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Granular transfer molding of multimodal powders

Hyunick Shin, Joosun Kim, Hae-Weon Lee*, Jongho Lee, Sang-Woo Kim, Huesup Song

Nano-Materials Research Center, Korea Institute of Science and Technology, 131 PO Box, Cheongryang, Seoul 136-791, South Korea

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Abstract

Relatively homogeneous green compacts were prepared with the powders of multimodal particle size distribution by granular transfer molding (GTM) using the premixed granules. The homogenous granules were prepared by rapid granule formation by solvent exchange even with multimodal powders. In order to obtain optimum green microstructure, it is necessary to control resin migration and granule deformation with the help of resin solubility and molding temperature. The process mechanism of granular transfer molding could be divided into four steps: granule arrangement under external field, local deformation of granules accompanied by individual particle packing, resin curing in the presence of a liquid vehicle, and liquid removal.

Keywords: A. Shaping; D. Carbides; Multimodal powder; Packing; Granule; Segregation; Solubility

1. Introduction

Due to their excellent properties at elevated temperature, silicon carbide ceramics have been widely used for high temperature applications [1–5]. Among various silicon carbide ceramics, reaction-bonded silicon carbide (RBSC) ceramics have considerable advantages in an economical viewpoint since the costs of production and raw materials are relatively low compared to other ceramic materials [4,6–8]. Above all, the RBSC ceramics have an extraordinary advantage over common ceramic fabrication techniques in that they can be readily fabricated into the near-net-dimension components by infiltrating reactive liquid into porous solid preforms.

Recently, reaction-formed silicon carbide (RFSC) ceramics have been extensively studied to further improve mechanical properties at ambient and elevated temperatures. These were produced by reactive infiltration of silicon melt into carbonaceous porous preform [6–12]. Despite the greatly improved mechanical properties of RFSC ceramics due to lower residual silicon content, the excessive shrinkages associated with resin curing and debinding hamper the fabrication of large pieces of structural components [10,13].

On the other hand, the fabrication of RBSC radiant tubes by loose powder loading and firing approach might be the most economical processing route introduced thus far [4]. However, the RBSC radiant tubes produced by loose powder packing retained a substantial amount of residual silicon in the range 32–50 vol.%. Since the residual silicon content is closely related to the mechanical properties at elevated temperature, the application of those radiant tubes might be limited to relatively lower use temperatures [3,8,14–16].

In our previous study, a continuous reaction infiltration was successfully employed to fabricate a RBSC radiant tube by a double-walled preform method where process shrinkage was reduced to a negligible level in the presence of a network structure of component particles [17,18]. The multimodal powders used in the mixture inevitably resulted in the segregation of component particles at relatively high centrifugal field due to the large difference in size, in addition to resin segregation by capillary flow. However, it is necessary to achieve packing uniformity of the preform in order to take advantage of high packing density of multimodal powders for low residual silicon in RBSC ceramics [19–21].

Therefore, the primary objective of the present study was to investigate the feasibility of transfer molding process using premixed granules composed of multimodal powders in order to obtain improved packing uniformity. Additionally, the packing behavior of

* Corresponding author. Tel.: +82-2-958-5523; fax: +82-2-958-5529.

E-mail address: hwlee@kist.re.kr (H.-W. Lee).

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premixed granules as studied in terms of types of liquid vehicle, molding temperature, and solids loading.

2. Experimental procedures

Starting powders used in this study were three grades of α-SiC powders with mean particle sizes in the range 5–150 μm (GC #100, #400, #2500, Showa Denko, Japan) and two grades of silicon powder with mean particle sizes of 70 and 2000 μm. The polymeric component used in this study as a binder as well as an additional carbon source was phenol resin (KNG 100, Kolon Chemical, Korea). HMT (hexamethylene tetramine, Junsei, Japan) was used as a curing agent and 1-butanol was used as a liquid medium for suspension preparation.

