

Research Article

Microstructure and Glass Phase of Inorganic Binder Coated on Mold for Thin Casting

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A new dual dipping process has been introduced for the increase in the fracture strength of casting mold through the effective glassification of inorganic binder precursors. Two different dipping processes have been employed to investigate the reactivity of the precursors. Process I is that the substrate was coated with a sodium oxide (Na_2O) precursor through dipping in the solution, and then a silicon dioxide (SiO_2) precursor was coated onto the substrate coated with the Na_2O precursor. Process II is the inverse coating sequence for process I. In the case of the mold prepared by process I, the glass phase converted from the precursors is uniformly observed at the surface of the particle and the interface between particles, compared with that by process II, inducing that the fracture strength of the mold prepared by process I is significantly improved. In addition, when the PDMS without a sol-gel reaction was used as the SiO_2 precursor, especially in process II, the glass phase is not absolutely observed at the surface of the particle owing to the evaporation of PDMS and Na ion during the heat treatment, resulting in the collapse of the mold sample after the heat treatment.

1. Introduction

Recently, the convert mold process has been introduced to fabricate molds in a thin casting [1, 2]. The convert mold process has many advantages, such as high strength, excellent collapse, easy processability, and high thermal stability, making it useful in fabricating components of automobile and aircraft. Typically, the convert mold process is divided into five main processes: (1) fabricating the starting mold coated with an organic binder, (2) dipping the coated mold into a slurry containing inorganic binder precursors, (3) 1st drying for 1 h at 80°C, (4) 2nd drying for 1 h at 200°C, and (5) heat treatment for 1 h at 1000°C, resulting in the conversion of the organic binder-coated mold to the inorganic binder-coated mold [3, 4]. The hydrolysis and condensation reactions (generally called a sol-gel reaction) and glassification take place during the above (3 and 4) and (5) processes, respectively [5–7]. The

mechanical and thermal properties of the mold are induced from the glass phase generated during the heat treatment process, even though the organic binder is decomposed after the heat treatment. Therefore, the generated glass phase must be homogeneously formed on the surfaces of starting particles in the mold as well the conversion efficiency of inorganic binder precursors into the glass phase should be increased, which are related to the reactivity between precursors. Our early work has researched about the new inorganic precursors without the sol-gel reaction instead of the inorganic binder used in the conventional convert mold process, showing a higher glassification efficiency of inorganic binder precursors and a better fracture strength. In addition, the morphology and structure of inorganic binder obtained after the dry and heat treatment processes were investigated in detail [8, 9]. However, the previous works were related to the new precursors for the increase in the strength of the mold.

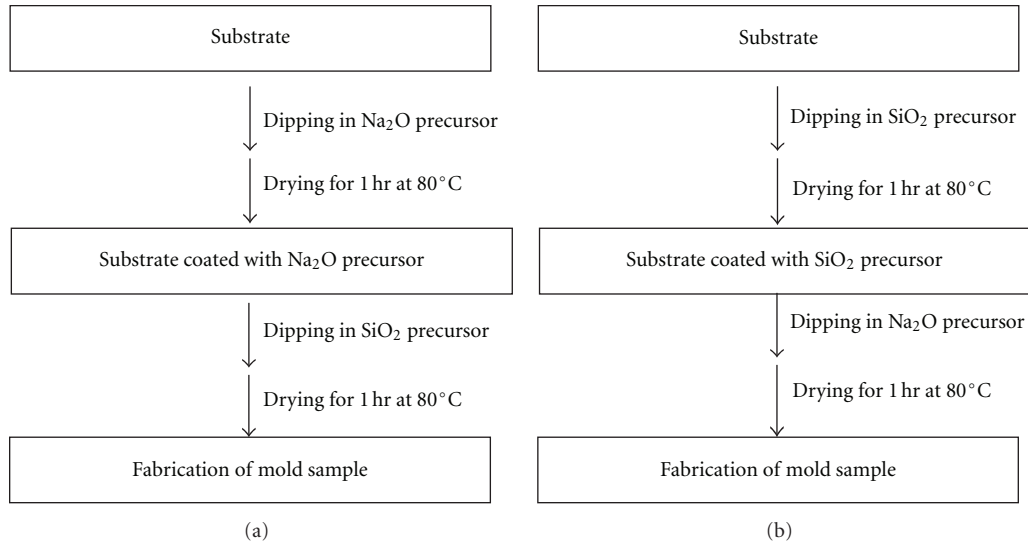


FIGURE 1: Schematic diagram for fabricating mold samples through the new dual dipping process: (a) process I and (b) process II.

