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Room-Temperature Freeze Casting for Ceramics with Nonaqueous Sublimable Vehicles in the Naphthalene–Camphor Eutectic System

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Freeze casting for Al_2O_3 was accomplished at room temperature with nonaqueous sublimable vehicles in the naphthalene–camphor eutectic system with a eutectic temperature of 31°C. A fully dense sintered body (>99.5% of theoretical density (T.D.)) was obtained with a eutectic composition vehicle, whereas at most 90% T.D. was obtained with an off-eutectic (i.e., hypo- or hypereutectic) composition vehicle due to formation of large uniquely shaped voids. Microstructural observation suggested that growing pro-eutectic crystals rejected the suspended Al_2O_3 particles to form large voids during the solidification process. At the eutectic composition, formation of fine lamellar microstructure in a solidified vehicle is considered to inhibit particle rejection resulting in large voids.

I.   Introduction

FREEZE casting followed by a freeze-drying process[1,2] has been used in complex-shape forming for ceramics, like other colloidal processing techniques such as conventional slip casting, injection molding, and gel casting.[3–5] The details of these colloidal ceramic processing techniques were recently reviewed.[6–8] Freeze casting is a forming technique where a ceramic slurry, which is usually aqueous and sometimes containing silica-sol, is frozen in a 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, no troublesome binder burnout process, and so on. However, in the freeze casting technique, we need special efforts to obtain an extremely cold temperature, e.g., < −40°C.

To eliminate this expensive freezing process under extremely cold temperature and troublesome freeze-drying under 0°C, the authors have recently developed a new freeze casting technique capable of manufacturing near room temperature using a molecular compound, camphene ($C_{10}H_{16}$), as a vehicle and showed that an almost fully dense Al_2O_3 sintered body was obtained.[9] Since camphene is a natural, nontoxic material, this technique is even environmentally friendly unlike other room-temperature freeze casting techniques[10,11] with toxic materials as a vehicle. Among such materials, naphthalene ($C_{10}H_8$) and camphor ($C_{10}H_{16}O$) are promising candidates for a vehicle of room-temperature freeze casting, even though they are a little toxic, because they have (1) low liquid viscosity as water so that concentrated slurries can be made, (2) negative volume change (shrinkage) during solidification unlike water to contribute a higher green density, and (3) higher vapor pressure in a solid state for easy freeze-drying. Their properties,[12,13] as well as those of water,[14] are summarized in Table I. However, their solidification temperatures, especially

180°C for camphor, are too high for room-temperature freeze casting where the preferable solidification temperature range is 30–60°C.

The binary system of naphthalene and camphor, both of which are molecular compounds, is a known eutectic system with a eutectic temperature of 31–32°C.[15,16] The phase diagram of the naphthalene–camphor system by Robinson *et al.*[16] is shown in Fig. 1. Because of the convenient eutectic temperature, the naphthalene–camphor alloy has been studied by metallurgists as a model for solidification.[17–19] This eutectic alloy seems suitable for a vehicle for room-temperature freeze casting in terms of not only a convenient solidification temperature of 31–32°C but also a low liquid viscosity, negative volume change during solidification, and higher vapor pressure, all of which are expected from the properties of pure naphthalene and pure camphor.

In this paper, we report the trial of using a eutectic vehicle for room-temperature freeze casting for ceramics. The eutectic naphthalene–camphor alloy with a manageable solidification temperature is chosen as a vehicle. We also investigate the effect of vehicle composition (eutectic or off-eutectic) on the microstructure of final sintered ceramics.

II.   Experimental Procedure

(1)   Materials

We chose alumina as a ceramic example, using a common α-Al_2O_3 powder (AG16, Alcoa Chemical, Pittsburgh, PA) with a median size (d_{50}) of 0.4 μm, a specific surface area of 8.6 m^2/g, and a density of 3.91 g/cm^3 (all from the manufacturer's specifications). As a vehicle, naphthalene (>99.6%, $C_{10}H_8$, Alfa Aesar, Ward Hill, MA) with a melting temperature of 80°C (from the manufacturer's specifications) and DL-camphor (>96%, $C_{10}H_{16}O$, Alfa Aesar/Avocado Organics, Ward Hill, MA) with a melting temperature of 173–175°C (from the manufacturer's specifications) were used without further purification. To produce stable Al_2O_3 suspensions, a commercial liquid product of amine derivative of a fatty acid condensation polymer (Perfad 9100, UNIQEMA, Everburg, Belgium) with a measured density of 0.963 g/cm^3 was adopted as the colloidal dispersant.

