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Powder preparation for a shell mold using a new coating process

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Abstract

A new coating process in the powder preparation for a shell mold has been developed to increase the fracture strength of the shell mold. It is due to the homogeneous formation of a glass phase on the starting particles and the increase in the glassification efficiency by the reduction in the loss of inorganic precursors. The inorganic binder system used for the new coating process is composed of tetraethyl orthosilicate (TEOS) and sodium methoxide (NaOMe) as the silica (SiO_2) and sodium oxide (Na_2O) precursors, respectively. Three different coating processes are employed for the powder preparation with a high glassification efficiency. In process I, the starting particles are coated with NaOMe, and then TEOS are coated on the particles treated with NaOMe. Process II is the reverse sequence of process I. Process III involves coating of the particles with a mixture of TEOS and NaOMe. The particles coated with an individual or mixture precursor were fixed with an organic binder and then heated at 1000 °C for 1 h. Molds prepared through the new coating processes, especially process III, show a higher fracture strength value compared with that of the conventional convert mold process, which may be caused by the increase in the glassification efficiency of the precursors. Powder prepared by process III shows a more uniform coating of the glass phase than those by other processes, resulting from an enhancement in the phase mixing between SiO_2 and NaOH molecules.

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1. Introduction

The convert mold process for preparing shell molds used in the foundry industry has many advantages, such as high strength, enhancement of collapse, easy processability, and high thermal stability, making it useful in fabricating automobile and aircraft components [1,2]. Typically, the convert mold process is divided into five main processes: (1) forming the starting mold coated with an organic binder, (2) dipping the coated mold into a slurry with inorganic precursors, (3) first drying for 1 h at 80 °C, (4) second drying for 1 h at 200 °C, and (5) heat-treating for 1 h at 1000 °C, resulting in the conversion of the organic-coated mold to the inorganic-coated mold [3,4]. The hydrolysis and condensation reactions (generally called a sol–gel reaction) take place during the third and fourth processes, and glassification is generated during the fifth process [5–7]. The mechanical and thermal properties in the mold are induced from the glass phase generated during the heat treatment process (fifth process). In addition, in the convert mold process, an inorganic binder (or precursor) is generally coated on the organic binder which is used to fix the mold shape. Therefore, the inorganic precursor is easily lost by burning of the organic binder with a low decomposition temperature during the heat treatment. This causes a reduction in the glassification efficiency of inorganic precursor. Therefore, the inorganic precursor should be coated on the starting particles prior to the organic binder for the reduction in the loss of inorganic precursor. It improves homogeneity of coating with the inorganic precursor on the surfaces of particles and increases conversion of the inorganic precursor into the glass phase, enabling the preparation of a mold with high thermomechanical properties.

In this work, a new coating process for enhancing the addition effect of inorganic precursor is introduced. Namely, the inorganic precursor was coated on the starting powder preparatory to the organic binder, and then the organic binder

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was added to form the mold. In addition, the preparation method for the powder with a high glassification efficiency was divided into two processes: in the first process, individual inorganic precursors were independently coated on the starting particles through the continuous coating process, and in the second process, the mixed inorganic precursor was coated on the starting particles. The coating morphology and surface microstructure of the powders prepared by the new coating processes were compared with those by the conventional convert mold process, using various analytical techniques. The relationship between fracture strength and coating process is discussed based on the microstructures observed before and after heat treatment.

2. Experimental

The inorganic binder system for fabricating the powder through the coating process was prepared using tetraethyl orthosilicate (TEOS, Sigma–Aldrich Korea, Yongin, Korea) as a SiO_2 precursor, and sodium methoxide (NaOMe, Sigma–Aldrich Korea, Yongin, Korea) as a Na_2O precursor. In this work, three different coating processes were employed to fabricate the powder, as shown in Fig. 1. In the first process (process I), the starting particle composed of SiO_2 and Al_2O_3 was coated with the Na_2O precursor, and then the treated particle was recoated with the SiO_2 precursor (Fig. 1(a)). In the second process (process II), the coating sequence of process I was inverted (Fig. 1(b)). Process III involved coating of the starting particle with a mixture of TEOS and NaOMe (Fig. 1(c)). The solution of TEOS and NaOMe mixed with 40 and 60 wt%, respectively, was stirred for 1 h at room temperature. The precursor-coated particles were dried at 80 °C for 1 h. The dried particles were mixed with poly(vinyl alcohol) (PVA) used as an organic binder, and formed with a pressure of 60 MPa with a cuboid shape of 10 mm × 10 mm × 50 mm. The prepared mold samples were heat-treated at 1000 °C for 1 h. Basic formulations and experimental ranges to prepare the powder and mold samples through the coating process are shown in Table 1.

