidated layer e and the specific surface area per unit volume of powder S_0 is expressed by the Kozeny–Carman equation.[23]

$$Q = \frac{1}{k_c S_0^2} \cdot \frac{e^3}{(1-e)^2} \cdot \frac{P}{\mu H} \tag{2}$$

$$k_c = k_o (l_e / H)^2 \tag{3}$$

where l_e is the real length of the flow channel in the consolidated layer and k_o is a constant defined by the shape of the cross section of the flow channel. The term k_c is called the Kozeny constant. For many systems, the value $k_c = 5$ as suggested by Carman has been applied.[23] By comparison between eqns (1) and (2): eqn (4) is obtained.

$$k = \frac{1}{k_c S_0^2} \cdot \frac{e^3}{(1-e)^2} \tag{4}$$

Figure 3 shows the change in the heights of the piston/suspension interface h and in that of the consolidated layer H during filtration at the constant pressures of 2·5, 5·0 and 10·0 MPa. The higher the pressure applied on the suspensions, the

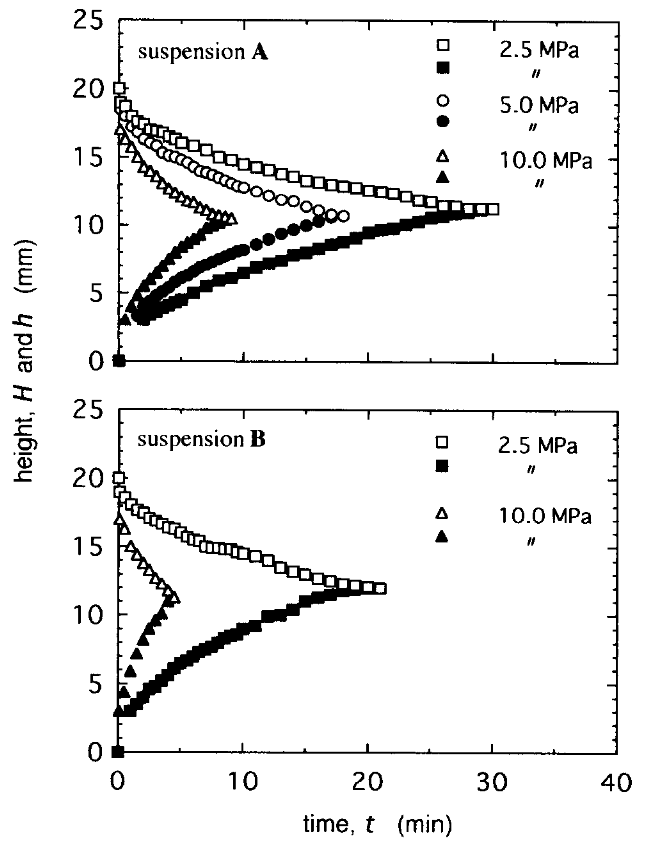

Fig. 3. Change in the heights of piston/suspension interface h (open marks) and consolidated layer H (closed marks) during filtration at constant pressure.

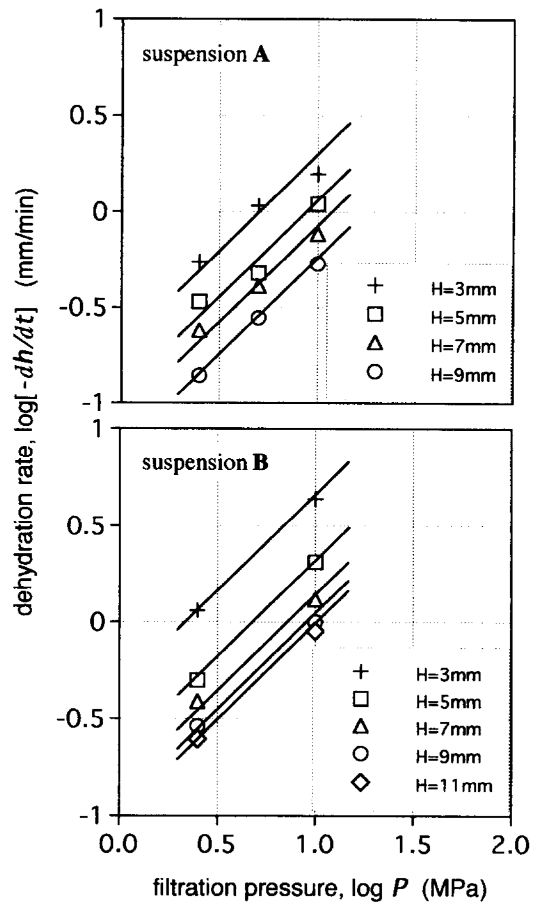

Fig. 4. Relation between filtration pressure and dehydration rate.