(2)   Fabrication Procedure

First, three kinds of liquid vehicles with either (1) hypoeutectic (naphthalene-rich), (2) eutectic, or (3) hypereutectic (camphor-rich) composition in the naphthalene–camphor eutectic system was prepared. Appropriate amounts of solid naphthalene, solid camphor, and a liquid dispersant were put into high-density polyethylene bottles with Al_2O_3 milling media. They were sealed and ball-milled inside a drying oven for 1 h at 55°C for hypoeutectic and eutectic composition, and at 60°C for hypereutectic composition to make liquid vehicles made of a molten naphthalene–camphor alloy and dispersant. After confirming that the vehicles became completely liquid, an appropriate amount of prewarmed Al_2O_3 powder was added into the liquid vehicles, and they were again ball-milled inside the same drying oven at the same temperatures for 20 h to produce stable, dispersed slurries. Slurries with initial solid content of 20, 30, 40 and 48 vol%, all

Table I. Some Physical Properties of Naphthalene, Camphor, and Water

	Chemical formula	Solidification temperature (°C)	Volume change during solidification	Liquid viscosity (mPa·s)	Vapor pressure in solids (Pa)
Naphthalene	$C_{10}H_8$	80	Negative	0.91 (80°C)	1.3×10^2 (52°C)
Camphor	$C_{10}H_{16}O$	180	Negative	0.63 (180°C)	1.3×10^2 (41°C)
Water	H_2O	0	Positive	1.0 (20°C)	1.3×10^2 (−20°C)

with 3 wt% dispersant (to 100 wt% Al_2O_3 powder), were prepared in 10–20 cm³ batches.

During the warm ball-milling process, the naphthalene vapor and the camphor vapor in the sealed bottle should be in equilibrium with the slurry. Because the naphthalene vapor pressure and the camphor vapor pressure are different and these vapors are lost when the bottle is opened, the naphthalene ratio to camphor in the warm ball-milled slurries will be changed from the initial charged ratio. As is explained in detail later, microstructural observation of solidified naphthalene–camphor alloys revealed that the initial charge of 40 wt% naphthalene–60 wt% camphor became the eutectic composition, which is 35 wt% naphthalene–65 wt% camphor according to the phase diagram,[16] after the warm ball-milling in this work. Initial charges of 56 wt% naphthalene–44 wt% camphor, 40 wt% naphthalene–60 wt% camphor, and 31 wt% naphthalene–69 wt% camphor were used as hypoeutectic, eutectic, and hypereutectic vehicles, respectively. Measured liquid densities of hypoeutectic (56 wt% naphthalene–44 wt% camphor) and eutectic (40 wt% naphthalene–60 wt% camphor) compositions are both 0.983 g/cm³ at 55°C, and that of hypereutectic (31 wt% naphthalene–69 wt% camphor) composition is 0.964 g/cm³ at 60°C. Examples of the charged weight of each material for 48 vol% Al_2O_3 slurries are shown in Table II.

Warm ball-milled slurries were poured into a cylindrical depression on the surface of polyurethane molds at room temperature. The size of the mold was 10 mm in diameter and 5 mm in depth. The slurries solidified typically within 20 min to yield solid rigid green bodies. After demolding, green bodies were placed in ambient atmosphere with an airflow rate of 0.01–0.05 m/s to sublime the frozen naphthalene–camphor alloy from the green

bodies. Judging from the weight change, this sublimation process typically finished in 60 h. During this freeze-drying process, neither crack formation nor measurable shrinkage was observed. After the freeze-drying process, the cast bodies were sintered at 1600°C (ramping rate of 5°C/min) for 4 h without a special binder burnout process. The fabrication procedure described above is summarized in Fig. 2.

(3) Characterization

The density of sintered bodies was measured using the water displacement method based on the Archimedean principle. The microstructure of the sintered bodies was observed with scanning electron microscopy (SEM; XL-30, Philips Electronics N.V., Eindehoven, The Netherlands). The microstructure of solidified naphthalene–camphor alloys was observed with optical microscopy (OM; BH2-UMA, Olympus, Tokyo, Japan) in the transmission mode by dropping molten liquid alloys without ceramic powder and the dispersant onto a slide glass.