The microstructure of the particles treated by various process conditions was observed using a scanning electron microscope (SEM, JEOL Model JSM-5610, Tokyo, Japan), and the element analysis of each particle was carried out using an energy dispersive X-ray spectrometer (energy resolution = 133 eV, Oxford Inst., Oxford, UK). The fracture strength of mold samples after heat treatment was measured using a universal testing machine (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 fracture strength.

3. Results and discussion

The reaction mechanisms of the two precursors used in this work, that is, TEOS and NaOMe, are as follows [3,4]:

Hydrolysis reaction:

$$NaOR + H_2O \rightarrow ROH + NaOH \quad (1)$$

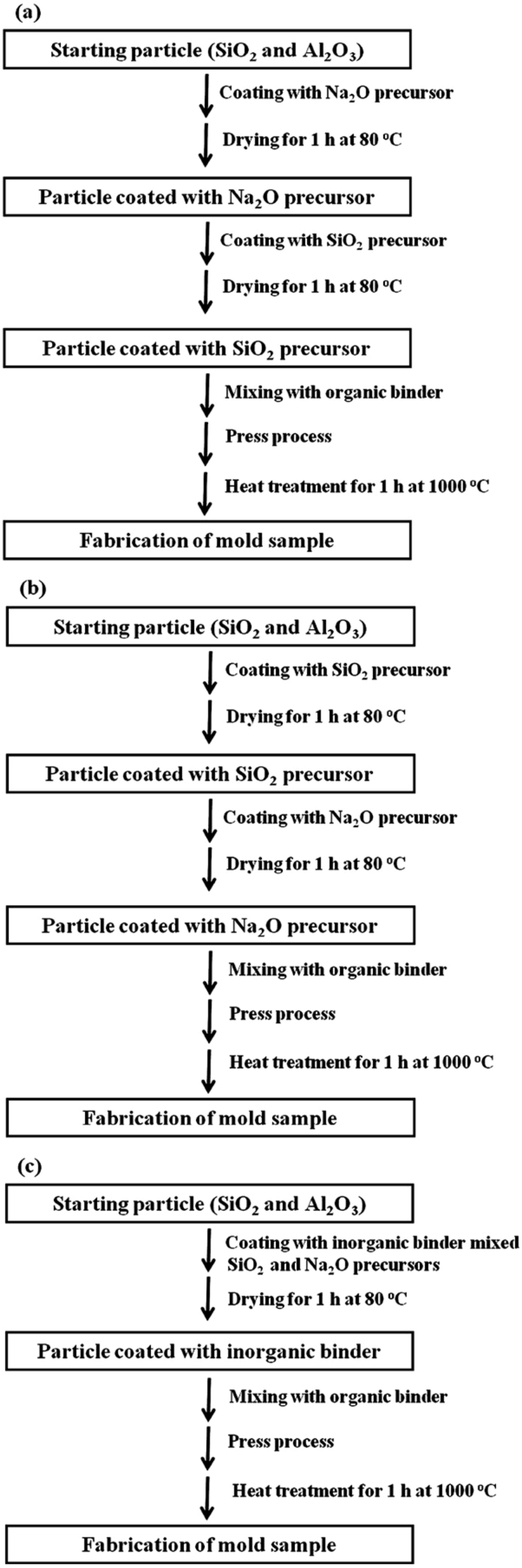

Fig. 1. Schematic diagram for fabricating the mold sample through the new coating process: (a) process I, (b) process II, and (c) process III.

Table 1
Basic formulations and experimental ranges to prepare the powder and mold samples.