faster is the filtration rate obtained. However, the packing density of the consolidated bodies is pressure-insensitive over the applied pressure range for both suspensions as shown in Table 1. The green densities of the compacts consolidated from suspension B are lower than those from suspension A.

Figure 4 shows the relation between filtration pressure P and dehydration rate $Q(= -\mathrm{d}h/\mathrm{d}t)$. From the Reynolds' law, when the flux of liquid in a capillary is slow, the flow obeys a laminar flow ($Q \propto P^1$), and when the flux becomes faster, the flow becomes turbulent ($Q \propto P^{1/2}$).[24] The slope of 1 for both suspensions shows that the flows of the filtrates in the consolidated layers are laminar.[19] For both the suspensions A and B, the permeabilities of the consolidated layers were calculated by using eqn (1). Figure 5 shows the permeability changes during the filtration. The permeabilities at different heights of the consolidated layers are also shown on the right side of the figure. Permeabilities are nearly constant during filtration for both the suspensions. This result indicates that the consolidation and particle packing proceed uniformly during the filtration for both the suspensions. The slight decrease in the permeability at the final stage of filtration is probably due to the partial compression of the cake by the piston.

Table 1. Relative green density, void fraction, permeability and Kozeny constant of the compacts consolidated from the suspensions A and B

	Filtration pressure P (MPa)	*Green density*	*Void fraction e*	*Permeability k (m²)*	*Kozeny constant kc*
(A)	2·5	0·485	0·515	$1{\cdot}05\times10^{-17}$	5·76
	5·0	0·493	0·507	$9{\cdot}79\times10^{-18}$	5·70
	10·0	0·485	0·515	$8{\cdot}14\times10^{-18}$	7·43
(B)	2·5	0·476	0·524	$1{\cdot}76\times10^{-17}$	3·76
	10·0	4·479	0·521	$1{\cdot}71\times10^{-17}$	3·75

Kozeny constants were also calculated by using eqn (2). A specific surface area of the raw powder ($16{\cdot}2\,\mathrm{m^2\,g^{-1}} = 9{\cdot}80\times10^7\,\mathrm{m^2\,m^{-3}}$) was used as S_0 for the calculation. The specific surface area of the raw powder was measured after outgassing in vacuum at 400°C by the BET method using nitrogen as adsorbate. The calculated results are shown in Table 1. As described above, the value $k_c = 5$, experimentally found by Carman using micron-sized powders, has been applied for many systems without any confirmation. Grace has pointed out cases which depart from $k_c = 5$ for some submicron-sized powders, for example $k_c = \sim 50$, and considered the reason to be the flocculation of the particles since small particles are easy to flocculate.[25] There has been other reports of k_c measured for submicron-sized powder. Sobue *et al.* have reported $k_c = 6{\cdot}2$ for $0{\cdot}52\,\mu\mathrm{m}$ Si_3N_4 powder.[15] We