Suspension was prepared in 1-butanol at 76 wt.% of solids loading with 11.4 wt.% of phenol resin addition. The starting silicon carbide powders were composed of 49, 29, and 22 wt.% of 150, 35, and 5 μm powders, respectively. The prepared suspension was added drop-wise into 5 wt.% HMT aqueous solution kept at 85 °C. The drop-wise added suspension was continuously stirred for 2 h at 85 °C in order to facilitate solvent exchange. After cooling to room temperature, the resulting powder granules were separated by filtering and dried at 50 °C for 10 h. The dried granules were physically classified using a sieve and the classified granules in the range 250–500 μm were used for transfer molding and characterization.

Granular transfer molding was carried out at 1500 rpm using an aluminum mold of 65 mm diameter. Granules of 150 g were added into the aluminum mold in the presence of liquid vehicles such as ethanol, butanol, and water, and the mold was kept rotating at 60–110 °C for 1–2 h for partial curing of phenol resin. The molding temperature was measured using an infrared thermometer (THI-500, TASCO, Japan) on the graphite-coated mold surface. Once the transfer molding was complete, the samples were further dried at 70 °C for 10 h in order to completely cure the phenol resin.

The cured samples were heat-treated and carbonized in vacuum at 1200 °C for 1 h. The carbonized samples were characterized using mercury porosimeter (Pore Sizer 9320, Micromeritics, USA) and optical microscope (ICS, Sometech, Korea). True density of the carbonized sample was measured using a helium pycnometer (AccuPyc 1330, Micromeritics, USA).

3. Results and discussion

Fig. 1 shows the polished cross-sections of granules prepared by a liquid condensation process, where a homogeneous suspension in non-aqueous solvent was granulated by adding droplets of suspension into non-solvent liquid medium [22,23]. Despite the multi-modal characteristics of starting silicon carbide powders, the granules were relatively homogeneous in terms of packing uniformity and binder distribution by maintaining the homogeneity of suspension structure into granule structure. Hereafter, the transfer molding using suspensions with dispersed individual particles will be designated powder transfer molding (PTM), while that using granules of premixed particles, granular transfer molding (GTM).

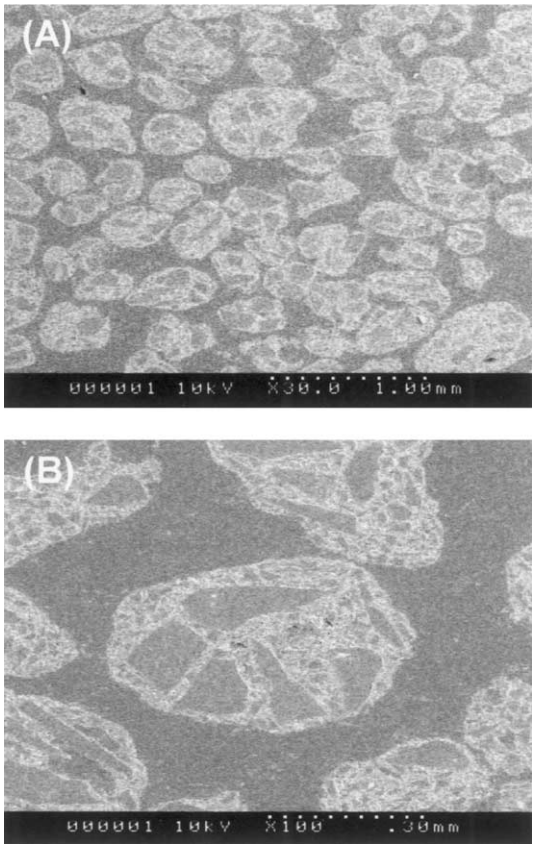

Fig. 1. SEM micrograph of premixed granules: (A) low and (B) high magnifications.

The granular transfer molding requires a proper amount of liquid vehicle for granule flow and mold filling. Mercury porosimetry was used to estimate the required amount of liquid vehicle for granular transfer molding. Fig. 2 shows plots of pore size distribution and cumulative intrusion as a function of pore channel diameter for the premixed granules in the size range 250–500 μm. Even though there exist three peaks in the pore size distribution curve shown in Fig. 2(A), the peak observed at coarser pore diameter is believed to be associated with the pores formed between loosely packed premixed granules. The intergranular porosity estimated from Fig. 2(B) is ~16.5%, while the intragranular porosity is ~7%.