Run number	1st coating precursor	2nd coating precursor	Organic binder	Condition	Fracture strength (MPa)
Run-1	–	–	–	Conventional convert mold process	4.20 ± 1.21
Run-2	NaOMe	–	–	W/o heat treatment	–
Run-3	TEOS	–	–	W/o heat treatment	–
Run-4	NaOMe	TEOS	–	W/o heat treatment	–
Run-4-1			PVA	Coating process I	6.80 ± 1.68
Run-5	TEOS	NaOMe	–	W/o heat treatment	–
Run-5-1			PVA	Coating process II	5.71 ± 0.82
Run-6	TEOS + NaOMe		–	W/o heat treatment	
Run-6-1			PVA	Coating process III	10.13 ± 0.92

Sol–gel reaction:

$$(\mathrm{RO})_3\mathrm{Si}[\mathrm{O-Si(OR)_2}]_n\mathrm{OR} + (n+2)\mathrm{H_2O} \rightarrow (n+1)\mathrm{SiO_2} + 2(n+2)\mathrm{ROH} \quad (2)$$

where NaOR, ROH, NaOH, $(RO)_3Si[O–Si(OR)_2]_nOR$, and SiO_2 denote sodium alkoxide, alcohol, sodium hydroxide, alkyl silicate, and silica, respectively [5]. Sodium alkoxide is hydrolyzed to form sodium hydroxide (by Eq. (1)), and alkyl silicate is hydrolyzed to form silica and alcohol (by Eq. (2)). In addition, silica is a continuous glass phase by the sol–gel reaction of silicate whereas NaOH generated just by the hydrolysis reaction is a solid particle.

Heat-treatment reaction:

$$2\mathrm{NaOH} + \mathrm{SiO_2} \rightarrow \mathrm{Na_2O \cdot SiO_2} + \mathrm{H_2O} \quad (3)$$

The glass phase of sodium silicate ($Na_2O·SiO_2$) is produced by the reaction between sodium hydroxide and silica at a temperature of about 1000 °C [8], which can give strength to the mold. Therefore, the homogeneous glassification on the surfaces of the starting particles and the glassification efficiency of precursors are important factors in increasing mechanical properties of the mold.

Typical cross-sectional morphologies of the particles treated under various conditions are presented in Fig. 2, which are observed in the particles after the hydrolysis or sol–gel reactions following the drying process. As mentioned above, the particle with the NaOH generated by the hydrolysis reaction of NaOMe represent the particulate layer with a polygonal shape (denoted by the dotted arrows in Fig. 2(a)), while the particle with the SiO_2 by the sol–gel reaction of TEOS shows the layer with a continuous solid state on the surface of the starting particle (denoted by the solid arrows in Fig. 2(b)). In the SEM image of the particle prepared through process I (Fig. 2(c)), the layers of SiO_2 and NaOH are not independently observed on the surface of the starting particle, meaning that