III. Results and Discussion

Figure 3 shows the relative density of Al_2O_3 sintered bodies as a function of the charged solid content (Al_2O_3 volume fraction) in
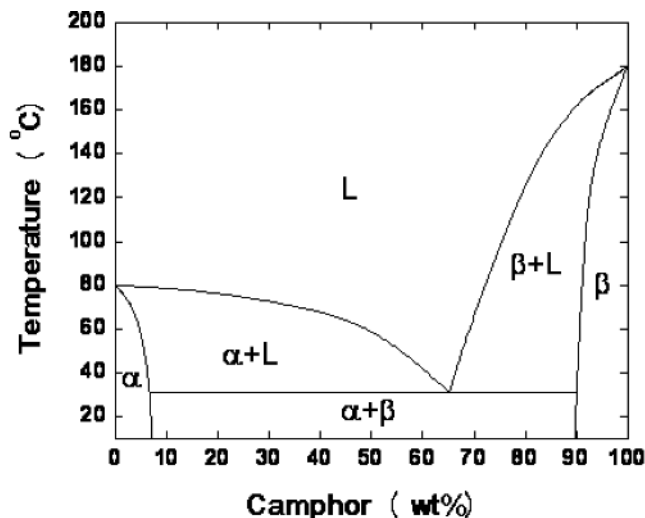

Fig. 1. Naphthalene–camphor phase diagram.[16]
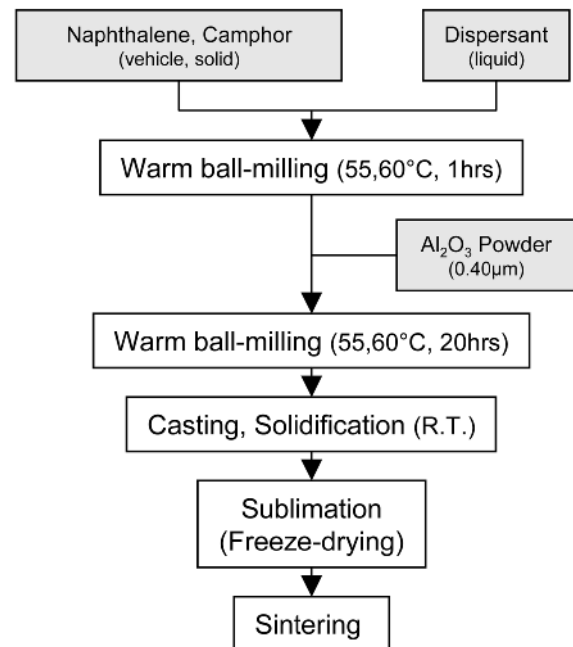

Fig. 2. Schematic chart of the fabrication procedure.

Table II. Example of the Charged Weight for 48 vol% Al_2O_3 Slurries

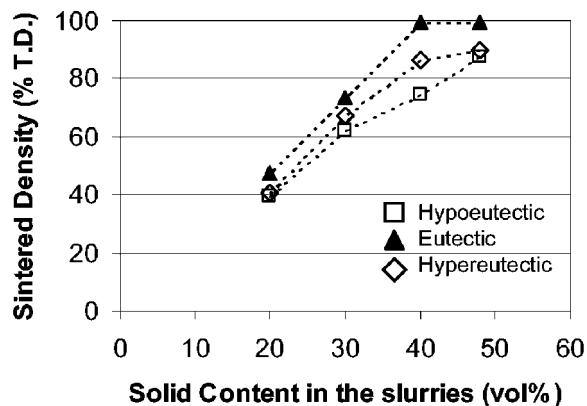|	Naphthalene-to-camphor ratio	Al_2O_3 (g)	Dispersant (g)	Naphthalene (g)	Camphor (g)
Hypoeutectic	56 wt% N–44 wt% C	41.37	1.24	5.60	4.40
Eutectic	40 wt% N–60 wt% C	41.37	1.24	4.00	6.00
Hypereutectic	31 wt% N–69 wt% C	42.18	1.27	3.10	6.90

Fig. 3. Relative density of Al_2O_3 sintered bodies as a function of the charged solid content in the slurries.

the slurries with hypoeutectic, eutectic, and hypereutectic compositions. Almost fully dense bodies (>99.5% of theoretical density (T.D.)) were obtained from the 48 vol% slurry with eutectic composition. It is noted that even 40 vol% slurry with eutectic composition gives sintered bodies with more than 98% T.D. However, at most around 90% T.D. was obtained from 48 vol% slurries, which were practically almost at maximum solid content in this work, with hypo- and hypereutectic compositions.