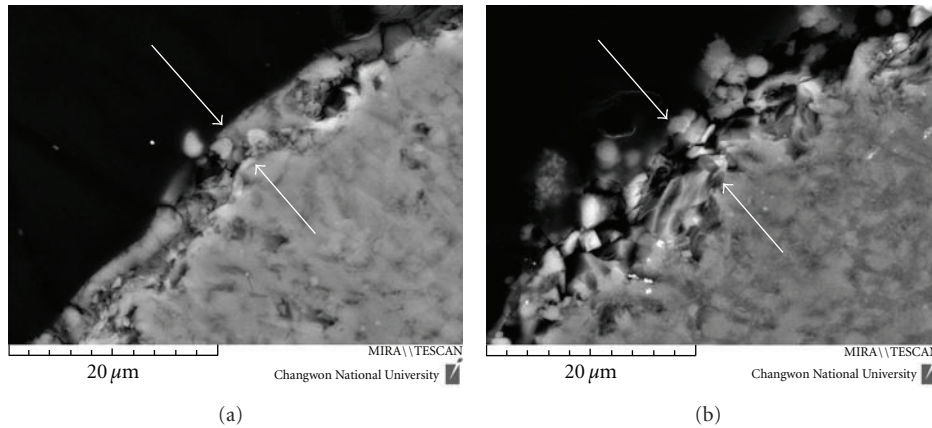


FIGURE 2: SEM morphologies of particle surfaces in mold samples prepared by (a) process I and (b) process II before the heat treatment. TEOS was used as the SiO_2 precursor. Arrows indicate the coated layers in each particle.

For that reason, in this work, a new dipping process has been introduced for inducing the uniform coating of glass phase and improving the conversion efficiency of inorganic binder precursors into the glass phase, leading to the optimum fracture strength of the mold for the thin casting. The inorganic binder system consisted of a mixture of alkyl silicate (or siloxane compound) and sodium alkoxide used as the silicon dioxide (SiO_2) and sodium oxide (Na_2O) precursors, respectively. Respective precursors were independently coated on the particles of the mold through the continuous dipping process, called a dual dipping process, compared with the convention process dipped into a mixture with two precursors at a time. The properties of mold samples prepared by the dual dipping process were measured using various analytical techniques. The influences of precursor species and dipping sequence in the dual dipping process on fracture strength have been investigated and discussed based on the microstructures observed before and after the heat treatment.

2. Experimental Procedure

Composite binder systems for fabricating mold samples through the dual dipping process were prepared using tetraethyl orthosilicate (TEOS, Sigma-Aldrich Korea, Yongin, Korea) of silicate type or poly(dimethyl siloxane) (PDMS, bp 160°C , Sigma-Aldrich Korea, Yongin, Korea) of siloxane type used as a SiO_2 precursor, and sodium methoxide (NaOMe, Sigma-Aldrich Korea, Yongin, Korea) used as an Na_2O precursor. The size of a substrate prepared with the bead composed of SiO_2 and Al_2O_3 was $10 \times 10 \times 50$ mm, which was coated with an organic binder of phenol resin. In this work, two different dual dipping processes were employed for preparing mold samples, as shown in Figure 1. In the first process, the substrate was coated with the Na_2O precursor, and then the treated substrate was coated with the SiO_2 precursor, which is process I. In the second process, the coating sequence of process I was inverted, which is process II. The mold samples coated with the precursors were dried

