

# Ternary-phase binder system for preparing a mold with high strength in sand casting

Eun-HeeKim, Erdenechuluun Tumenbayar, Yeon-Gil Jung, Jing Zhang

**Abstract**— A binary-phase inorganic precursor is applied to prepare a mold with shape maintenance during heat treatment ( $\geq 1000$  °C) in casting process. With a conventional binary-phase precursor, the strength of the mold is induced by a glass phase of sodium silicate generated by the reaction of tetraethyl orthosilicate (TEOS) and sodium methoxide (NaOMe), which is insubstantial for the casting of large objects. Therefore, in this work, a ternary-phase inorganic precursor consisted of TEOS, NaOMe, and  $\text{Al}(\text{OH})_3$  was used in the fabrication process of the mold to improve mold strength. The mold sample was first coated with the ternary-phase system, and then dipped into the second binary-phase binder system. Sodium aluminosilicate (nepheline) is synthesized in the ternary-phase system in temperatures of both 1000 and 1200 °C, while only sodium silicate is generated in the binary-phase system. The strength of the mold prepared with the ternary-phase system is more enhanced than that with the bi-phase system, due to the newly synthesized phases. The amount of TEOS and glassification temperature affects the strength of the mold, with a higher strength shown under a heat treatment of 1000 °C. The relationship between the composition ratio in the ternary-phase system and the mold strength is discussed extensively.

**Index Terms**—Mold, Precursor, Strength, Ternary-phase system.

## I. INTRODUCTION

Conventionally, a sand mold is used in the foundry industry because it is a simple process with high productivity [1–4]. However, it has a number of disadvantages, such as the generation of blowholes by the burning of the organic binder and casting defects because of the low mobility of molten metal. Therefore, the thin-wall casting of a complex shape less than a thickness of 5 mm has been generally performed using a precision-casting technique, so-called investment casting. However, this method has many drawbacks such as the increment of production costs, the complex and long process, and the limitation of product size. Therefore, Sasaki upgraded the sand mold process using an inorganic binder [5]. The inorganic binder is usually composed of silicate and sodium alkoxide, as silica ( $\text{SiO}_2$ ) and sodium oxide ( $\text{Na}_2\text{O}$ ) precursors, respectively [6–8]. In this binary-phase system, the mechanical properties of the mold are caused by the cohesive strength of the glass phase

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generated at the interface between starting particles [9–11]. Specifically, the fracture strength arises from the glass phase synthesized through the sol-gel reaction and glassification taking place between silicate and sodium alkoxide [12–14]. During the above reactions, the organic binder coated on the surface of the particle is substituted by the inorganic binder of the glass phase, which is called an organic-inorganic conversion process. However, the strength of the mold is limited due to the intrinsic strength of the binary system and the low converting efficiency from the precursor to the glass phase. Also, the unreacted  $\text{Na}_2\text{O}$  can be the cause of efflorescence in the mold.

In this work, a ternary-phase system has been introduced and combined with the binary-phase system to effectively improve the mechanical properties of the casting mold. Aluminum hydroxide ( $\text{Al}(\text{OH})_3$ ) was used as an alumina ( $\text{Al}_2\text{O}_3$ ) precursor to create a new compound showing increased strength and a stable phase at high temperatures above 1000 °C. Ceramic bead of mullite composition was used instead of conventional sand powders (such as artificial sand, chamotte, and chromite), due to excellent thermal resistance with temperature to molten metal at the casting temperature. The possible processes of a ternary-phase system to enhance the mold strength are proposed, and the relationship between fracture strength and ternary-phase composition is discussed, with a focus on the interface microstructure and process.