To examine the cause of the differences in the sintered densities, microstructural observation was conducted for sintered bodies. Figures 4 and 5 summarize microstructures of Al_2O_3 sintered bodies from 48 vol% slurries with hypoeutectic (Figs. 4(a) and 5(a)), eutectic (Figs. 4(b) and 5(b)), and hypereutectic (Figs. 4(c) and 5(c)) compositions. No voids except some small closed pores are observed in the sintered body from the eutectic composition slurry (Figs. 4(b) and 5(b)). This microstructure is almost the same as that of a sintered body by conventional dry pressing (Figs. 4(d) and 5(d)). On the other hand, relatively large uniquely shaped voids were observed in the bodies from off-eutectic (i.e., hypo- and hypereutectic) composition slurries. Long-plate-shaped voids surrounded by almost fully dense regions were observed in the sintered body from the hypoeutectic composition slurry (Figs. 4(a) and 5(a)), and distorted dendrite-shaped voids surrounded by almost fully dense regions were observed in the sintered body from the hypereutectic composition slurry (Figs. 4(c) and 5(c)). It is hence concluded that the reason why an almost fully dense Al_2O_3 sintered body was not obtained from an off-eutectic composition slurry is the formation of large uniquely shaped voids.

To examine the origin of these uniquely shaped voids, microstructural observation of solidified naphthalene–camphor alloys themselves was conducted. Molten liquids of naphthalene–camphor alloys, which had either the same hypoeutectic, eutectic, or hypereutectic composition as Al_2O_3 slurries, were prepared in the same manners as the slurries, then dropped onto a slide glass to solidify, and observed with an optical microscope. Typical solidified microstructures of each composition are shown in Fig. 6.
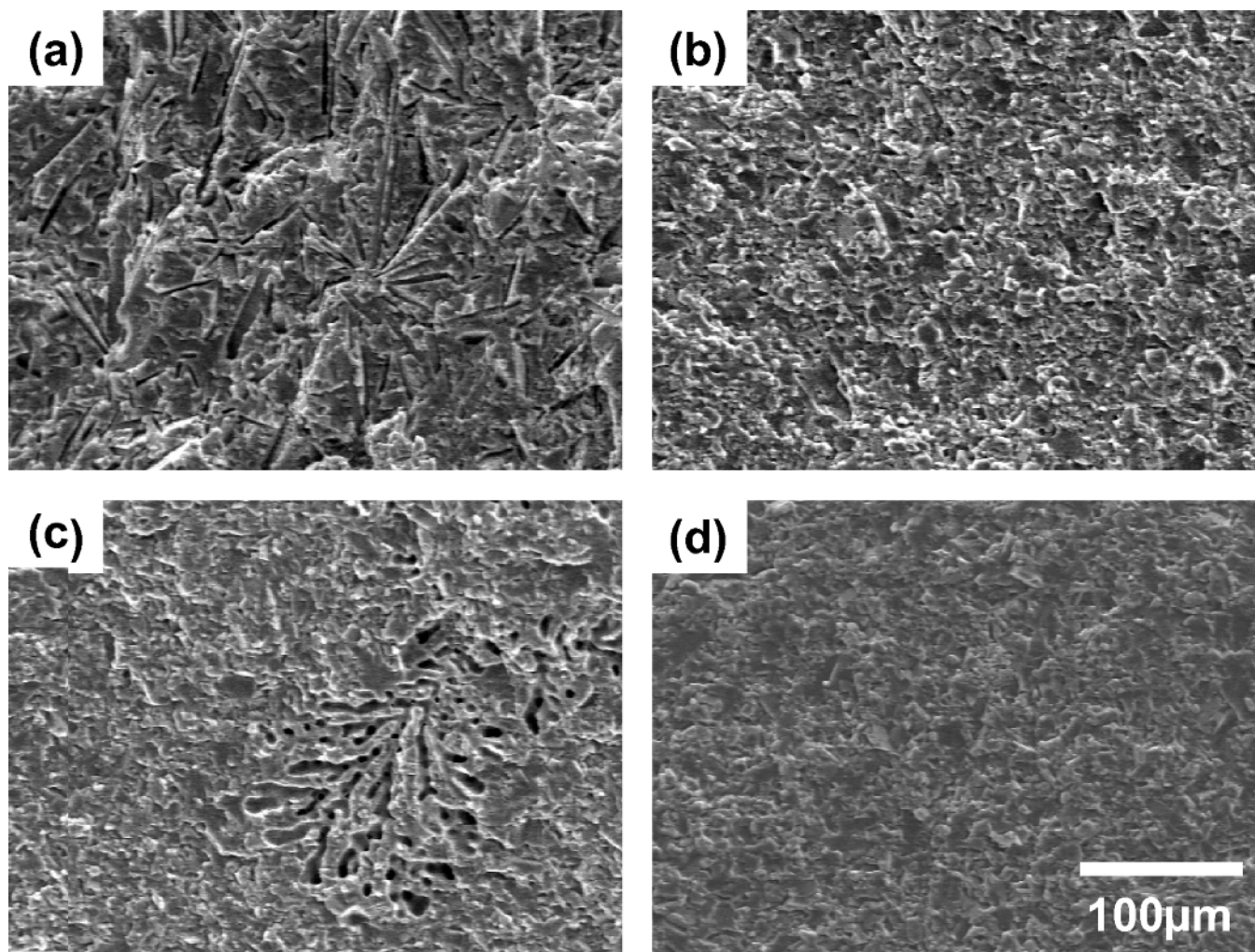

