journal

New Freeze-Casting Technique for Ceramics with Sublimable Vehicles

Kiyoshi Araki* and John W. Halloran**

Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109

A new ceramic freeze-casting technique capable of manufacturing near room temperature with a sublimable vehicle was accomplished. Fluid-concentrated slurries of Al_2O_3 powder in molten camphene ($C_{10}H_{16}$) were prepared at 55°C. These slurries were quickly solidified (frozen) at room temperature to yield rigid solid green bodies, followed by frozen camphene removal by sublimation (freeze-drying) with negligible shrinkage. Sintering without any special binder burnout process yielded sintered bodies with over 98% theoretical density. The proposed advantages include (1) elimination of extremely cold temperatures, (2) elimination of troublesome binder burnout process, and (3) fast manufacturing cycle due to quick solidification.

I. Introduction

IN GENERAL, ceramics are hard to form in complex shapes because the forming technique is basically based on powder processes. Among the powder processing techniques, colloidal processing techniques are usually used in complex-shape forming for ceramics. These include conventional slip casting, widely used (wax-based) injection molding, gelcasting,[1–3] and freeze-casting.[4–7] The details of these colloidal processing techniques as well as novel colloidal processing techniques were recently reviewed.[8–10]

Among these colloidal processing techniques, freeze-casting is one of the simplest techniques. Freeze-casting is a forming technique where a ceramic slurry, which is usually aqueous and sometimes containing silica–sol, is frozen in a nonporous mold under extremely cold temperature, e.g., −40°C, and followed by demolding and vehicle removal by sublimation, i.e., freeze-drying, to obtain a green body. This technique has many advantages such as a fast manufacturing cycle, no drying cracks, and no troublesome binder burnout process. In freeze-casting, however, special efforts need to be made to obtain an extremely cold temperature and to conduct a slow freeze-drying process under 0°C.

The objective of this work is to develop a new freeze-casting technique capable of manufacturing near room temperature to eliminate expensive processes under extremely cold temperatures. To do this, an alternative vehicle needs to be selected instead of water. The requirements for the alternative vehicle are (1) appropriate solidification temperature, which should be higher than the room temperature but should not be too high (e.g., <70°C), (2) liquid viscosity similar to water so that concentrated slurries can be made, (3) small volume change during solidification to avoid problems associated with solidification shrinkage (or expansion), and (4) higher vapor pressure in solid state (the vapor pressure of ice is 0.10 kPa[11] at a freeze-drying temperature of −20°C) for

freeze-drying. Other than these requirements, the vehicle should be safe and inexpensive.

There could be many potential candidates for such a vehicle. In this paper, we discuss an organic molecular compound, camphene ($C_{10}H_{16}$, 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane, CAS 79-92-5), as a vehicle. Camphene is a cyclic hydrocarbon as shown in Fig. 1. At room temperature it is a soft crystalline solid material. It is a natural material, a terpenoid, and commonly used in fragrance compounds. Camphene has a melting temperature around 44°–48°C, low liquid viscosity of 1.4 mPa·s at 47°C[12] and manageable solidification shrinkage of −3.1%.[12] Solid camphene has a vapor pressure of 1.3 kPa[13] just below the melting temperature, high enough for convenient freeze-drying at room temperature. It is safe and inexpensive. Thus, camphene seems a good candidate for a vehicle of new freeze-casting capable of near-room-temperature manufacturing.

II. Experimental Procedure

(1) Materials

We chose alumina using an α-Al_2O_3 powder (AG16, Alcoa Chemical, Pittsburgh, PA) with a median size (d_{50}) of 400 nm, specific surface area of 8.6 m^2/g, and density of 3.91 g/cm^3 (all from the manufacturer's specifications). For the vehicle, (±)-camphene ($C_{10}H_{16}$, Alfa Aesar/Avocado Organics, Ward Hill, MA) with a melting temperature of 44°–48°C (from the manufacturer's specifications) and a measured liquid density of 0.833 g/cm^3 at 55°C was used without further purification. A dispersant is needed for stable colloid dispersions of alumina in liquid camphene. After evaluating several commercial dispersants, we chose Perfad 9100 (UniQema, Everburg, Belgium), an amine derivative of a fatty acid condensation polymer. The measured density of the Perfad 9100 is 0.963 g/cm^3.