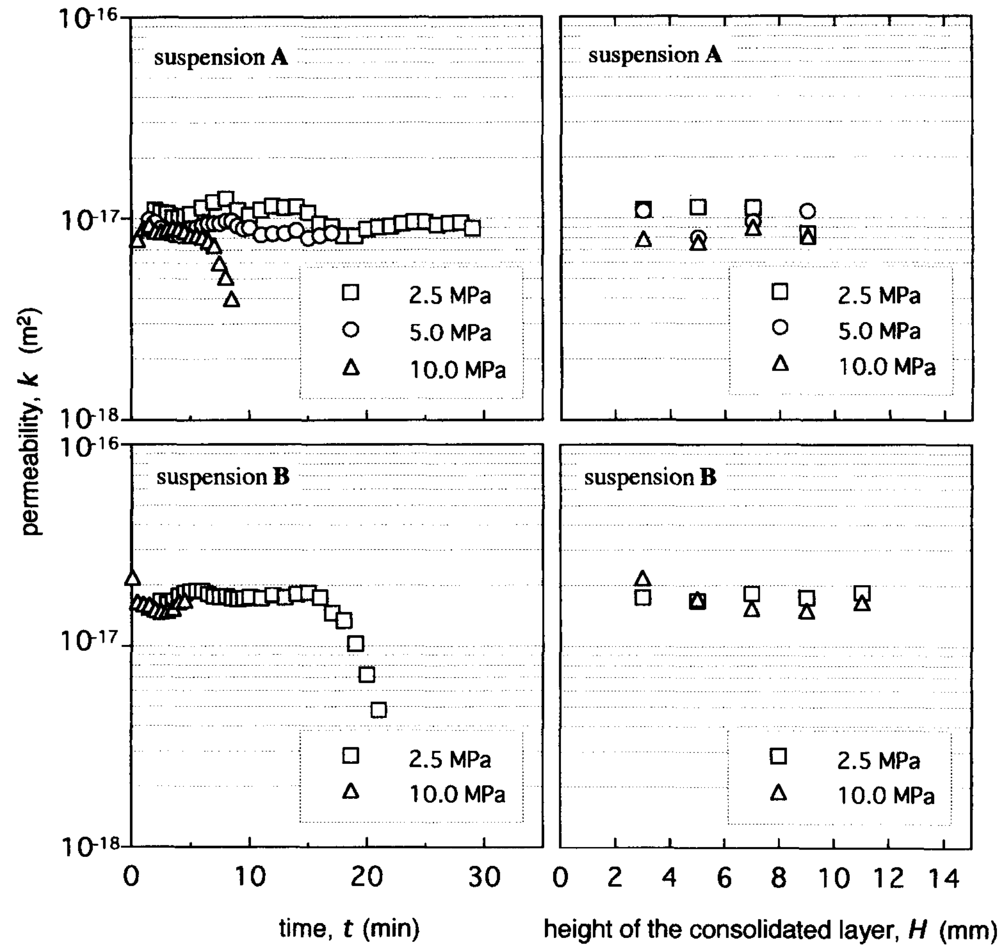

Fig. 5. Permeability changes for the suspensions during the formation of consolidated layers.

have reported $k_c = 4{\cdot}1\text{–}5{\cdot}6$ for well-dispersed 0·1 μm alumina powder.[19]

In this study, the calculated k_c of the suspension A is 5·8–7·4, while the k_c of suspension B is 3·8. These values are seen as close to 5. Our result indirectly supports the validity of $k_c \approx 5$ for 60 nm-sized powder. The reason why k_c of the suspension B is smaller than that of the suspension A is probably due to an overestimation of the specific surface area. The specific surface area measured for raw powder has been used for the calculation of k_c, but the real specific surface area for a flocculated suspension can well be smaller than that of a raw powder.

3.3 Sintering characteristics

The sintering characteristics were investigated using compacts filtrated at 2·5 or 5 MPa. Figure 6 shows the impact of the dispersion of the suspensions and the effect of the following CIP treatment on the density of the sintered bodies. CIP treatment is effective in improving the green density for both compacts. The compacts prepared from suspension A show good sinterability, and the relative density reaches more than 99% at 1300°C regardless of CIP treatment. However, in the case of compacts from suspension B, the relative density sintered at 1300°C without CIP is 96·5%. The inferior sinterability of the latter is improved by CIP treatment at 400 MPa, and the relative density then reaches more than 99%. By sintering at 1400°C, the relative density reaches 100% for all