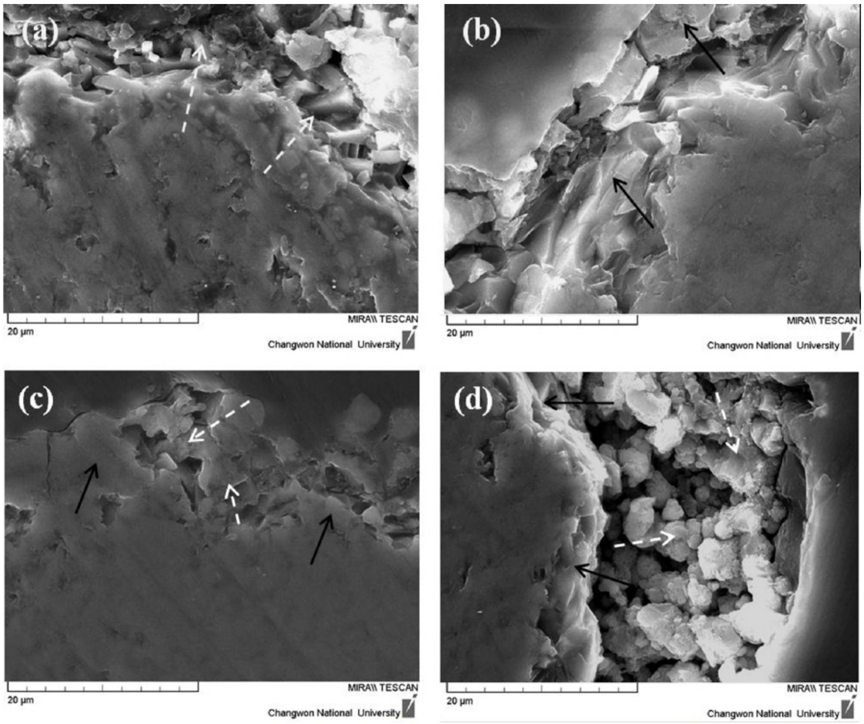

Fig. 2. SEM morphologies of the particles coated with inorganic precursors: (a) NaOMe, (b) TEOS, (c) process I, and (d) process II. White and black arrows indicate the NaOH and SiO_2 phases, respectively.

TEOS has permeated between the NaOH particles. Therefore, it can be assumed that a single layer with a mixture of SiO_2 and NaOH phases is formed. However, in the case of Fig. 2(d), the layers of SiO_2 and NaOH are observed on the surface of the particle, indicated by the solid and dotted arrows, respectively. This is because the continuous glass state of SiO_2 restricts the infiltration of NaOMe. These phenomena can be confirmed in the element analysis results for the particles prepared through each coating process, presented in Fig. 3. The starting particle used in this work is mostly composed of SiO_2 and Al_2O_3, with Al and Si elements homogeneously dispersed on the surface of the particle. In Figs. 3(a-2) and (a-4), the Na and Si are uniformly observed on the surface of the particle because of the mixture of SiO_2 and NaOH, as mentioned in the SEM morphology. However, in the case of Fig. 3(b-2), a considerable amount of Na is detected on the outside of the particle, meaning that the phases of SiO_2 and NaOH exist separately, compared with the particle treated by process I. It could be expected that the mold prepared through process I has a higher fracture strength than that prepared by process II, caused by the