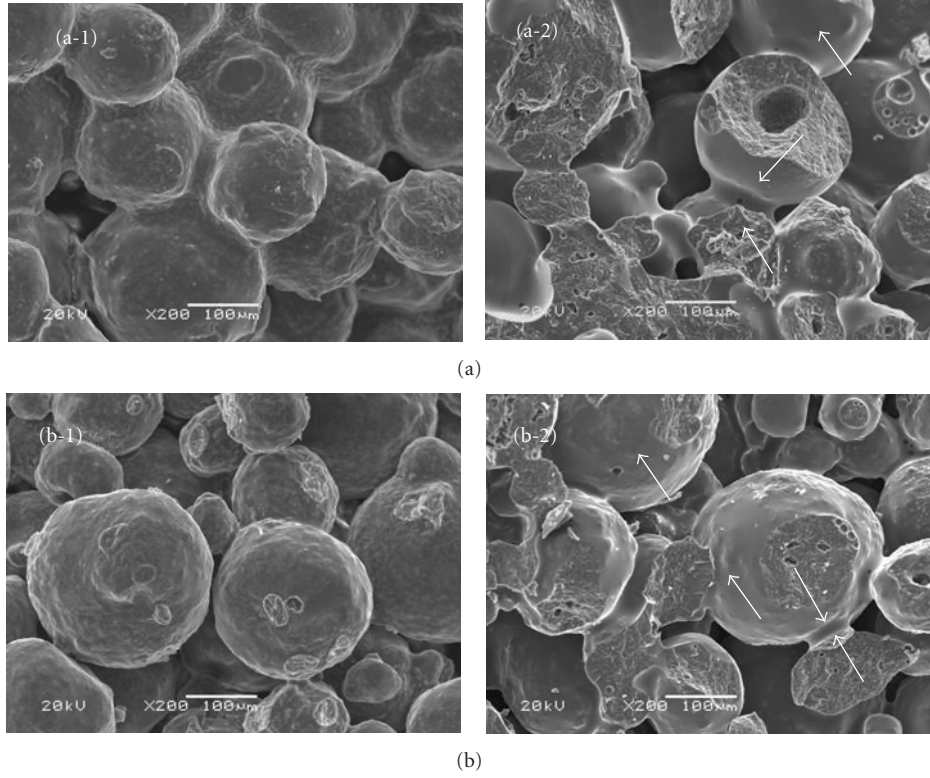


FIGURE 3: SEM morphologies on the fracture surfaces of mold samples through process I as a function of SiO_2 precursor: (a) TEOS and (b) PDMS. Each number indicates SEM morphologies before and after the heat treatment, respectively. Arrows indicate the glass phase formed in mold samples.

TABLE 1: Basic formulations and experimental ranges to prepare mold samples through the new dual dipping process.

Run number	SiO_2 precursor	Na_2O precursor	Process	Condition of heat treatment
Run-1	TEOS		Process I	1000°C for 1 h
Run-2	PDMS	NaOMe		
Run-3	TEOS		Process II	
Run-4	PDMS			

at 80°C for 1 h after each coating or dipping process, and then heat-treated at 1000°C for 1 h. The molten metal based on iron (Fe) was poured into the real mold prepared through process I with TEOS as the SiO_2 precursor for thin casting. Basic formulations and experimental ranges for preparing the mold through the dual dipping process are shown in Table 1.

The surface morphology and microstructure before and after the heat treatment were observed using a scanning electron microscope (SEM, JEOL Model JSM-5610, Tokyo, Japan). The fracture strength of mold samples after the heat treatment was measured using a universal testing machine (UTM, Instron 5566, Instron Corp., Norwood, MA, USA) in the bending mode at a rate of 0.5 mm min⁻¹. Tests were carried out at room temperature, and five runs were performed to determine the standard deviation of the

strength. The support spans of the low and upper noses were 2.5 cm and 1.0 cm, respectively.

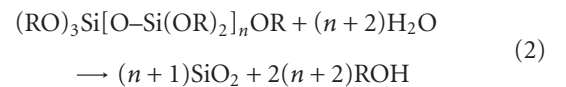
3. Results and Discussion

The reaction mechanism of precursor materials is divided into hydrolysis reaction, sol-gel reaction, and heat-treatment stages [3, 4], as shown in the following reactions.

Hydrolysis reaction:

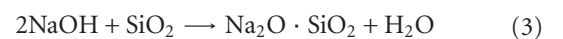


Sol-gel reaction:



where NaOR, ROH, NaOH, $(\text{RO})_3\text{Si}[\text{O}-\text{Si}(\text{OR})_2]_n\text{OR}$, and SiO_2 denote sodium alkoxide, an alcohol, sodium hydroxide, alkyl silicate, and silicon dioxide (silica), respectively [5, 10]. NaOR is hydrolyzed to form NaOH (by (1)), and alkyl silicate is hydrolyzed to form silica and alcohol (by (2)).