## II. EXPERIMENTAL PROCEDURE

### A. Sample Preparation

The inorganic binder used for preparing the mold for thin-walled casting was composed of tetraethyl orthosilicate (TEOS; Sigma-Aldrich Korea, Yongin, Korea) as a  $\text{SiO}_2$  precursor, sodium methoxide (NaOMe; Sigma-Aldrich Korea) as a  $\text{Na}_2\text{O}$  precursor, and  $\text{Al}(\text{OH})_3$  (Sigma-Aldrich Korea, Yongin, Korea) as a  $\text{Al}_2\text{O}_3$  precursor. Bead powder (nominal particle size of 0.39 mm, Itochu Ceratech Corporation, Seto, Japan) was used as a starting material for the mold [15], which was prepared by the resin-coated sand (RCS) process. Formulations for the investigation of compounds generated in the ternary-phase system are shown in Table 1. Basic formulations and experimental ranges for preparing mold samples using the binary- and ternary-phase systems are

shown in Table 2. The size of the mold sample used as a substrate was 10 mm  $\times$  10 mm  $\times$  50 mm, which was determined and prepared by a commercial casting company. In addition, the variation of inorganic precursors after the hydrolysis reaction and heat treatment was checked using only inorganic precursors. The hydrolysis reaction of the

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precursors was conducted at 80 °C for a period of 24 h, dried at room temperature (RT) for a period of 3 days, and then heat treatment was at 1000 °C with a dwell time of 1 h. The mold samples coated with the organic binder were first dipped into a solution of the ternary-phase system (TEOS/NaOMe/Al(OH)<sub>3</sub>), and then a second dipping into a solution of the binary-phase system (TEOS/NaOMe) was conducted at room temperature. To verify the effectiveness of the ternary-phase system, the mold sample as reference was prepared after dipping into the only binary-phase system. The individually dipped samples were dried at 80 °C for a period of 24 h, and then heat treated at 1000 °C or 1200 °C with a dwell time of 1 h in ambient atmosphere. Detailed processes through the binary-phase and combined-phase systems are shown in Fig. 1.

Table 1. Basic formulations to investigate the compounds generated in inorganic precursors

Composition	Composition ratio (mole)	Condition
TEOS : NaOMe	1 : 1	Dry process: 80 °C, 24 h → RT, 3 days  Heat treatment: 1000 °C, 1 h
TEOS : Al(OH) <sub>3</sub>		
NaOMe : Al(OH) <sub>3</sub>		
TEOS : NaOMe : Al(OH) <sub>3</sub>	1 : 1 : 1	

Table 2. Basic formulations and experimental ranges to prepare the mold samples using the binary- and ternary-phase systems

Run number	1 <sup>st</sup> inorganic Precursor (mole ratio)		2 <sup>nd</sup> inorganic Precursor (mole ratio)	Dry process	1 <sup>st</sup> heat treatment	2 <sup>nd</sup> heat treatment
Run 1-1	TEOS : NaOMe	0.18 : 1.5	TEOS : NaOMe	80 °C, 24 h	1000 °C	1000 °C, 1 h
Run 2-1	TEOS : NaOMe : Al(OH) <sub>3</sub>	01:01:01	(0.18 : 1.5)	24 h	1000 °C	1 h
Run 2-2					1200 °C	
Run 3-1					1000 °C	
Run 3-2					1200 °C	
Run 4-1	05:01:01				1000 °C	
Run 4-2					1200 °C	

To evaluate the properties, such as Young's modulus ( $E$ ) and hardness ( $H$ ), glass samples were prepared using SiO<sub>2</sub> (Sigma-Aldrich Korea, Yongin, Korea), Na<sub>2</sub>O (Sigma-Aldrich Korea, Yongin, Korea), and Al<sub>2</sub>O<sub>3</sub> (Sigma-Aldrich Korea, Yongin, Korea) powders as starting materials. Compositions of the samples are shown in Table 3. The prepared powders were mixed by dry milling at about 210rpm for 24h. The mixed powders were grinded for 5min. The prepared powders were heat-treated at 1600 °C for 1h.