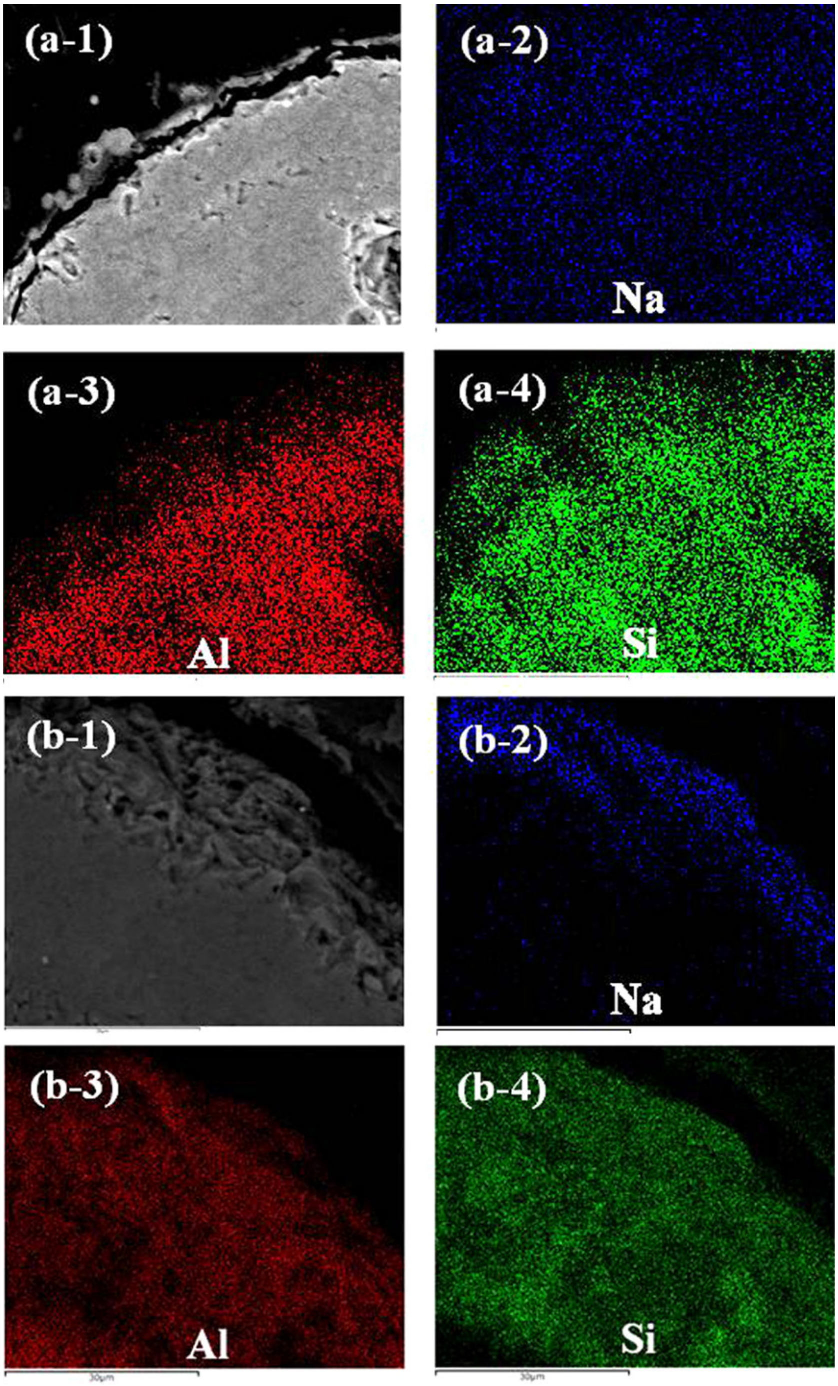

Fig. 3. Element analysis results of the particles prepared through process I (a) and process II (b). Each number presents SEM morphology of particle, and elements of Na, Al, and Si, respectively.

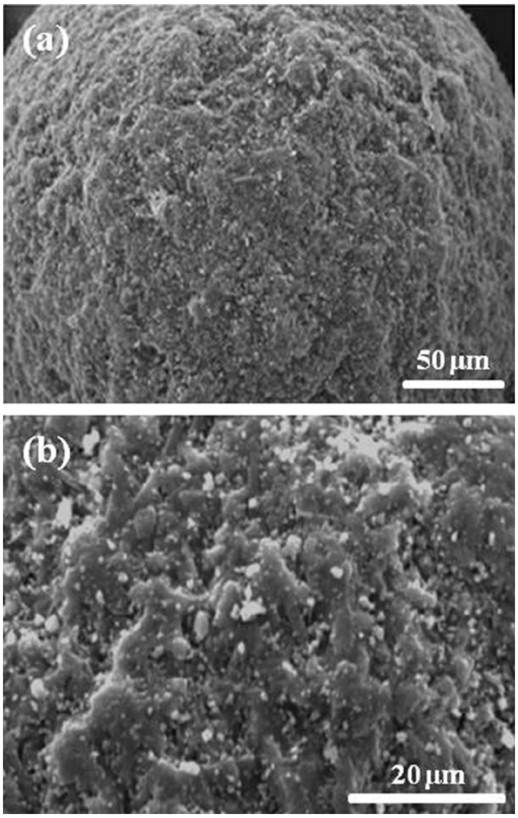

Fig. 4. SEM morphology of the particle prepared through process III before heat treatment: (a) low magnification and (b) high magnification.

improvement in the glassification efficiency because of the homogeneous mixing between the SiO_2 and NaOH phases at the surface of the particle.