Fig. 4. Fracture surface of sintered bodies from (a) hypoeutectic, (b) eutectic, and (c) hypereutectic composition slurries. Fracture surface of sintered body by (d) uniaxial dry pressing at 200 MPa is also shown as a comparison.
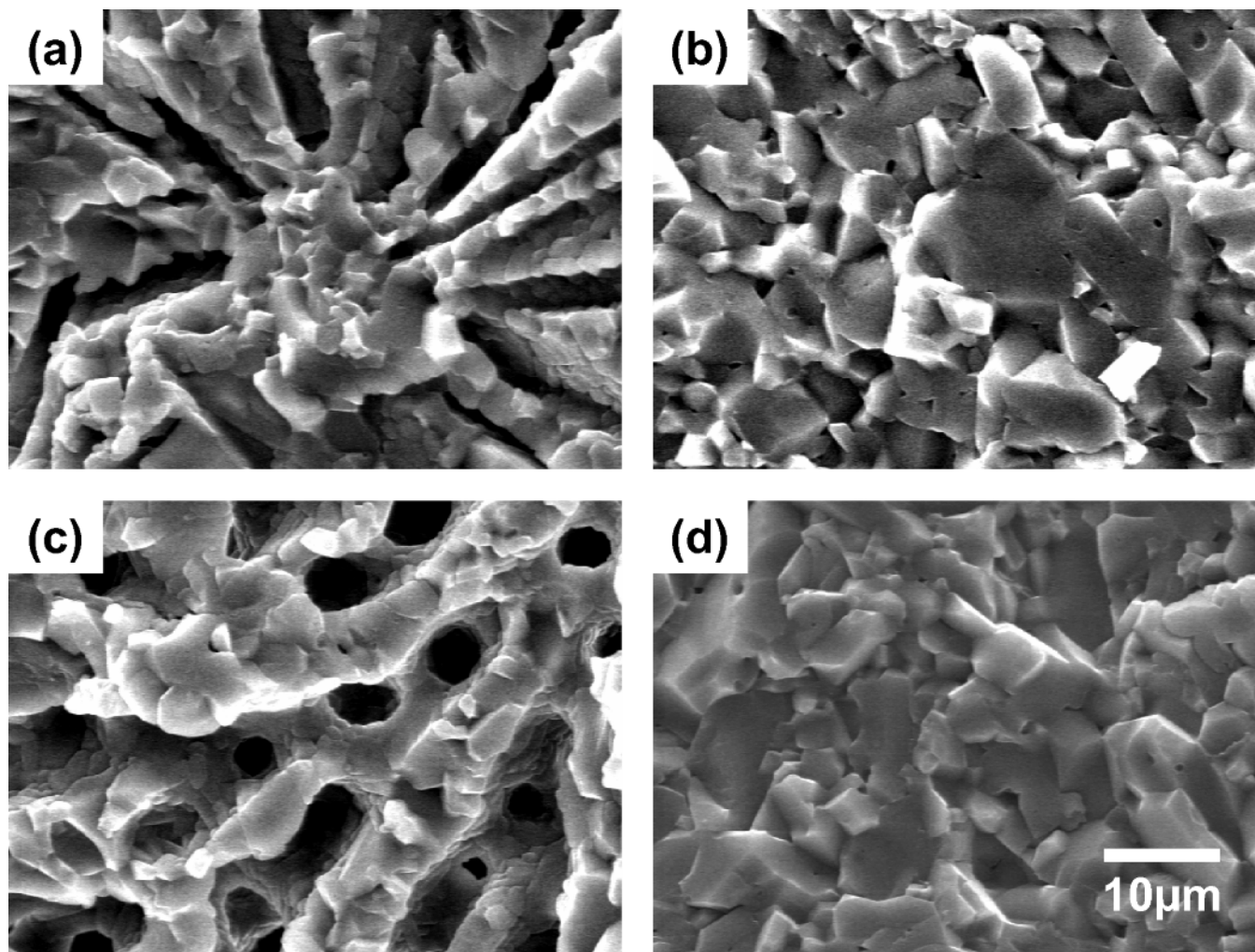
Fig. 5. Fracture surface of sintered bodies from (a) hypoeutectic, (b) eutectic, and (c) hypereutectic composition slurries. Fracture surface of sintered body by (d) uniaxial dry pressing at 200 MPa is also shown as a comparison. Magnification in this figure is higher than that in Fig. 4.