(2) Fabrication Procedures

Suspensions were prepared by conducting ordinary ceramic processing at 55°C, using "warm ball-milling". The process is summarized in Fig. 2. Appropriate amounts of Al_2O_3 powder, dispersant, and solid camphene were put into sealed high-density polyethylene bottles with prewarmed Al_2O_3 milling media. They were ball-milled inside an oven at a temperature of 55°C for 20 h to produce stable, dispersed slurries. A sealed bottle prevented the loss of camphene by evaporation during warm milling. Camphene has a vapor pressure of 2.0 kPa at 55°C[14] (equivalent to the vapor pressure of water at 18°C). Because some camphene vapor will be lost when the bottle is opened, the actual solid content in the slurry (volume fraction of the powder in the slurry) becomes higher than that in the initial composition by about 3 vol%. For example, the initial solid content of 45.0 vol% became the actual solid content of 48.2 vol% after ball-milling at 55°C for 20 h. The initial solid content was calculated by using the volume of the Al_2O_3 powder, dispersant, and camphene at 55°C on the assumption that the volume of the liquid portion in the slurry is the same as the sum of the dispersant and molten camphene volume. The actual solid content in the slurry was calculated with the weight change after complete sublimation of camphene from the cast bodies made by the slurry on the assumption that the weight change corresponds to

---
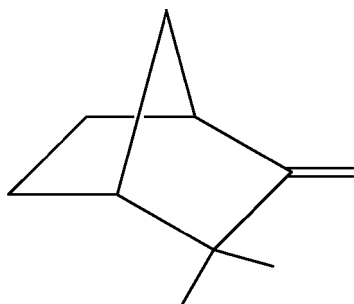
Fig. 1. Structural formula of camphene, $C_{10}H_{16}$.

Fig. 3. Measured viscosity of 43.6 vol% Al_2O_3 slurry as a function of the dispersant (Perfad9100) content in Al_2O_3/camphene/Perfad9100 system. Measurement was conducted at 55°C at constant shear rate of 100 s^{-1}.

the camphene weight in the slurry after warm ball-milling. Hereafter, the term, solid content, means this actual solid content.

The warm slurries were poured into aluminum or polyurethane molds at room temperature. The typical cavity size of the mold was 10- or 55-mm diameter and 5-mm depth. After the casting, the solidification was completed within 30 s to yield a solid frozen body.

After demolding, green bodies were placed in an ambient atmosphere to sublime (freeze-dry) the frozen camphene from the cast bodies. Judging from the weight change, this sublimation process typically finished in 24 h. Negligible shrinkage was observed during sublimation. The cast bodies were sintered at 1100°, 1300°, 1500°, and 1600°C (ramping rate of 5°C/min) for 4 h without any special binder burnout process.

(3) Characterization

The viscosity of the alumina–camphene suspensions was measured in the steady shear mode on a rheometer (CS-50, Bohlin, East Brunswick, NJ) at shear rate of 10–1000 s^{-1}. We used a cone-and-plate measurement geometry (Bohlin, CP-4/40) having a 0.15-mm gap between the cone and the lower plate. The temperature of the measurements was controlled by indirect heating of the lower plate and set at 55 ± 1°C. A solvent trap was used to minimize evaporation of camphene.

The sublimation behavior was observed by measuring the mass change of the demolded cast bodies. Thermogravimetric analysis and differential thermal analysis (TG/DTA) were conducted to observe the burnout behavior of the residual organics in the camphene-free body after sublimation. The density of sintered bodies was measured using the Archimedes method. The microstructure of the sintered bodies was observed with a scanning
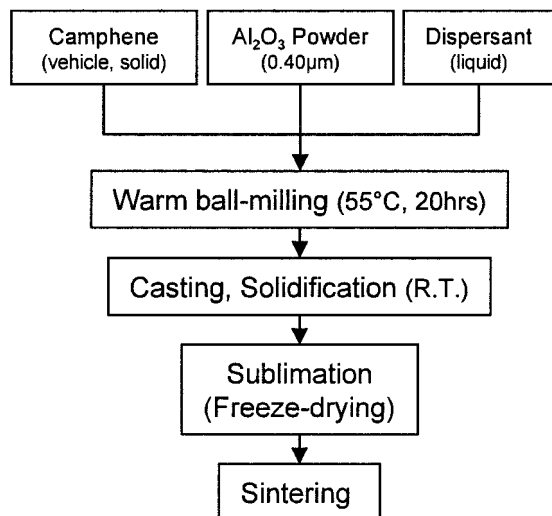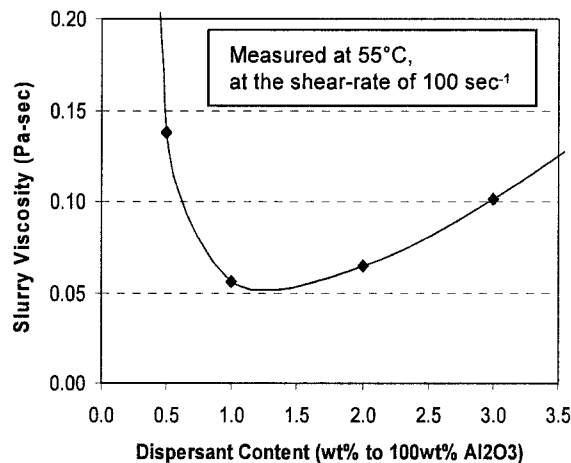
electron microscopy (SEM; XL-30, Philips Electronics N.V., Eindehoven, The Netherlands).