Typical cross-sectional morphologies and the element analysis results of the particles prepared through process III before heat treatment are shown in Figs. 4 and 5, respectively. The TEOS of the continuous solid state and the NaOMe of the particulates are homogeneously mixed and then coated on the surface of the starting particle (Fig. 4), resulting in the Na and Si are uniformly observed on the surface of the particle (Fig. 5). Surface morphologies of the particles prepared as a function of process are shown in Fig. 6. The glass phase is observed at the interface between particles and on the surface of particles, independent of the process employed. The particle prepared by the conventional convert mold process shows a less homogeneous glass phase (indicated by the solid arrow in Fig. 6(a)), compared with those by the new coating processes, caused by the loss of inorganic precursors by the decomposition of organic binder during the heat treatment. In the mold prepared by process III, the glass phase is the most homogeneously dispersed at the interface between particles and on the surface of the particles, as shown in Fig. 6(d), resulting from the high glassification efficiency by the homogeneous mixture of each inorganic precursor. In addition, in process I, the glass phase is well and uniformly developed because of the increase in the contact area between SiO_2 and NaOH existing simultaneously in the mixture layer, as shown in Fig. 6(b). However, in Fig. 6(c), the glass phase of sodium silicate is locally and partially seen on the surface of the particles. In the case of process II, the glassification is reduced because of the low reaction between the SiO_2 and NaOH molecules being in the double layer as well as the evaporation of elemental Na present at the outside of the particle. It is verified that the Na strongly affects the generation of glass phase, showing the higher strength in the mold prepared by process I than by process II.

Fig. 7 shows photographs of the mold prepared through process III. Two solid phases (SiO_2 and NaOH) generated by hydrolysis and/or condensation reactions (see Fig. 7(a)) are converted into the glass phase of sodium silicate (Na_2SiO_3) during the heat treatment, having a white solid phase, as shown in Fig. 7(b). These results imply that the new process can be applied to fabrication of mold having high thermomechanical properties for precision thin casting.

The fracture strengths of molds prepared through each process were measured at room temperature, and the results are shown in Table 1. The new coating processes introduced in this work are designed to decrease the loss of inorganic precursors by the coating of organic binder onto the inorganic precursors. It induces the enhancement of glassification efficiency of the precursor. Therefore, the fracture strengths in mold samples prepared by the new processes are significantly increased compared with that of the conventional convert mold process. In addition, the fracture strength value of the mold sample

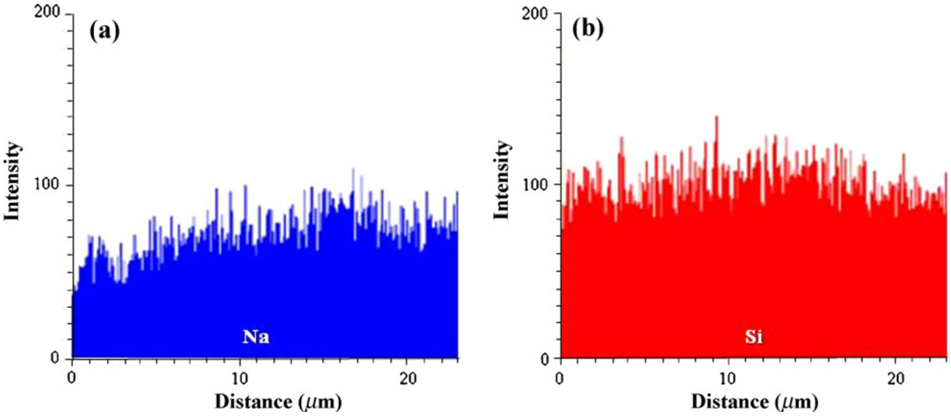

Fig. 5. Element analysis results of the particle prepared through process III before heat treatment: (a) Na element and (b) Si element.