Almost uniform microstructure is observed in the solidified eutectic alloy, as shown in Fig. 6(b). On the other hand, a lot of faceted long plates surrounded by a matrix region are observed in the solidified hypoeutectic alloy, as shown in Fig. 6(a). Precipitates shaped like six-pointed stars are observed also in the solidified hypereutectic alloy, as shown in Fig. 6(c).

According to the naphthalene–camphor phase diagram (Fig. 1), the long-plate-shaped precipitates in the hypoeutectic composition (Fig. 6(a)) and the six-pointed-star-shaped precipitates in the hypereutectic composition (Fig. 6(c)) are considered as pro-eutectic naphthalene-rich phase, α, and pro-eutectic camphor-rich phase, β, respectively. The faceted plate morphology of the pro-eutectic naphthalene-rich phase, which is almost the same as the one in Fig. 6(a), in the naphthalene–camphor system has been observed and well described by many researchers.[16–19] As for the pro-eutectic camphor-rich phase in this system, six-pointed-star-shaped precipitates, which were the same as the ones in Fig. 6(c), were observed by Robinson *et al.*[16] They also observed that the growth of precipitates with initial six-pointed-star shapes tended to be dendritic in the latter stages of precipitation.[16]

As for large voids, it is well known that large voids are formed during freezing because of rejection of suspended particles by large ice crystals, which sometimes exhibit dendritic growth, in the aqueous freeze casting technique.[20–22] It is also known that rejection of ceramic particles by growing crystals occurs also in nonaqueous media during solidification.[23] The authors actually showed that, in an Al_2O_3/molten camphene ($C_{10}H_{16}$) slurry with relatively low solid contents, the suspended particles are rejected by growing camphene dendrites to form large voids, which well

replicate the shape of large camphene dendritic crystals, during freezing.[24]

From the above discussion, it seems reasonable that large uniquely shaped voids in Al_2O_3 sintered bodies from off-eutectic composition slurries are formed by the rejection of suspended particles by growing pro-eutectic crystals. Indeed, the long-plate-shaped voids (Figs. 4(a) and 5(a)) in sintered bodies from hypoeutectic composition slurry well replicate the faceted plate morphology of pro-eutectic naphthalene-rich phase[16–19] (Fig. 6(a)). The dendrite-shaped voids (Figs. 4(c) and 5(c)) in sintered bodies from hypereutectic composition slurry are considered to replicate the dendritic morphology of pro-eutectic camphor-rich crystals,[16] which are in the latter stage of the growth of the six-pointed-star-shaped precipitates (Fig. 6(c)).