Heat-treatment reaction:



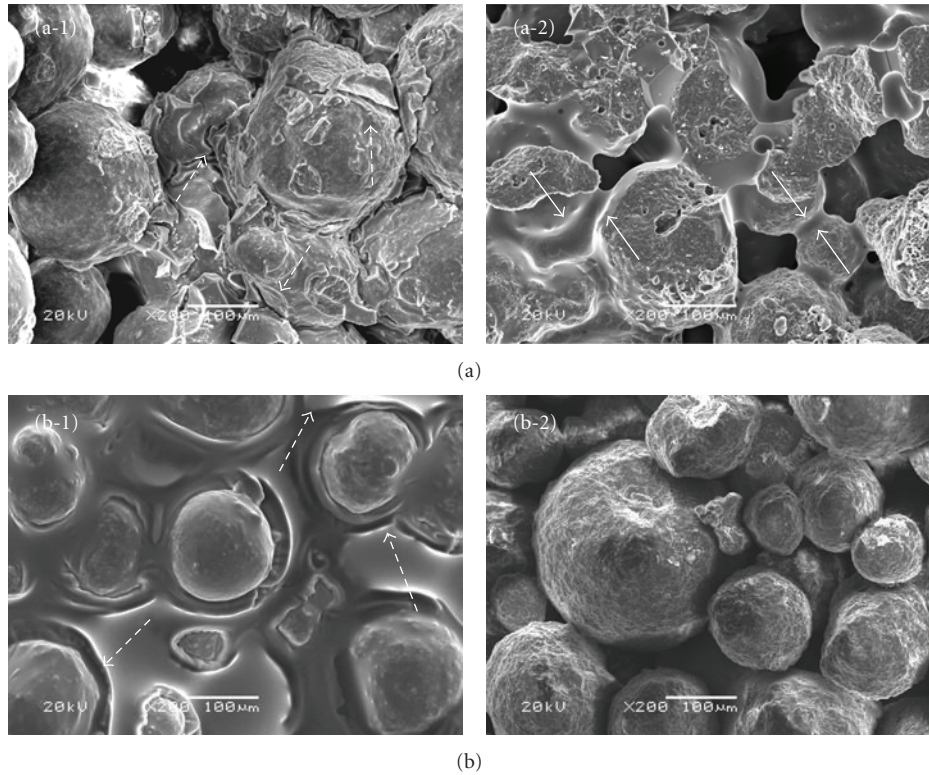


FIGURE 4: SEM morphologies on the fracture surfaces of mold samples through process II as a function of SiO_2 precursor: (a) TEOS and (b) PDMS. Each number indicates SEM morphologies before and after the heat treatment, respectively. Dotted and solid arrows indicate the crack created (series-1) and glass phase formed (series-2) in mold samples, respectively.

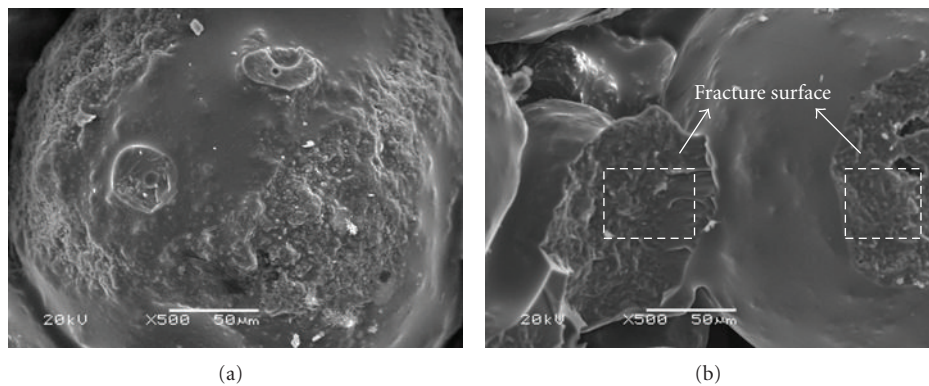


FIGURE 5: SEM morphologies of particle surfaces in mold samples prepared by (a) conventional process and (b) process I with TEOS as the SiO_2 precursor after the heat treatment.

The glass phase of sodium silicate ($\text{Na}_2\text{O}\cdot\text{SiO}_2$) is produced by the reaction between sodium hydroxide and silica at a temperature of about 1000°C [11], which can give a certain strength to the mold. Therefore, the inorganic precursors should be homogeneously coated on the surfaces of starting particles and the conversion efficiency of the precursors coated on the substrate (starting particles) should be increased to improve the fracture strength.