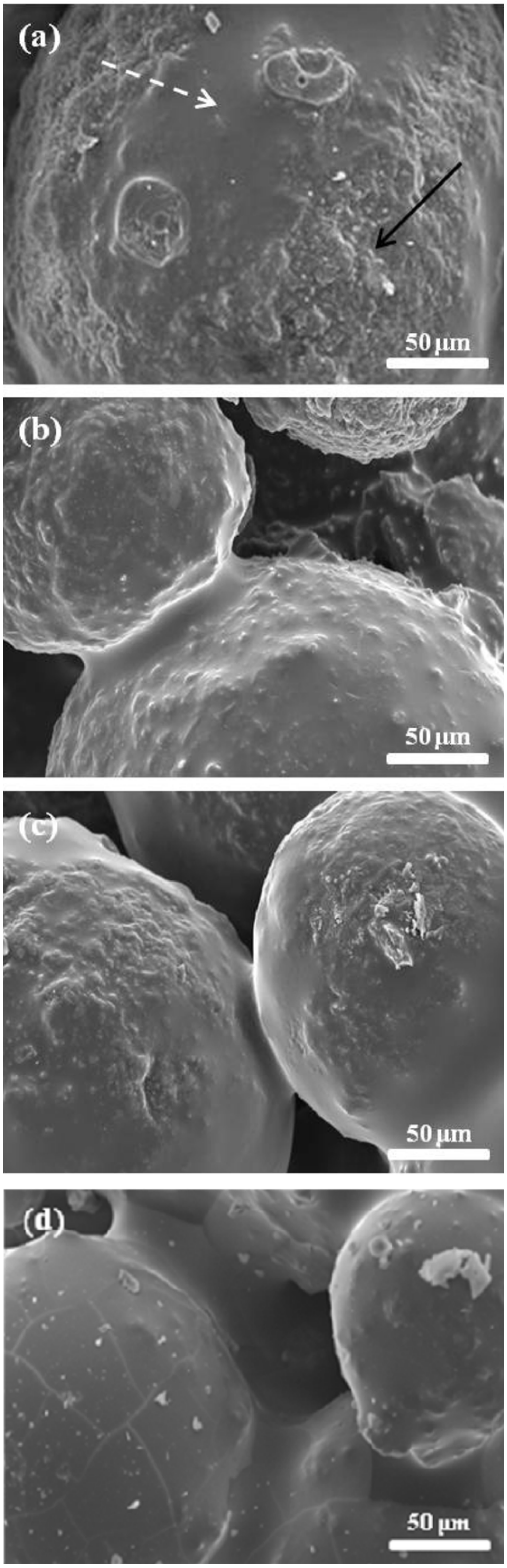

Fig. 6. SEM morphologies of particles after heat treatment in mold samples prepared by (a) conventional convert mold process, (b) process I, (c) process II, and (d) process III.

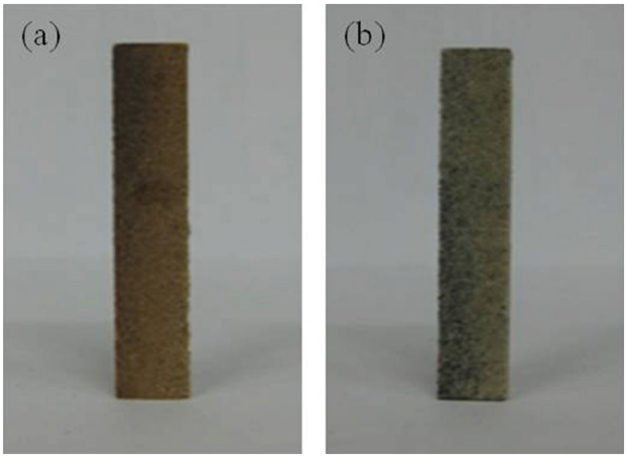

Fig. 7. Photographs of the mold samples prepared through process III: (a) before heat treatment and (b) after heat treatment. Photograph of each sample is real size of 10 mm × 10 mm × 50 mm.

prepared by process III is higher than those of processes I and II because of the high glassification efficiency and the uniform glassification by the high mixing effect between precursors.

4. Conclusions

A new coating process in the powder preparation of a shell mold has been developed to enhance the coating effect of inorganic precursors, related to the coating of inorganic precursor prior to organic binder on the starting particles, compared with the conventional mold process. It induces the homogeneous formation of the glass phase on the surface of starting particle and the increase in the glassification efficiency of inorganic precursor. Namely, the new coating process significantly reduces the loss of inorganic precursors by burning of organic binder occurred in the conventional mold process, leading to an improvement in the fracture strength of shell mold. In the surface morphology of the particles prepared by process III, the glass phase is well and uniformly formed both at the interface between particles and on the surface of the particles. This is because the high reactivity between SiO_2 and NaOH existing in the mixture precursor increases the glassification efficiency. However, the glass phase generated under process II is locally and partially seen on the surface of the particles in the mold, resulting from the evaporation of elemental Na present at the outside of the mold and the low reactivity between the two inorganic precursors. Therefore, the fracture strength of the mold sample prepared by process III is higher than those prepared by processes I and II, whereas the conventional convert mold process results in the lowest fracture strength, indicating that the new coating process can provide a high strength mold.

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