III. Results and Discussion

(1) Rheology

The rheological behavior of slurries in this work is worth investigating because not only it gives quality control factors for casting but also a highly loaded, fluid slurry of Al_2O_3 in liquid camphene is novel. The effect of the dispersant content to the slurry viscosity was first examined. Suspensions with 43.6 vol% Al_2O_3 were prepared with different amounts of the dispersant. The dispersant content here is defined as the mass ratio of the dispersant to Al_2O_3 powder. The relationship between the dispersant content and the slurry viscosity at 55°C is shown in Fig. 3. As is often observed in ceramic slurries, the viscosity dramatically decreases with a small amount of dispersant and gradually increases with the increase of excess amount of the dispersant. A fixed dispersant content of 2.0 wt% of the Al_2O_3 powder was used for additional experiments.

The steady shear behavior, measured at 55°C, of Al_2O_3 slurries with various volume fraction of solids is shown in Fig. 4. All the slurries, except for the solid content of 33.1 vol% exhibiting
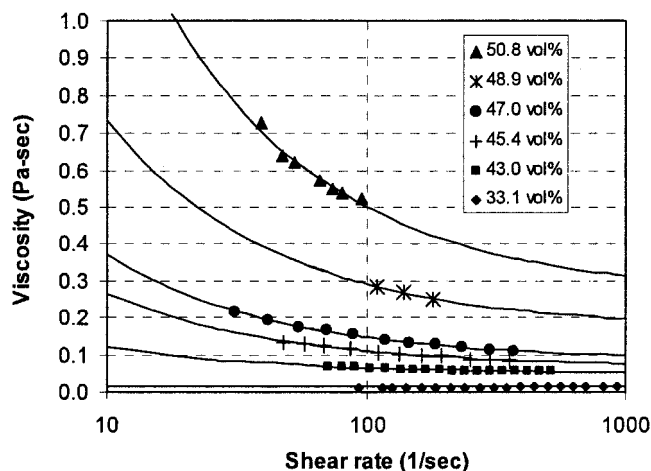

Fig. 2. Schematic chart of the fabrication procedure.

Fig. 4. Steady shear viscosity at 55°C of the Al_2O_3/camphene/Perfad9100 system at different volume fractions of solids. The data, except for 33.1 vol% exhibiting Newtonian behavior, are fitted to the high shear form of the Cross model, Eq. (2), with a common exponent, $p = \frac{2}{3}$.

Table I. Fitting Parameters Using Equation (2) for Steady Shear Data in Figure 4

Solid content	η_∞	$(\eta_0 \cdot \eta_\infty)/b$	p	Correlation factor (R^2)
0.508	0.261	5.1653	2/3	0.9750
0.489	0.170	2.6145	2/3	0.9909
0.470	0.0851	1.3256	2/3	0.9975
0.454	0.0673	0.9239	2/3	0.9656
0.430	0.0495	0.3327	2/3	0.9843

Table II. Fitting Parameters, ϕ_m (Maximum Volume Fraction of Solids) and n (Exponent), Using Equation (3), with Reported Values in Other Nonaqueous Ceramic Slurries

ϕ_m	n	Powder	Vehicle	Ref.
0.61	2.9	Al_2O_3	Camphene	This work
0.64	1.6	Al_2O_3	Acrylate monomer	Ref. 19
0.565	1.7	Al_2O_3	Acrylic triblock copolymer	Ref. 20
0.53	2	Al_2O_3	Paraffin wax	Ref. 21
0.54	2.4	Si_3N_4	Decalin	Ref. 18

almost Newtonian behavior, are characterized by shear-thinning behavior. Both the degree of shear thinning and the viscosity at the specific shear rates increase with the increase of the solid content.