Typical cross-sectional morphologies of particles in mold samples prepared by the dual dipping process used TEOS as

the SiO_2 precursor before the heat treatment are presented in Figure 2. The NaOH generated by the hydrolysis reaction of NaOMe has a particle layer with a polygonal shape, while the SiO_2 by the sol-gel reaction of TEOS shows a layer with a continuous solid state on the surface of particle. The layer with a mixture of SiO_2 and NaOH phases observed in the SEM image of the particle surface prepared through process I (Figure 2(a)) is due to the permeation of SiO_2 precursor between the generated NaOH particles. However, in the case of Figure 2(b), two layers with SiO_2 and NaOH

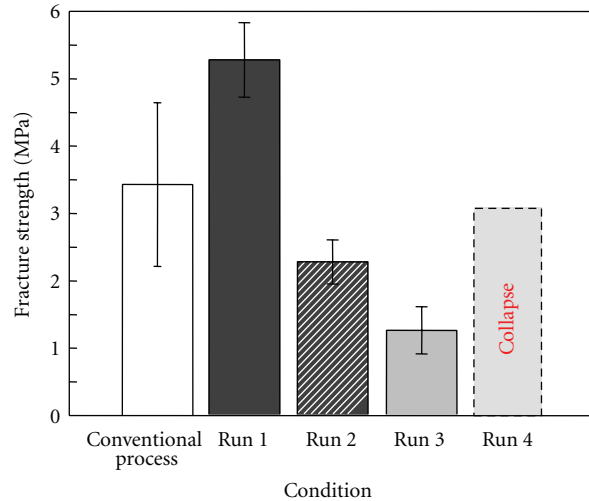


FIGURE 6: Fracture strength of mold samples after the heat treatment as functions of process and SiO₂ precursor.

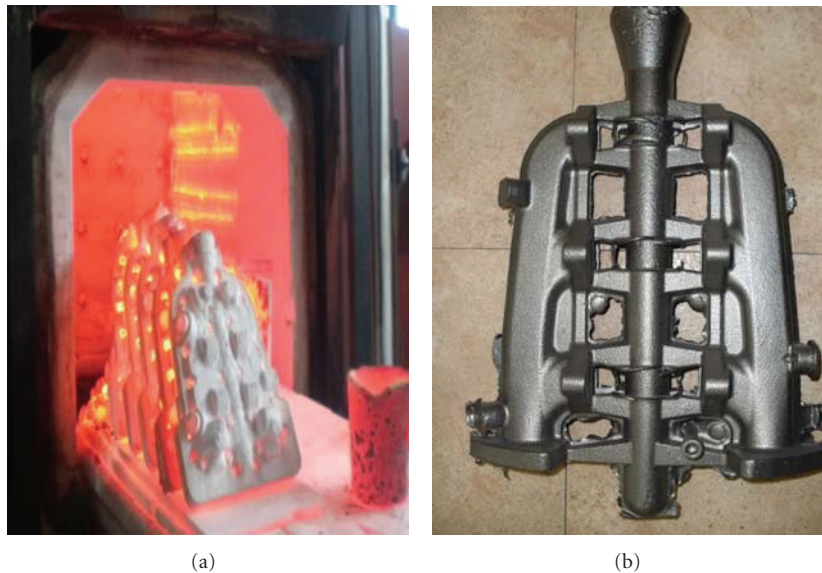


FIGURE 7: Photographs of real mold through process I with TEOS as the SiO₂ precursor after the heat treatment at 950°C and fabricated product: (a) real mold and (b) casted product.

phases are independently formed on the surface of particle. This is because the continuous glass phase of SiO₂ restricts the infiltration of Na₂O precursor. Therefore, the layer formed by process I shows thinner thickness than that by process II. In process I, the mixture phases of SiO₂ and NaOH are converted into the glass phase of Na₂O·SiO₂ prior to the evaporation of Na ion decomposed from NaOH during the heat treatment, whereas in process II, NaOH existed at the outside of the layer is easily degraded and partially evaporated in the heat treatment. Therefore, the layer prepared by process I would be mainly composed of Na₂O·SiO₂, while in process II the layer would have the mixture composition of Na₂O·SiO₂ and SiO₂. In addition, the inorganic precursors in process II have the lower

conversion efficiency into the glass phase than those in process I owing to the easy evaporation of Na ion used to decrease the formation temperature of glass phase. It could be expected that the mold prepared through process I has a higher fracture strength than that prepared by process II.