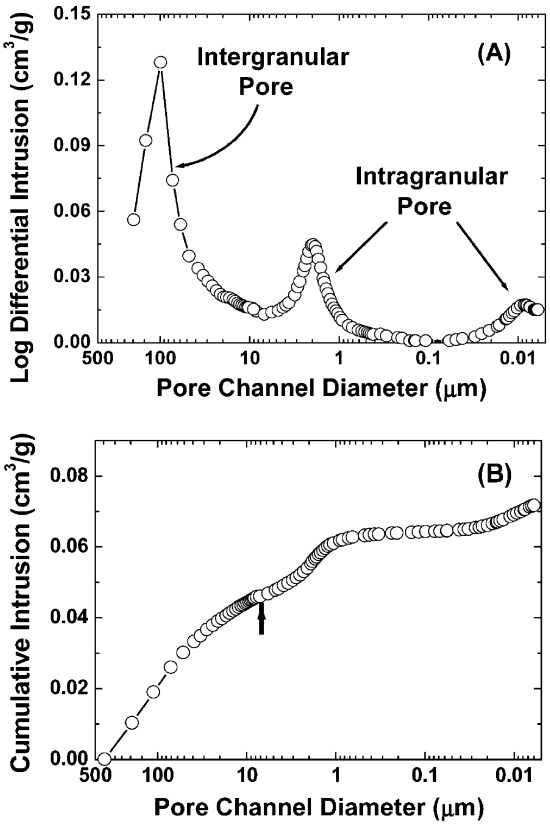

Fig. 2. Plots of the pore characteristics for premixed granules measured by mercury porosimetry: (A) pore size distribution and (B) cumulative intrusion curves.

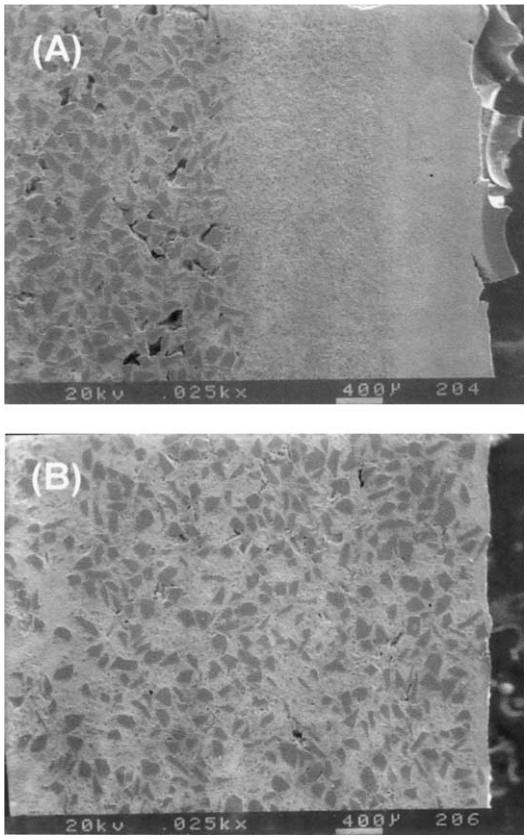

Fig. 3. SEM micrographs of debinded samples prepared by (A) powder transfer molding and (B) granular transfer molding.

Fig. 3 shows a comparison of packing structure for the samples prepared by both PTM and GTM. Although the suspensions with quite high solids loading, e.g. 60 vol.%, were used in PTM in order to prevent segregation of component particles due to size differences, the debinded sample by PTM shown in Fig. 3(A) shows that considerable segregation of component particles took place. It is also evident that there occurred substantial segregation of binder in addition to the particle segregation. The binder segregation is likely to be associated with the liquid migration through the capillaries formed by the component particles.

On the other hand, the sample prepared by GTM in Fig. 3(B) shows considerably reduced surface segregation of component particles as well as binder phases since the granules with quite high packing density allow a very limited deformation and restrict the binder phase to local redistribution. This indicates that, for the powders with multimodal particle size distribution, the transfer molding with controlled granule structure and composition might be beneficial for maintaining packing uniformity and homogeneous binder distribution.