One of the simplest and widely accepted models for shear-thinning behavior is the Cross model,[15] which expects constant low- (η_0) and high-shear (η_∞) viscosity with a shear-thinning region in between and described as

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + b\dot{\gamma}^p} \quad (1)$$

where η is the slurry viscosity at a specific shear rate of $\dot{\gamma}$, and b, p are constants. Near the high-shear rate limit, where $b\dot{\gamma}^p \gg 1$, the Cross equation can be described as

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{b} \dot{\gamma}^{-p} \quad (2)$$

Although the measured viscosity data in Fig. 4 is limited, it was possible to fit these data to the Cross Eq. (2), with a common exponent, $p = 2/3$, which is the recommended value in the original Cross paper.[15] The fitting parameters in Table I are used to estimate the high shear viscosity.

Figure 5 shows the relatively high shear viscosity, which is defined as η_∞ from the Cross model normalized by the viscosity of the slurry with no solids (liquid camphene in this case, 1.4 mPa·s at 47°C[12]), as a function of the volume fraction of solids. By fitting the obtained data to the modified Krieger–Dougherty equation[16–18]

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-n} \quad (3)$$

where η_r is the relative high shear viscosity, ϕ is the volume fraction of the solids, and both ϕ_m and n are fitting parameters, the values of $\phi_m = 0.61$ and $n = 2.9$ for the Al_2O_3/camphene/
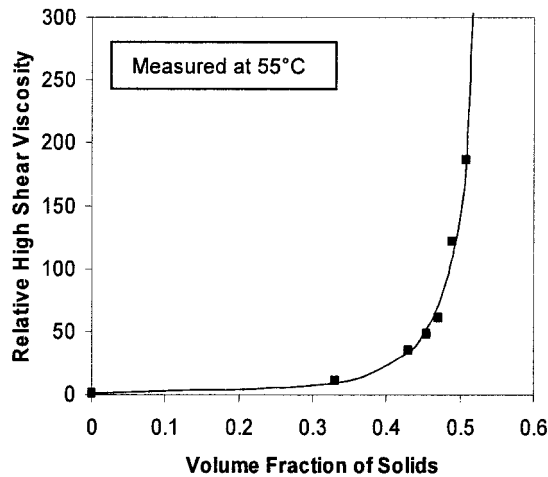
Perfad9100 slurry was obtained. The fitting parameter, ϕ_m, describes the maximum volume fraction where the slurry viscosity becomes infinite (maximum packing fraction; 0.64 for random close packing). The parameter n describes the degree of increase in viscosity. Table II lists the fitting parameters, ϕ_m and n, in other nonaqueous ceramic slurries reported earlier.[18–21] The value of n in this work seems slightly higher than other values reported. This difference may be ascribed to the uncertainty in the estimate of the η_∞ values in this work, which were obtained from the measurement with the limited shear rate range. Another reason for a higher n value may be ascribed to the effect of the viscous dispersant, Perfad 9100, which has a relatively high viscosity of 1.4–2.4 Pa·s.[22] As is mentioned in the experimental procedures, the amount of dispersant is proportional to the solid content (volume fraction of solids). Thus, there is little dispersant in the slurry with lower solid content, whereas there is ~4 vol% dispersant in the slurry with 50.8 vol% solid content. Since it was not known how much dispersant is in the liquid portion of slurries compared with the amount adsorbed onto the Al_2O_3 powders, the dispersant effect on slurry viscosity was neglected. The addition of viscous dispersant, however, may increase the slurry viscosity at higher solid content, in this case making the n value apparently larger.

(2) Sublimation Behavior

To examine the rate of sublimation, a 50.6 vol% Al_2O_3 slurry at 55°C was cast to make a disk, 55-mm diameter and 5-mm thickness. After demolding (within 1 min after casting), the green body was placed in a fume hood to sublime the frozen camphene from the green body. Ambient temperature was kept 25 ± 2°C and the airflow rate of ambient atmosphere was 0.01–0.05 m/s. The cast body was placed on pins so that the sublimation occurs also from the bottom side. Sublimation was measured from mass loss. Shrinkage during the freeze-drying process was negligible.