Table 3. Composition of the glass samples employed to evaluate mechanical property

Sample	SiO <sub>2</sub> (mol%)	Na <sub>2</sub> O(mol%)	Al <sub>2</sub> O <sub>3</sub> (mol%)
1	0.75	0.25	-
2	0.65	0.25	0.1
3	0.5	0.25	0.25

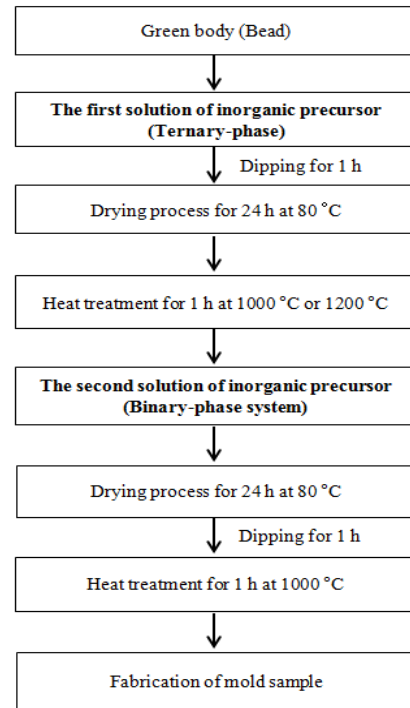


Fig. 1. Schematic diagram of processes for preparing mold samples.

### B. Characterization

The compounds converted from the inorganic precursors or synthesized by the reaction between inorganic precursors during heat treatment were analyzed using an X-ray diffractometer (XRD, Philips X-pret MPD, Model PW3040, Eindhoven, Netherlands). The microstructure of the fracture surface in mold samples was observed using a scanning electron microscope (SEM; Model JSM-5610; JEOL, Tokyo, Japan). The fracture strengths of mold samples before and after heat treatment were measured using a universal testing machine (Instron 5566; Instron Corp., Norwood, MA, USA) with the bending mode at a rate of 0.5 mm · min<sup>-1</sup>. Tests were carried out at room temperature, and five runs were performed to determine the standard deviation of the fracture strength. To obtain both mechanical properties,  $E$  and  $H$ , each sample was cold-mounted using an epoxy resin. The mounted samples were polished using silicon carbide paper and polished using the 3 and 1 μm diamond pastes. The mechanical properties were evaluated using a nano-indenter (Nano Instruments, MTS Systems Corp., Eden Prairie, USA) with a Berkovich tip (radius of tip < 100 nm). The measured condition was as follows; Poisson's ratio of 0.25, Maximum load of 25 mN. In nano-indentation,  $E$  and  $H$  can be determined using the stiffness as calculated from loading and unloading, respectively, in the slope of the load vs. displacement curve. To obtain reliable values, more than 10 points were tested for each result. All indentations were performed at room temperature.

### III. RESULTS AND DISCUSSION

The strength of mold sample prepared using inorganic precursors is induced by the glass phase synthesized by a reaction between inorganic precursors during the heat treatment. The efficiency of conversion from inorganic precursor to glass phase are directly related to the strength of mold. Therefore, in this work, the ternary-phase system was introduced to the conventional binary-phase system to increase the efficiency of conversion and to synthesize a new phase with temperature-stable properties, such as strength and phase stability. Generally, in the Si-Al-M-O composite, the addition of M (Na, B, Ca, Mg, Zr, and Cr, and so on) decreases the melting temperature of the composite, as shown in Fig. 2 [16]. Specifically, this means that the glass phase is easily synthesized and the efficiency of glassification is enhanced due to the reduction of the reaction temperature between precursors, this could be called the glassification temperature. The Na element is selected as additive (M) in this work because the composite can be converted to the glass phase depending on the amount of Na added in the ternary-phase system.

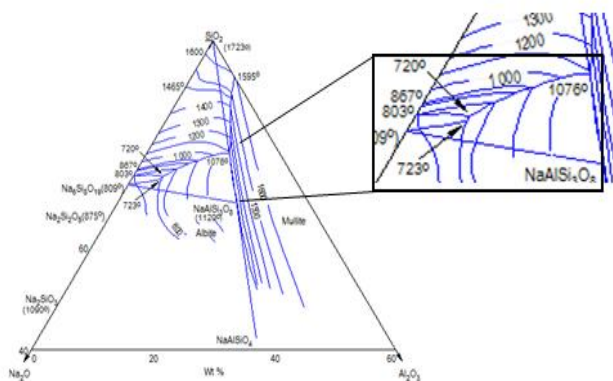
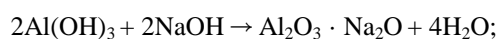
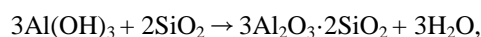
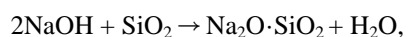
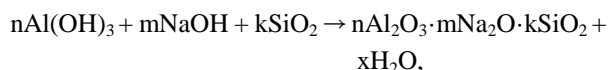


Fig. 2. Phase diagram of SiO<sub>2</sub>-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> [16]. Melting temperature as a function of additive in the ternary-phase system is represented by the Table.