Fig. 4 shows the polished cross sections of debinded samples prepared by GTM using various liquid media including ethanol, 1-butanol and water. All samples were consolidated below the boiling temperatures of the liquid vehicles used. The sample prepared in ethanol shows a relatively homogeneous packing structure of component particles with little surface segregation of resin phase. However, the sample prepared in 1-butanol shows considerably increased thickness of surface segregation layer with increased pore volume in the internal packing layer. Finally, the sample prepared in water shows almost no segregation of resin phase in the surface, but it contains a fairly large number of macropores inside the packing layer.

This can be explained by the fact that the three liquid vehicles used in this study have a different solubility parameter with respect to the phenol resin, as summarized in Table 1 [24]. Since 1-butanol has a very similar solubility parameter and degree of hydrogen bonding to those of phenol resin, it is expected that the phenol resin has the highest miscibility with 1-butanol among the liquid vehicles used in the present study. On the other hand, water is almost completely immiscible with phenol resin so that water is expected to be distributed between the granules without solubility effects. In this case, the granules should be deformed and/or bonded solely by softening of phenol resin at the molding temperature. In this viewpoint, it is apparent that the external pressure applied by centrifugal field was not high enough to deform the granules, resulting in the

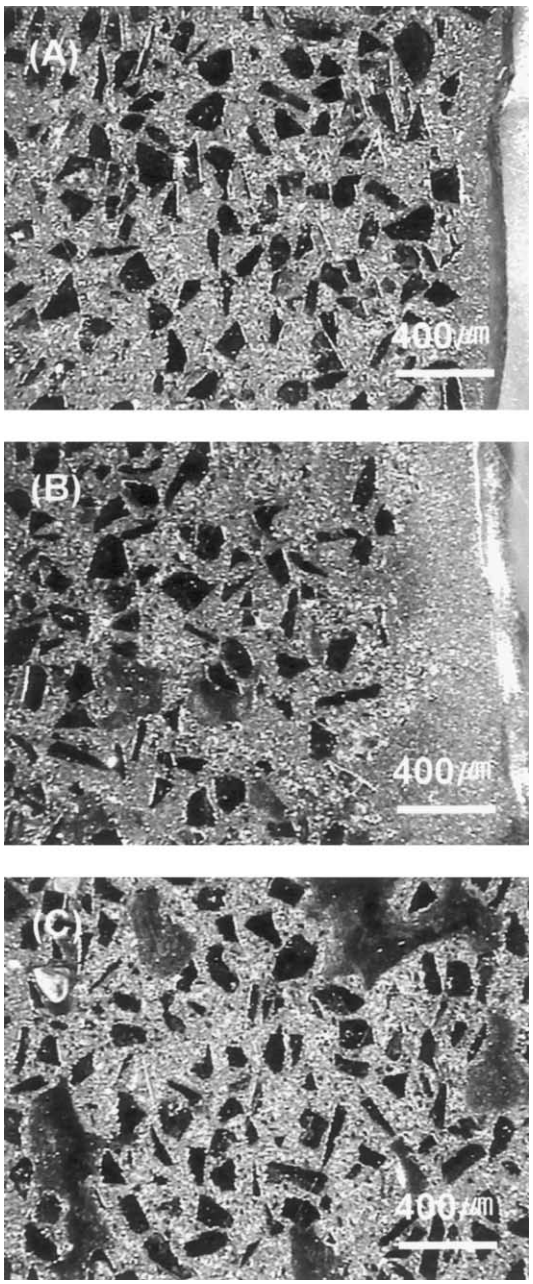

Fig. 4. Optical micrographs of debinded samples prepared by granular transfer molding in various liquid vehicles: (A) ethanol, (B) 1-butanol, and (C) water.