The morphologies on the fracture surfaces of mold samples prepared through process I as a function of SiO₂ precursor are shown in Figure 3. The surfaces of particles coated with the precursors are changed from rough to smooth during the heat treatment, caused by the generation of glass phase. In the case of PDMS used as the SiO₂ precursor (Figure 3(b)), the glass phase is not fully developed at the interface and/or on the surface of particles. PDMS without the sol-gel reaction remains as a liquid phase and

is easily evaporated during the heat treatment. However, TEOS is already converted into solid-phase silica before the heat treatment. Therefore, the fracture strength of samples prepared with PDMS could be significantly decreased, compared with that with TEOS. Typical SEM morphologies on the fracture surfaces of mold samples prepared by process II before and after the heat treatment are shown in Figure 4 as a function of SiO₂ precursor. In process II, cracks are formed at the interface between particles and on the surface of particles before the heat treatment, denoted by the dotted arrow, whereas these cracks are not observed in process I (Figure 3). This is because the evaporation of alcohol used as the solvent of NaOMe. In process I, the evaporation of Na ion is disturbed by the layer of SiO₂ precursor, whereas Na ion can be freely evaporated in process II, as pointed out in Figure 2. It is verified that the Na strongly affects the generation of glass phase, causing the higher strength in the mold prepared by process I than process II. In addition, in Figure 4(b-2), the glass phase is not presented at the interface and on the surface after the heat treatment, arising from the nonformation of glass phase owing to the easy evaporation of Na ion and PDMS existed as liquid phase during the heat treatment. Figure 5 is the SEM images of particle surfaces in the mold samples prepared by the conventional process and process I using TEOS as the SiO₂ precursor. In Figure 5(b), the glass phase is homogeneous and uniform formed on the surface of particle. However, in Figure 5(a), the glass phase is locally and partially seen on the surface of particle.

The fracture strength of mold samples with the different processes and SiO₂ precursors was measured at room temperature, and the results are shown in Figure 6. In general, the fracture strengths of mold samples prepared by process I (Runs 1 and 2) represent higher values than that by process II (Runs 3) due to the high reactivity between precursors, already mentioned at the results of SEM morphology. The mold treated by PDMS without the sol-gel reaction, especially in process II, absolutely collapsed owing to the deterioration in the formation of glass phase by the evaporation of Na ion and PDMS. In addition, the fracture strength through Run 1 is significantly enhanced, compared with the conventional binder process, caused by the enhancement of conversion efficiency and by the homogeneous formation of glass phase through the dual dipping process. It indicates that the mold for thin casting with reasonable mechanical properties could be fabricated by the new dual dipping process using inorganic binder precursors, inducing the reduction of product price. In addition, the dipping sequence in the dual dipping process is an essential point for increasing the efficiency and homogeneity of glassification and the fracture strength in the mold. Figure 7 shows a photograph of the real mold prepared through process I with TEOS as the SiO₂ precursor after the heat treatment at 950°C for and the product fabricated by thin casting. The real mold prepared by the dual dipping process is perfectly produced and the casted product shows clean surface without defects such as dross, nonmetallic inclusions, and crack. Consequently, the new dual dipping process can be applied for preparing the mold for thin casting having high thermomechanical properties.

4. Conclusions

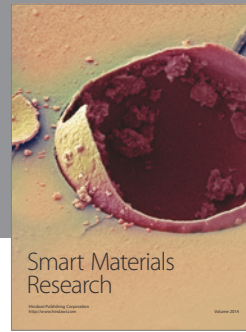
A new dual dipping process has been developed for the homogeneous formation of the glass phase on the surface of particles and at the interface between particles in the mold and to increase the reactivity between precursors, leading to the enhancement in the fracture strength of the mold. The glass phase is well and uniformly formed both at the interface and on the surface of particles in the mold prepared by process I, compared with that by process II. This is because the evaporation of Na ion generated by decomposition of NaOH is interrupted by the layers of SiO₂ precursor in process I, while Na ion existed at the outside of particle surface is easily and partially evaporated in process II. In addition, when PDMS is used as the SiO₂ precursor, the glass phase is partially or not absolutely formed in the mold, because PDMS existed as liquid phase without the sol-gel reaction after the dry process is deformed before the generation of glass phase during the heat treatment.

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