Even though there were no pro-eutectic crystals in the eutectic composition slurry, however, large voids could be formed in sintered bodies from the eutectic composition slurry. Since, as described earlier, large voids are often observed[20–22,24] in sintered bodies from one component vehicle slurry which has no pro-eutectic crystals, even non-pro-eutectic crystals could form large voids. To investigate the reason why there are no large voids in the sintered body from the eutectic slurry, further microstructural investigation was conducted for the solidified naphthalene–camphor alloy with the eutectic composition. Optical microscopy with a polarizer revealed that the eutectic has a little disordered lamellar microstructure of the naphthalene-rich and camphor-rich phases, and the lamellar spacing, which should be dependent on the cooling rate,[16] was about 10 μm, as shown in Fig. 7. Thus, in the
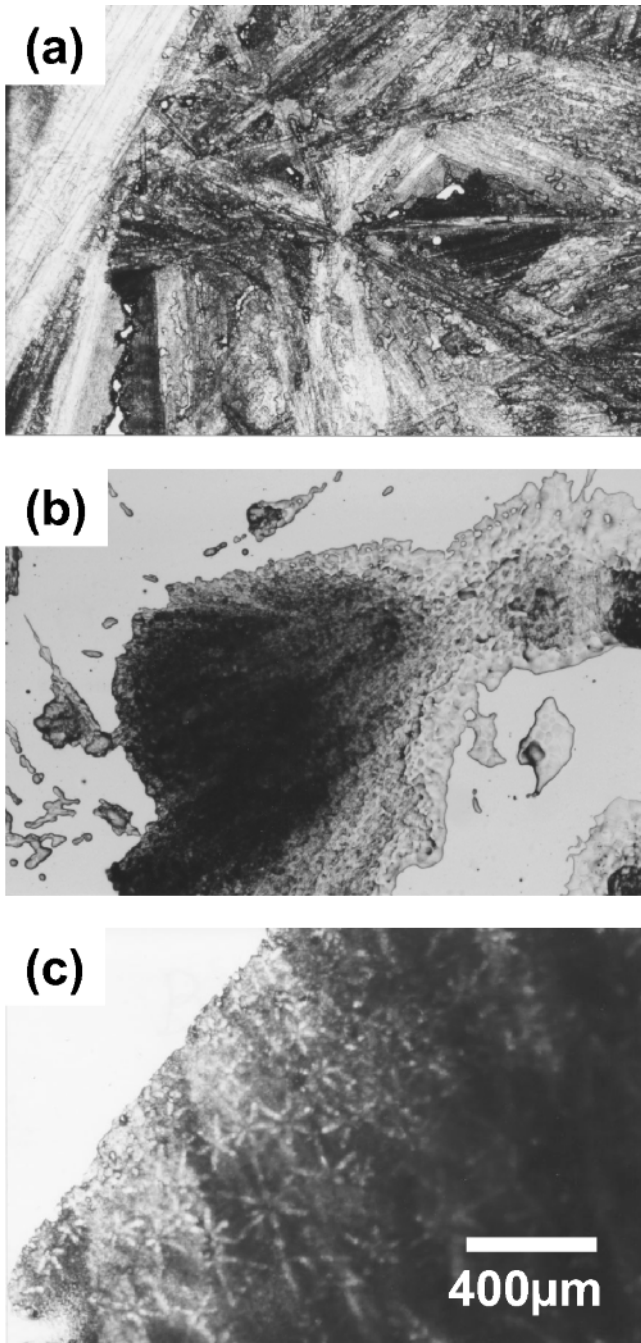
Fig. 6. Typical solidified microstructure of (a) hypoeutectic, (b) eutectic, and (c) hypereutectic alloys in the naphthalene–camphor system.

Fig. 7. Solidified microstructures of naphthalene–camphor alloy with the eutectic composition observed by an optical microscope (a) without and (b) with a polarizer. A distorted lamellar microstructure with a spacing of about 10 μm is observed on the center in (b).

Fig. 8. Schematic drawings of the effect of composition on microstructures in the naphthalene–camphor solidified alloys and resulting sintered bodies. Pro-eutectics in off-eutectic composition result in voids in sintered bodies.

eutectic composition slurry, the formation of fine lamellar microstructure is considered to inhibit particle rejection, resulting in large voids. The effect of vehicle composition (eutectic or off-eutectic) on the microstructure of naphthalene–camphor alloys and final sintered ceramics is schematically summarized in Fig. 8.