Figure 6 shows the relative mass change of the cast body as a function of time. Due to the sublimation of the frozen camphene in the cast body, the mass decreases rapidly initially and reaches steady value, about 84 wt% of the initial weight, after 24 h. This weight loss
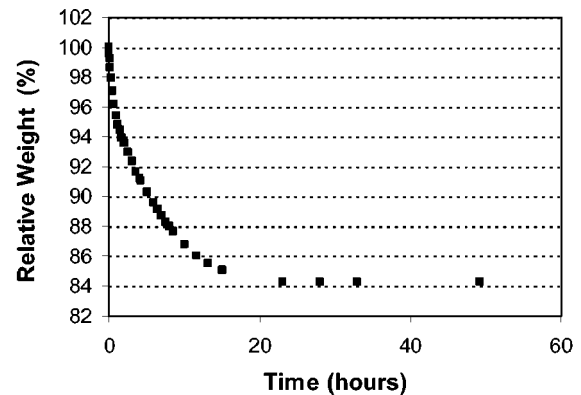
Fig. 5. High shear rate viscosity, η_r, at 55°C of the Al_2O_3/camphene/Perfad9100 system as a function of volume fraction of solids, ϕ. η_r is calculated from η_∞, in Table 1, divided by the slurry viscosity with no solids (1.4 mPa·s of liquid camphene). Obtained data are fitted to the modified Krieger—Dougherty equation, Eq. (3), using $\phi_m = 0.61$ and $n = 2.9$.

Fig. 6. Change of the relative weight in the cast body, 55-mm diameter and 5-mm height, made from 50.8 vol% Al_2O_3 slurry. The weight change corresponds to the amount of camphene in the as-cast body.
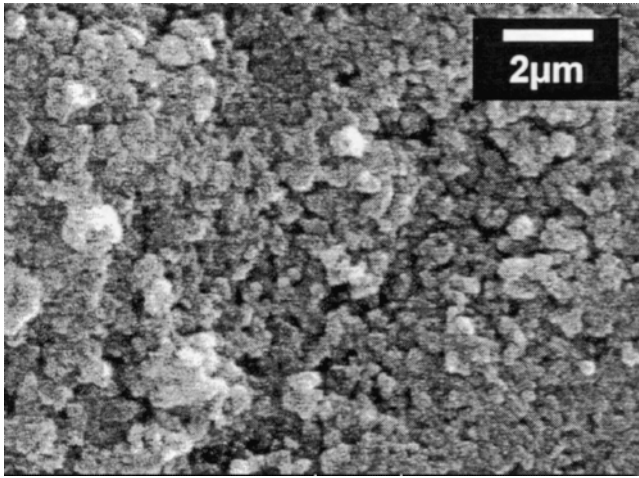
Fig. 7. Microstructure of freeze-dried Al_2O_3 green body made from the slurry with 45.4 vol% solid content.

of around 16 wt% corresponds to the camphene content in the as-cast body. The dispersant, Perfad 9100, did not evaporate.

Freeze-drying in ceramic process is a drying process where the slurry is first frozen, thereby converting the liquid vehicle to a solid form, and the solid vehicle is removed by sublimation. Freeze-drying of water/ice is usually conducted below −20°C to prevent the ice from melting and at low atmospheric pressure, less than 0.3 kPa, to lower the water vapor pressure in the drying chamber to promote sublimation. In our work, however, the room temperature is low enough to keep the camphene solid and the ambient atmosphere is enough for sublimation for the camphene, because a large gradient of camphene vapor pressure exists between a camphene surface and the surrounding atmosphere.
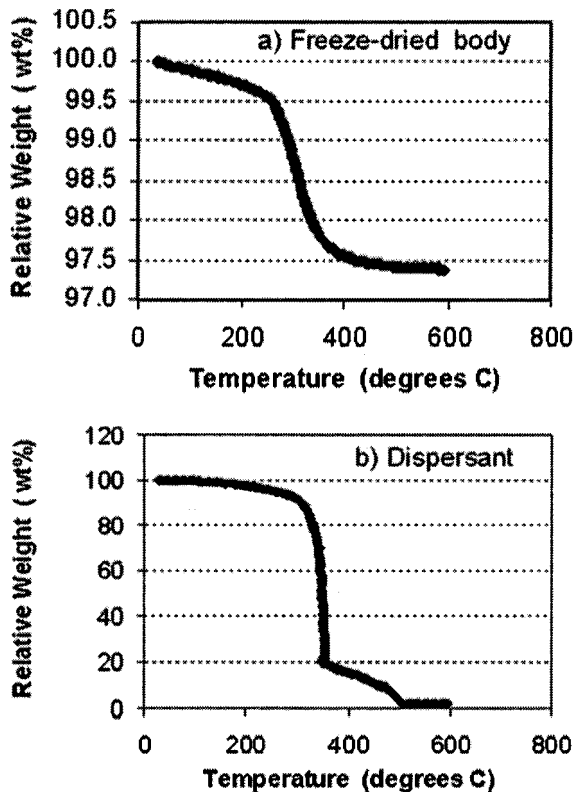