The ideal compounds which could be synthesized between or among precursors of TEOS, NaOMe, and Al(OH)<sub>3</sub> used in this study are as follows:



where  $n\text{Al}_2\text{O}_3 \cdot m\text{Na}_2\text{O} \cdot k\text{SiO}_2$ , NaOH, Na<sub>2</sub>O·SiO<sub>2</sub>, 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub>·Na<sub>2</sub>O are sodium aluminosilicate (nepheline), sodium hydroxide, sodium silicate, mullite, and sodium aluminate, respectively. The results of XRD analysis

for the compounds synthesized from inorganic precursors after a heat treatment at 1000 °C are shown in Fig. 3. All precursors of liquid status were converted into the solid status of amorphous phase by the sol-gel reaction before heat treatment, independent of the species of inorganic precursor. After a heat treatment of 1000 °C, TEOS/NaOMe, NaOMe/Al(OH)<sub>3</sub>, and TEOS/NaOMe/Al(OH)<sub>3</sub> systems were glassified into Na<sub>2</sub>SiO<sub>3</sub>, Na<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>, and NaAlSiO<sub>4</sub> (sodium aluminosilicate, nepheline), while in the composite of TEOS/Al(OH)<sub>3</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were independently detected. However, a 3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> phase (mullite) was not detected in XRD analysis contrary to expectations.

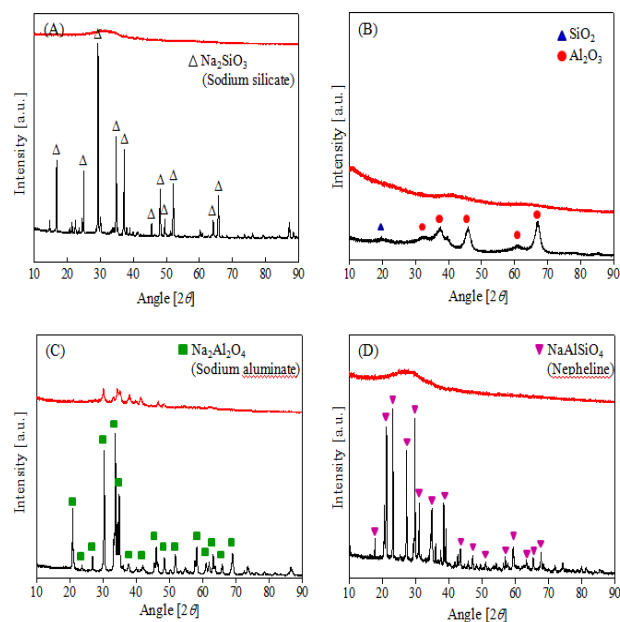


Fig. 3. Results of XRD analysis for compounds synthesized between or among inorganic precursors: (A) TEOS and NaOMe, (B) TEOS and Al(OH)<sub>3</sub>, (C) TEOA and NaOMe, and (D) TEOS, NaOMe, and Al(OH)<sub>3</sub>. Red and black lines represent composite powders before and after a heat treatment of 1000 °C, respectively.