In aqueous freeze casting, to avoid the formation of large ice crystals, cryoprotectants[20-22] such as dimethyl sulfoxide, sugar, glycerin, and glycerol are often added to the slurry. These cryoprotectants are considered to bind to water molecules and disrupt the complete crystallization of ice, resulting in a localized amorphous structure, thus reducing the size of growing crystals and inhibiting particle rejection.[22] Formation of fine lamellar microstructure in a solidified slurry with eutectic composition vehicle in this work can be another concept for inhibiting particle rejection in freeze casting technique, especially with sublimable organic vehicles.
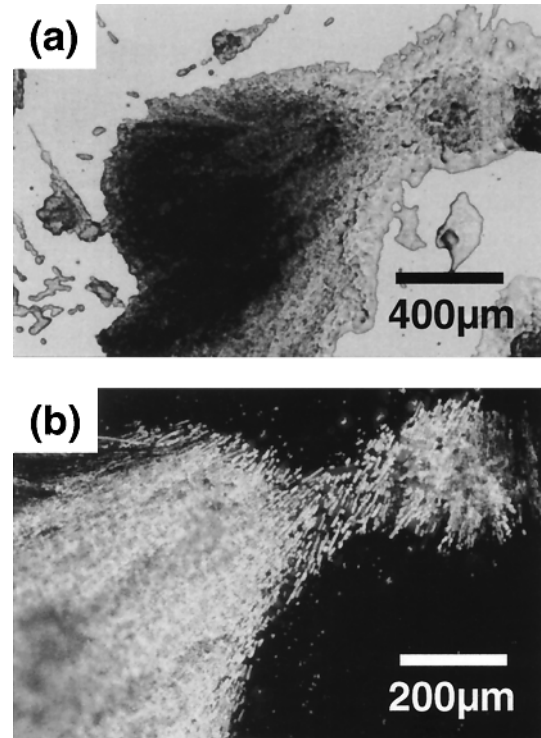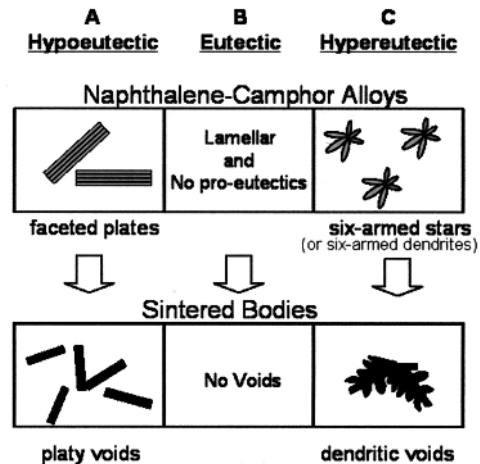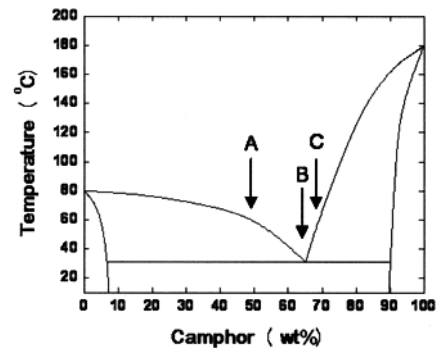
IV. Summary

Freeze casting for Al_2O_3 was accomplished at room temperature with nonaqueous sublimable vehicles in the naphthalene–camphor eutectic system with a eutectic temperature of 31°C. Three kinds of vehicles were prepared: (1) hypoeutectic (naphthalene-rich), (2) eutectic, and (3) hypereutectic (camphor-rich) composition vehicles. An almost fully dense sintered body (>99.5% T.D.) was obtained with the eutectic composition vehicle, whereas at most 90% T.D. was obtained with the off-eutectic (i.e., hypo- or hypereutectic) composition vehicle due to formation of large uniquely shaped voids. Long-plate-shaped voids and distorted dendrite-shaped voids were observed in sintered bodies from hypoeutectic and hypereutectic composition vehicles, respectively. Microstructural observation suggested that growing pro-eutectic crystals, i.e., naphthalene-rich α-phase and camphor-rich β-phase, respectively, rejected the suspended Al_2O_3 particles to form large voids during the solidification (freezing) process. At the eutectic composition vehicle, formation of distorted fine lamellar microstructure and no pro-eutectic crystals were observed. The fine lamellar microstructure is considered to inhibit particle rejection resulting in large voids. Like cryoprotectant addition to the slurry, adopting a eutectic composition vehicle can be another concept for inhibiting particle rejection in freeze casting, especially with sublimable molecular compound vehicles.

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