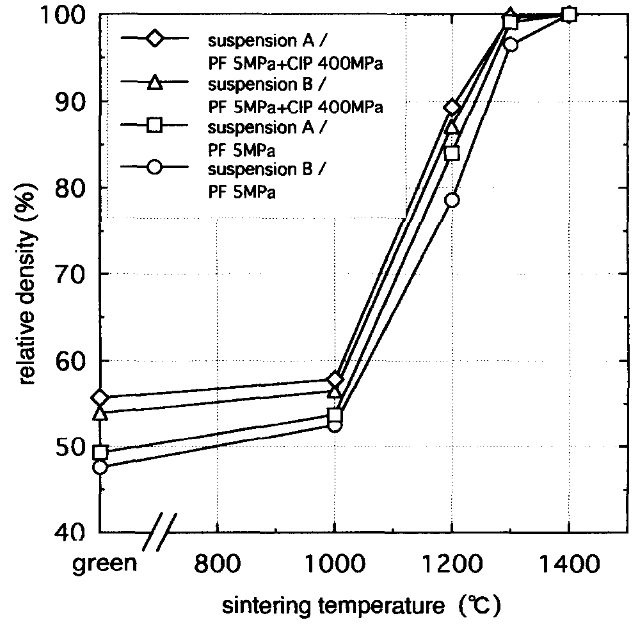

Fig. 6. Influence of the dispersion of the suspensions and of the following CIP treatment on the density of the sintered bodies.

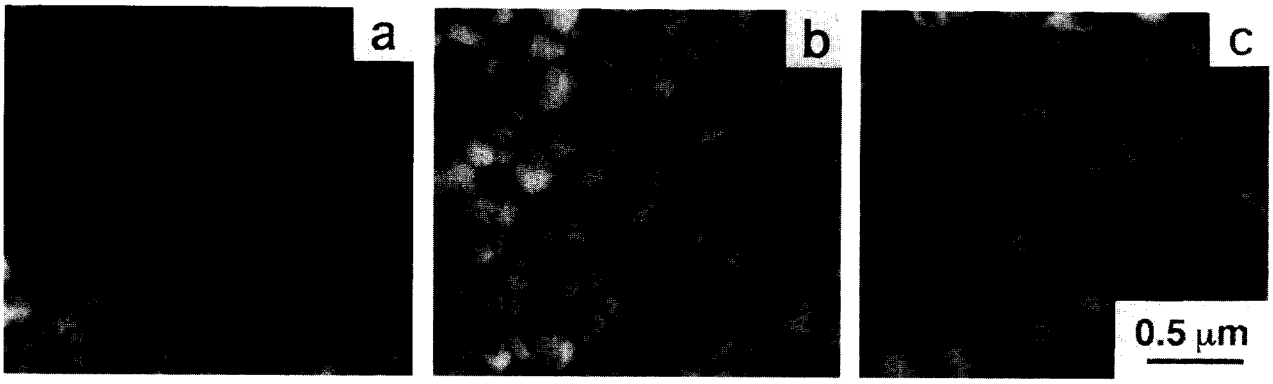

Fig. 7. SEM micrographs of the sintered bodies; (a) consolidated from suspension A and sintered at 1300°C, (b) consolidated from suspension B and sintered at 1300°C, (c) consolidated from suspension A and sintered at 1400°C. These three samples are sintered without CIP treatment after the consolidation by pressure filtration at 5 MPa.

compacts. Figure 7 shows SEM micrographs of the sintered bodies without CIP treatment. The samples were prepared from (a) suspension A sintered at 1300°C, (b) suspension B sintered at 1300°C and (c) suspension A sintered at 1400°C. Many pores are observed for the sample (b), and grain growth is observed for the sample (c). From the SEM observation of the other samples sintered at 1300°C, a similar microstructure was observed for samples prepared from suspension A without CIP, for suspension A with CIP and for suspension B with CIP. As mentioned before, although the rate of filtration is different between suspension A and B (the rate of B is almost double that of A), the formation of the consolidated layers proceeds uniformly during filtration for both suspensions. This result suggests a useful procedure for the processing of this powder, namely a combination of pressure filtration and a following CIP treatment using a slightly flocculated suspension. Slight flocculation helps to shorten the time for filtration. Flocculation also makes small pores in a consolidated body, but those pores are crushed by the following CIP treatment. After the filtration and CIP treatment, the compacts are sintered to > 99% at 1300°C like the compacts from a well-dispersed suspension. The most appropriate conditions for the preparation of suspension and consolidation should be determined from the detailed analysis of the filtration process and sintering behavior.