Table 1
Solubility parameter of phenol resin and various liquid vehicles [24]

Component	δ_d[a]	δ_p[b]	δ_h[c]	δ[d]
Phenol	18	5.9	14.9	24.1
1-Butanol	16	5.7	15.8	23.1
Ethanol	15.8	8.8	19.4	26.6
Water	15.5	16.0	42.4	47.9

[a] δ_d: dispersive term.
[b] δ_p: polar term.
[c] δ_h: hydrogen bond term.
[d] δ: total solubility term.

intergranular pores between the under-deformed granules. Among the liquid vehicles investigated, the green compact prepared with ethanol-base mixture showed the most favorable powder packing structure without macropores. The packing behavior of the granules in the various liquid vehicles suggest that the solubility of phenol resin in the granules plays a predominating role in controlling green microstructure of GTM compacts.

Although the solubility of phenol resin in the liquid medium clearly plays an important role in terms of the packing homogeneity of component particles and the presence of residual macro-pores, it should be pointed out that the solubility of phenol resin is closely related to its surface segregation through capillary migration, as shown in Fig. 4. The samples prepared in 1-butanol had a surface segregation layer of phenol resin of about three times as thick as in ethanol, reflecting that the solubility of liquid vehicle had significant effects on both granule deformation and resin segregation.

Fig. 5 shows mercury intrusion curves for the samples prepared by granular transfer molding in various liquid vehicles. The porosity values calculated using true density measured by helium pycnometer, e.g. 3.09 g/cm^3, were 29.8, 23.6, and 27.0% for 1-butanol, ethanol, and water, respectively. This is consistent with the microstructure observed in debinded samples in Fig. 4. Despite finer pore size characteristics, the sample prepared in high solubility 1-butanol shows considerably higher porosity which could be attributed to the highest degree of component segregation, particularly phenol resin. In contrast, the sample prepared in water shows intrusion curve of bimodal pore size distribution, which might be caused by relatively fast curing without phenol dissolution. The improved pore characteristics can be found in the sample prepared in ethanol with higher packing density and uniform pore size.

Essentially, the packing behavior in the GTM process could be divided into three steps: spatial rearrangement of granules, local deformation of granules with resin

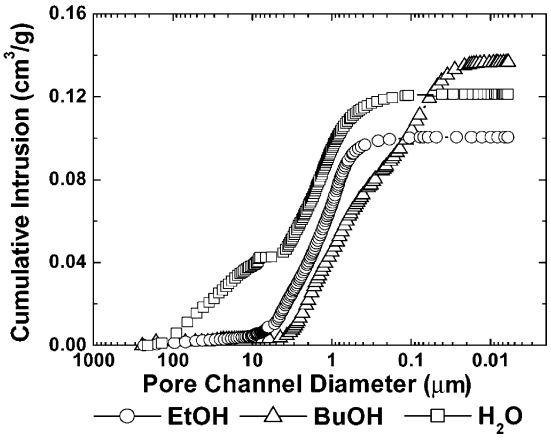

Fig. 5. Plots of the mercury intrusion curves for the samples prepared in various liquid vehicles.

dissolution, and resin curing. With respect to resin curing, the molding temperature should be optimized carefully since the temperature affects the kinetics of resin curing as well as solubility itself. If the molding temperature is too high, the surface segregation tends to increase due to the enhanced solubility. On the contrary, if the molding temperature is too low, the resulting compact can not maintain structural integrity due to insufficient resin curing. Therefore, it can be suggested that the GTM process has a competitive nature between granule deformation (particle packing) and resin curing.

Fig. 6 shows optical micrographs of samples prepared at 60 and 70 °C using ethanol-base mixtures containing premixed granules. As expected, the sample prepared at 60 °C had a relatively high volume fraction of macropores resulting from limited local deformation of premixed granules. On the other hand, the sample prepared at 70 °C revealed fairly homogeneous spatial distribution of component particles in the absence of macropores. This indicates that controlling curing rate might be another important parameter to obtain a homogeneous powder packing structure without resin segregation.

This was confirmed by the pore characteristics measured by mercury intrusion into debinded samples, as shown in Fig. 7. As expected, the porosity values calculated from mercury intrusion were ~30.9 and 23.6% for the samples prepared at 60 and 70 °C, respectively. The difference in porosity between those samples should be related to the variation granule deformation and curing behavior at the different temperatures.