The results of XRD analysis for the compounds synthesized before and after heat treatment in the binary- and ternary-phase systems shown in Table 2 are shown in Fig. 4. All of systems were amorphous status after the hydrolysis reaction in drying process. The mixture of TEOS and NaOMe showed a peak of Na<sub>2</sub>SiO<sub>3</sub> at a heat treatment of 1000 °C, where TEOS and NaOMe convert to the solid phases of SiO<sub>2</sub> and NaOH by hydrolysis reaction in drying process and then to the glass phase of Na<sub>2</sub>SiO<sub>3</sub> [17]. However, the mixture was converted to the amorphous phase at a heat treatment of 1200 °C. In the heat treatment of 1000 °C, the Na<sub>2</sub>SiO<sub>3</sub> synthesized by the chemical bond between SiO<sub>2</sub> and Na element generated from decomposition of NaOH. However, the mixture becomes the amorphous phase at a heat treatment of 1200 °C, due to the insufficient amount of Na element to react with SiO<sub>2</sub> by rapidly evaporation of Na element at 1050 °C [18]. In addition, in the Run 4 (TEOS/NaOMe/Al(OH)<sub>3</sub> = 5/1/1 in mole ratio) systems, cristobalite was a product together with NaAlSiO<sub>4</sub> at a heat treatment of 1000 °C, while only NaAlSiO<sub>4</sub> was synthesized in Runs 2 and 3 as shown in Figs. 4(b) and 4(c), respectively. However, NaAlSiO<sub>4</sub> was the only product at a heat treatment of 1200 °C, irrespective of the composition ratio.

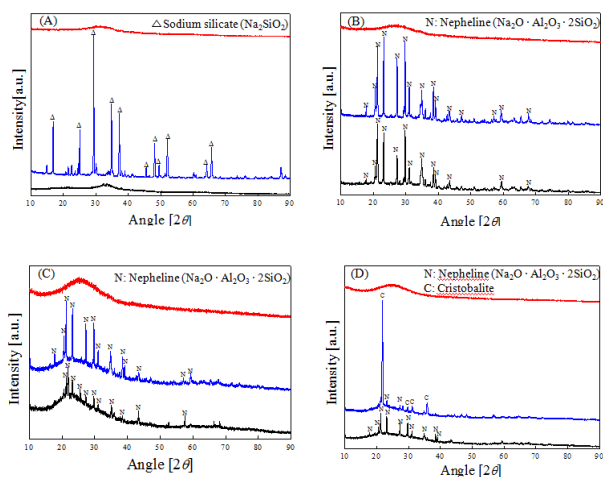


Fig. 4. Results of XRD analysis for compounds synthesized between/among inorganic precursors: (A) Run 1, (B) Run 2, (C) Run 3, and (D) Run 4, respectively. Red, blue, and black lines represent composite powders before and after a heat treatment of 1000 and 1200 °C, respectively.

The fracture strength values of the mold samples prepared through the binary- and ternary-phase systems are presented in Fig. 5. These were measured for the mold samples before and after heat treatment based on Table 2. A green strength of the mold samples show value of  $10.4 \pm 1.5$  MPa (mean  $\pm$  standard deviation) and a firing strength of  $7.2 \pm 0.3$  MPa after 1<sup>st</sup> and 2<sup>nd</sup> heat treatments of 1000 °C (Run 1-1). The higher green strength value is from the organic binder, and the strength after the heat treatment is from the glass phase of  $\text{Na}_2\text{SiO}_3$  shown in Fig. 4(A). In the samples prepared using the binary- and ternary-phase systems (dual-coating system), the strengths of the molds heat-treated at 1200 °C as the 1<sup>st</sup> heat treatment and at 1000 °C as the 2<sup>nd</sup> heat treatment were significantly improved (Run 2-2(B), Run 3-2(B), and Run 4-2(B)), synthesized by the chemical reaction of TEOS, NaOMe, and  $\text{Al}(\text{OH})_3$ . However, the strengths of the molds after the just 1<sup>st</sup> heat treatment after dipping into the ternary-phase system were lower than that prepared using the binary-phase system (Run 1-1(B)), independent of the heat treatment temperature. It means that the strength of mold indirectly related to the number of coating as well as composition of inorganic binder. The fracture strengths of molds heat-treated at 1000 °C as 1<sup>st</sup> heat treatment in the dual-heating process were decreased with an increasing content of TEOS in the ternary-phase system, but still showing a similar strength values with the mold prepared using the binary-phase system only.