Fig. 8. Weight changes of (a) the freeze-dried body during an early stage of the sintering process and (b) the dispersant, Perfad 9100, during thermal decomposition.
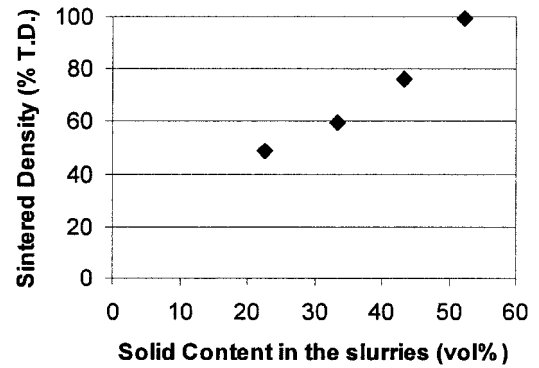

Fig. 9. Sintered density (in theoretical density (TD)) of Al_2O_3 cast bodies as a function of solid content in slurries. Sintering temperature was 1600°C.
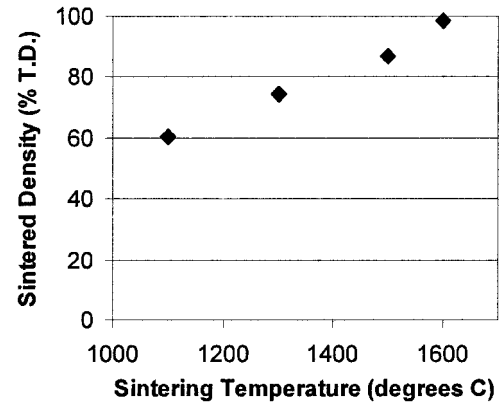

Fig. 10. Sintered density (in theoretical density (TD)) of Al_2O_3 cast bodies as a function of sintering temperature. All samples were fabricated from 50.8 vol% Al_2O_3 slurry.
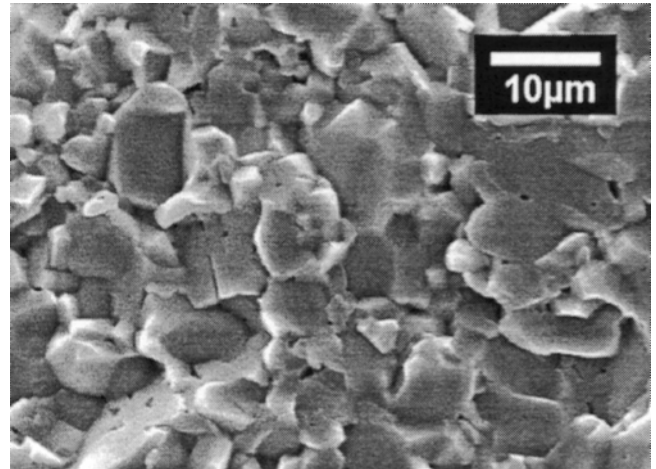

Fig. 11. Fracture surface of a sintered Al_2O_3 body with over 98% TD, fabricated by the new freeze-casting technique.

Relatively low sublimation enthalpy of camphene may also contribute to the fast freeze-drying without a freeze-dryer.