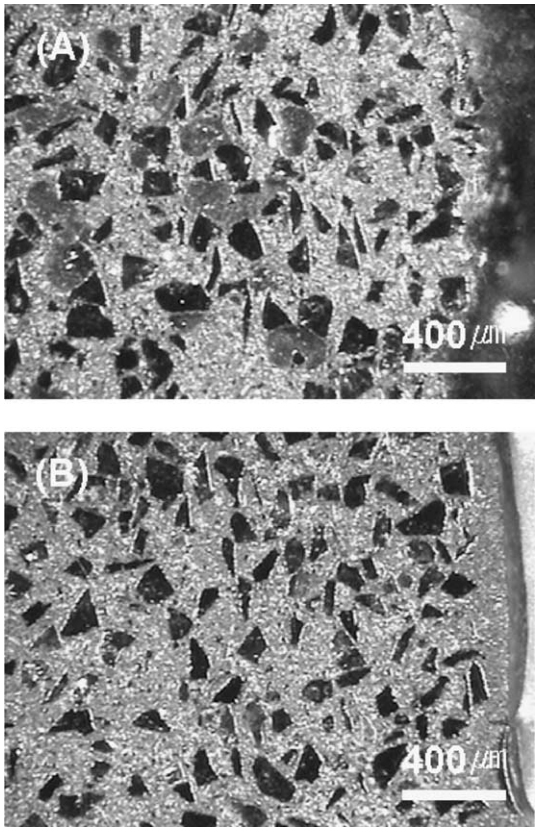

Fig. 6. Optical micrographs of debinded samples prepared by granular transfer molding at different molding temperatures: (A) 60 and (B) 70 °C.

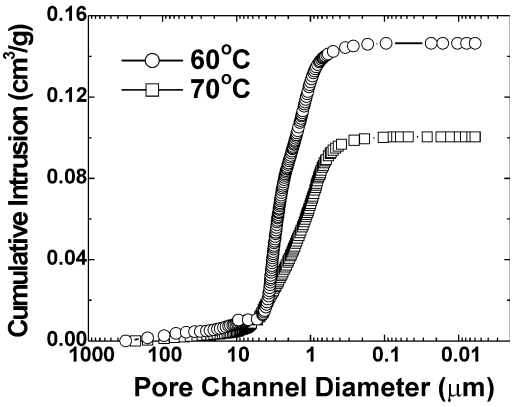

Fig. 7. Plots of the mercury intrusion curves for the samples prepared at different molding temperatures of 60 and 70 °C.

Fig. 8 shows the micrographs of debinded samples prepared by granular transfer molding using the ethanol-base mixtures of 66 and 75 vol.% solids loading. The sample prepared with 66 vol.% mixture shows relatively homogneous packing without macropores, while that with 75 vol.% does have a considerable

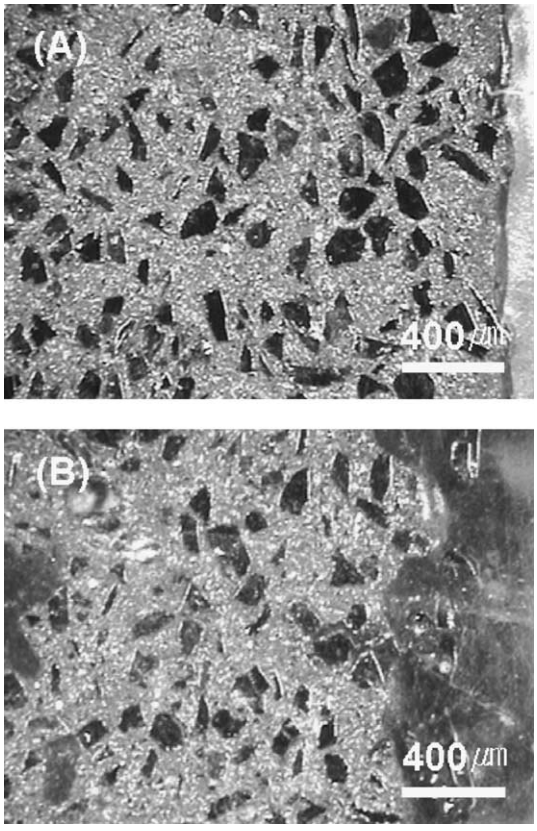

Fig. 8. Optical micrographs of debinded samples prepared by granular transfer molding at different solids loading: (A) 66 and (B) 75 vol.%.