The relative influence of uniaxial pressing (UP), pressure filtration (PF) and subsequent CIP treatment on the density of sintered bodies is also investigated. The uniaxial pressing was performed on the raw powder. Figure 8 shows the sinterabiltiy of six samples compacted in different ways: (1) UP at 100 MPa only, (2) UP at 100 MPa followed by CIP at 200 MPa, (3) UP at 100 MPa followed by CIP at 400 MPa, (4) PF of suspension A at 2·5 MPa only, (5) PF of suspension A at 2·5 MPa followed by CIP at 200 MPa and (6) PF of suspension A at 2·5 Mpa followed by CIP at 400 MPa.

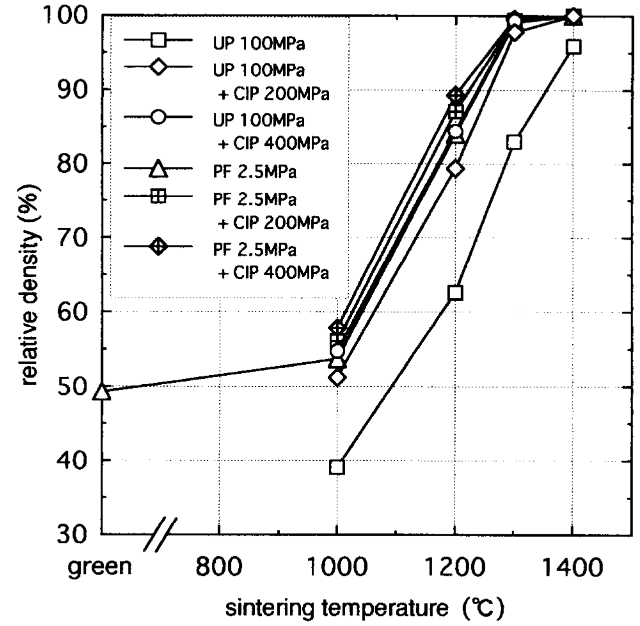

Fig. 8. Sinterability of six samples compacted in different ways; (1) UP at 100 MPa only, (2) UP at 100 MPa followed by CIP at 200 MPa, (3) UP at 100 MPa followed by CIP at 400 MPa, (4) PF of suspension A at 2·5 MPa only, (5) PF of suspension A at 2·5 MPa followed by CIP at 200 MPa and (6) PF of suspension A at 2·5 MPa followed by CIP at 400 MPa.

The green density of the compacts was improved by CIP for both the UPed and PFed samples. The relative sintered density of all PFed samples (4)–(6) and UPed at 100 MPa followed by CIP at 400 MPa (3) reaches more than 99% at 1300°C. The relative sintered density of the sample UPed at 100 MPa followed by CIP at 200 MPa (2) is 97·8% at 1300°C. The relative density of the sample UPed at 100 MPa only (1) is 95·9% even with sintering at 1400°C. As shown in Fig. 8, the sinterability of the compact prepared by PF of suspension A at 2·5 MPa (4) is equivalent to the sinterability of the compact prepared by UP at 100 MPa followed by CIP at 400 MPa (3). This result shows the high efficiency of colloidal processing for dense particle packing.

4 Conclusions

Y-doped zirconia aqueous suspensions with different rheological behavior were prepared by changing the amount of additional dispersant. A well-dispersed zirconia aqueous suspension with minimum viscosity was obtained at 0·65 wt% of dispersant. With reducing the dispersant to 0·40 wt%, the rheological behavior of the suspension was changed from pseudoplastic behavior to Bingham plastic. The consolidation of two suspensions, well-dispersed and insufficiently dispersed, respectively, was investigated by pressure filtration over the applied pressure range of 2·5 to 10·0 MPa. The flow of filtrate in the consolidated layer was laminar for both suspensions. The constant permeability of the filtrate during the filtration indicated uniform particle packing during the consolidation for both suspensions. The green compact consolidated from the well-dispersed suspension showed a good sinterability. CIP treatment at 400 MPa was able to increase the sintered density of the compact consolidated from the insufficiently dispersed suspension.

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