(3) Sintering

After freeze-drying, green bodies without vehicle were obtained with negligible shrinkage. Figure 7 shows the microstructure of freeze-dried Al_2O_3 green body made from the slurry with 45.4 vol% solid content. No macroscopic defects, cracks, or hard agglomeration were observed.

Fig. 12. U.S. penny (1 cent coin) replica made of Al_2O_3 sintered body.

Figure 8 shows the weight change of the freeze-dried body during the early stage in the sintering process, as well as the thermal decomposition behavior of the dispersant, Perfad 9100, itself. The freeze-dried body exhibits a rapid weight loss of about 2 wt% around 300°C (Fig. 8(a)). Judging from the amount of the weight loss and the decomposition behavior of Perfad 9100 itself (Fig. 8(b)), this weight loss in the freeze-dried body can be ascribed to the thermal decomposition of the Perfad 9100, which is the only organic remainder in the green body after freeze-drying. Due to the relatively low amount of organics, the freeze-dried body can be sintered without any special binder burnout process at a heating rate of 5°C/min.
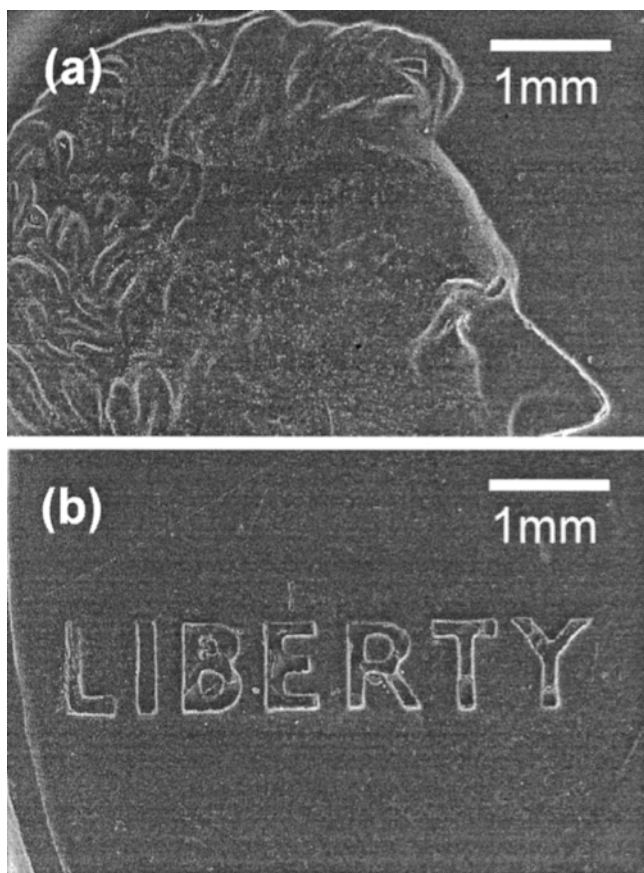

Fig. 13. SEM photographs of the replica shown in Fig. 12.

Figures 9 and 10 show sintered densities as a function of solid content in the slurries and sintering temperature, respectively. The sintered density increases with the increase of solid content in the slurry (Fig. 9) and the sintering temperature (Fig. 10). An almost fully dense body with 98.4% theoretical density (TD) is obtained with the solid content of 50.8 vol%, and the sintering temperature of 1600°C. Microstructural observation confirms the high sintered density as shown in Fig. 11.

To demonstrate the ability of this novel freeze-casting technique, some demo-castings were conducted with polyurethane molds. A picture of an U.S. penny replica made of Al_2O_3 sintered body and its magnified pictures are show in Figs. 12 and 13, respectively. Although further improvement is needed, relatively fine features are well-replicated.

IV. Summary

A new freeze-casting technique capable of manufacturing near room temperature with a sublimable vehicle is developed and discussed. Fluid concentrated slurries of Al_2O_3 powder in molten camphene ($C_{10}H_{16}$) were prepared at 55°C with a small amount of a dispersant. The rheology of the slurries is well-explained by the conventional theories for slurries with shear-thinning behavior. These slurries were quickly solidified (frozen) at room temperature to yield a rigid solid green body, where the frozen camphene was easily removed by sublimation (freeze-drying) with negligible shrinkage. Sintering could be conducted without any special binder burnout process, to yield over 98% TD sintered bodies. The proposed advantages include (1) elimination of extremely cold temperatures used in conventional freeze casting, (2) elimination of troublesome binder burnout process, and (3) fast manufacturing cycle due to quick solidification.