amount of macropores. The residual pores in Fig. 8(B) is believed to arise from the premature curing and limited rearrangement of premixed granules due to insufficient liquid vehicle. This indicates that there is an optimum amount of liquid vehicle required to properly control both granule rearrangement and curing rate. Assuming that the interparticle pores are readily filled with the liquid vehicle and the liquid vehicle in the interparticle pores is immobilized, the effective solids loadings of the mixtures used for the samples in Fig. 8(A) and (B) are approximately 69 and 79 vol.%, respectively. Therefore, it can be suggested that the solids loading of the mixture should be properly adjusted based on the granule characteristics in order to obtain homogeneous packing structure without defects.

Fig. 9 shows SEM micrograph for the RBSC samples prepared by granular transfer molding in ethanol at 70 °C and reaction-infiltrated at 1500 °C in vacuum for 1 h. The sample is nearly fully infiltrated and the component silicon carbide particles show fairly homogeneous spatial distribution throughout samples. This illustrates that granular transfer molding can be an alternative method to apply for the forming process of multimodal powders.

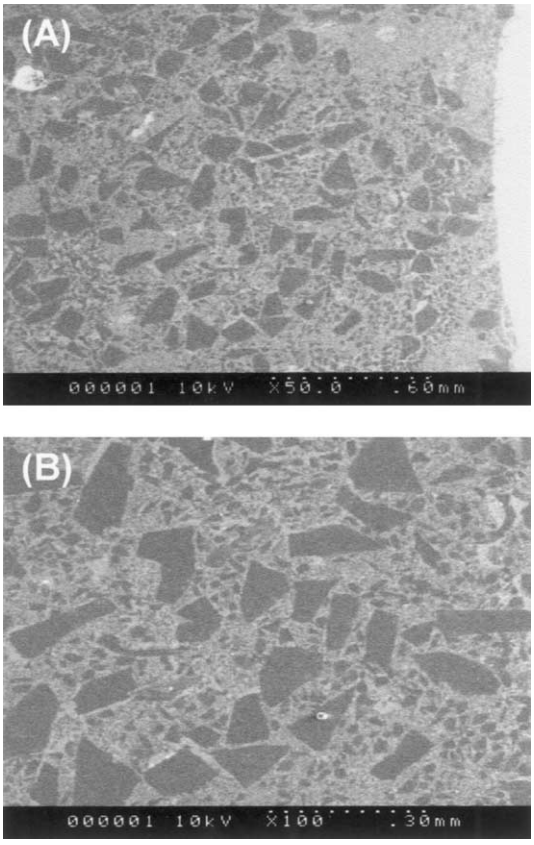

Fig 9. SEM micrographs of RBSC samples using the preform prepared by granular transfer molding in ethanol at 70 °C: (A) low and (B) high magnifications.

4. Summary

Relatively homogeneous green compacts were prepared with the powders of multimodal particle size distribution by granular transfer molding (GTM) using the premixed granules. Attempts were made to optimize the processing parameters such as liquid solubility, liquid amount and molding temperature. Optimum green microstructure was obtained by transfer-molding the premixed granules at 70 °C in the presence of ~30 vol.% ethanol as the liquid vehicle. The liquid solubility is important for controlling proper granule deformation as well as resin migration, while molding temperature plays a significant role in controlling macro-porosity. The macro-pores originated from either insufficient deformation of the premixed granules or entrapped vapor. The process mechanism in granular transfer molding could be divided into four steps: granule arrangement, local deformation of granules along with particle packing, resin curing and liquid removal. Consequently, a novel process called granular transfer molding might provide a forming route for the powders of multimodal particle size distribution in a wet state.

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