References

[1]O. O. Omatete, M. A. Janney, and R. A. Strehlow, "Gelcasting—A New Ceramic Forming Process," *Am. Ceram. Soc. Bull.*, **70** [10] 1641–49 (1991).

[2]A. C. Young, O. O. Omatete, M. A. Janney, and P. A. Menchhofer, "Gelcasting of Alumina," *J. Am. Ceram. Soc.*, **74** [3] 612–18 (1991).

[3]S. Morissette and J. A. Lewis, "Chemorheology of Aqueous Alumina–Poly(vinyl alcohol) Gelcasting Suspensions," *J. Am. Ceram. Soc.*, **82** [3] 521–28 (1999).

[4]H. Ballman "Unique New Forming Technique," *Ceram. Age*, **791**, 36–38 (1957).

[5]B. E. Novich, C. A. Sundback, and R. W. Adams, "Quickset Injection Molding of High-Performance Ceramics"; pp. 157–64 in Ceramic Transactions, Vol. 26, *Forming Science and Technology for Ceramics.* Edited by M. J. Cima. American Ceramic Society, Westerville, OH, 1992.

[6]R. W. Jones, "Near Net Shape Ceramics by Freeze Casting," *Ind Ceram.*, **20** [2] 117–21 (2000).

[7]S. W. Sofie and F. Dogan, "Freeze Casting of Aqueous Alumina Slurries with Glycerol," *J. Am. Ceram. Soc.*, **84** [7] 1459–64 (2001).

[8]F. F. Lange, "Powder Processing Science and Technology for Increased Reliability," *J. Am. Ceram. Soc.*, **72** [1] 3–15 (1989).

[9]W. M. Sigmund, N. S. Bell, and L. Bergström, "Novel Powder-Processing Methods for Advanced Ceramics," *J. Am. Ceram. Soc.*, **83** [7] 1557–74 (2000).

[10]J. A. Lewis, "Colloidal Processing of Ceramics," *J. Am. Ceram. Soc.*, **83** [10] 2341–59 (2000).

[11]*CRC Handbook of Chemistry and Physics*, 50th ed. Edited by R. C. Weast. The Chemical Rubber Co., Cleveland, OH, 1969.

[12]T. E. Daubert and R. P. Danner, *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*, Part 4. Taylor & Francis, London, U.K., 1989.

[13]D. R. Stull, "Vapor Pressure of Pure Substances Organic Compounds," *Ind. Eng. Chem.*, **39**, 517–40, (1947).

[14]*Vapor Pressure of Organic Compounds*. Edited by J. E. Jordan. Interscientific, New York, NY, and London, U.K., 1954.

[15]M. M. Cross, "Rheology of Non-Newtonian Fluids: A New Flow Equation for Pseudoplastic Systems," *J. Colloid Interface Sci.*, **20**, 417–37 (1965).

[16]I. M. Krieger and T. J. Dougherty, "A Mechanism for Non-Newtonian Flow in Suspensions of Rigid Spheres," *Trans. Soc. Rheol.*, **3**, 137–52 (1959).

[17]I. M. Krieger, "Rheology of Monodisperse Lattices," *Adv. Colloid Interface Sci.*, **3**, 111–36 (1972).

[18]L. Bergström, "Rheological Properties of Concentrated, Nonaqueous Silicon Nitride Suspensions," *J. Am. Ceram. Soc.*, **79** [12] 3033–40 (1996).

[19]T. M. Chu and J. W. Halloran, "High-Temperature Flow Behavior of Ceramic Suspension," *J. Am. Ceram. Soc.*, **83** [9] 2189–95 (2000).

[20]J. K. Montgomery, P. L. Drzal, K. R. Shull, and K. T. Faber, "Thermoreversible Gelcasting: A Novel Ceramic Processing Technique," *J. Am. Ceram. Soc.*, 85 [5] 1164–68 (2002).

[21]K. A. M. Seerden, N. Reis, J. R. G. Evans, P. S. Grant, J. W. Halloran, and B. Derby, "Ink-Jet Printing of Wax-Based Alumina Suspensions," *J. Am. Ceram. Soc.*, **84** [11] 2514–20 (2001).

[22]*Material Safety Data Sheet of the Perfad 9100*. UniQema, Everburg, Belgium, 1999.   □