The mechanical properties,  $E$  and  $H$ , measured as a function of composition ratio in the ternary composition of  $0.25\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(0.75-x)\text{SiO}_2$ , are shown in Fig. 6. Both properties of  $E$  and  $H$  in composites were enhanced with increasing the addition amount of  $\text{Al}_2\text{O}_3$ . It is due to enhancement in conversion efficiency from the ternary-phase precursor into  $\text{NaAlSiO}_4$ , as represented in Figs. 3 and 4. However, in mold samples, the composition ratio of Run 3 (TEOS/NaOMe/ $\text{Al}(\text{OH})_3 = 2/1/1$  in mole ratio) showed the highest strength value of  $5.7 \pm 0.7$  MPa after the first heat treatment at 1200 °C (Run 3-2 (B) in the dual-heating process and the reliable value with a narrow standard deviation of 0.6

MPa, which is a continuous coating caused by the amorphous phase as shown in Fig. 4(C). As a result, the introduction of the ternary-phase system is the desirable process in the fabrication of casting mold and  $\text{NaAlSiO}_4$  has a more favorable effect on the firing strength than  $\text{Na}_2\text{SiO}_3$  generated in binary-phase system. Therefore, the selection of the optimum precursor composition and heat treatment conditions are an essential component in achieving the maximum strength of the mold.

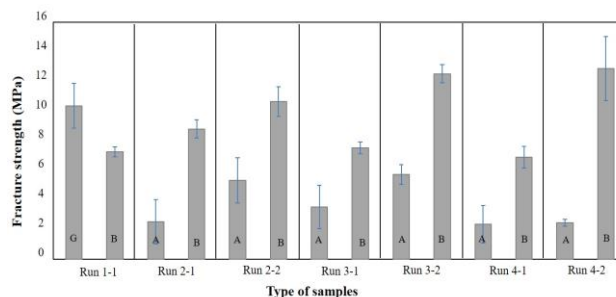


Fig. 5. Fracture strength of the mold samples prepared with the binary- and ternary-phase systems as functions of the composition ratio and heat treatment temperature, based on Table 2. G, A and B indicate the green strength, the firing strength values after 1<sup>st</sup> heat treatment, and 1<sup>st</sup> and 2<sup>nd</sup> heat treatments at 1000 °C, respectively.

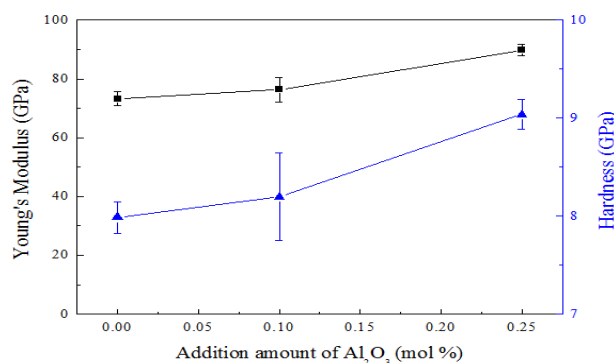


Fig. 6. Young's modulus ( $E$ ) and Hardness ( $H$ ) of composites in the ternary composition of  $0.25\text{Na}_2\text{O}-x\text{Al}_2\text{O}_3-(0.75-x)\text{SiO}_2$ .

The interface microstructures of particles in the molds prepared as a function of heat treatment temperature and the mole ratio in the ternary-phase system of TEOS, NaOMe, and  $\text{Al}(\text{OH})_3$  are shown in Figs. 7 and 8. The binary-phase system converts well to the glass phase at the interface between individual particles under a heat treatment of 1000 °C, which is indicated with arrow in Fig. 7(A). For the mold samples heat-treated at 1000 °C as the 1<sup>st</sup> heat treatment (Fig. 7),  $\text{NaAlSiO}_4$  is insufficiently generated due to the disproportioned composition ratio by an increase in the content of TEOS, and the glass at the interface between individual particles is not enough for strength development. However, when the mold samples were heat treated at 1200 °C as the 1<sup>st</sup> heat treatment in the dual-heating process (Fig. 8), the glass phase consisted of  $\text{NaAlSiO}_4$  that was well and uniformly distributed at the interface as well as on the surface of particles, which caused the improvement of the mold strength.

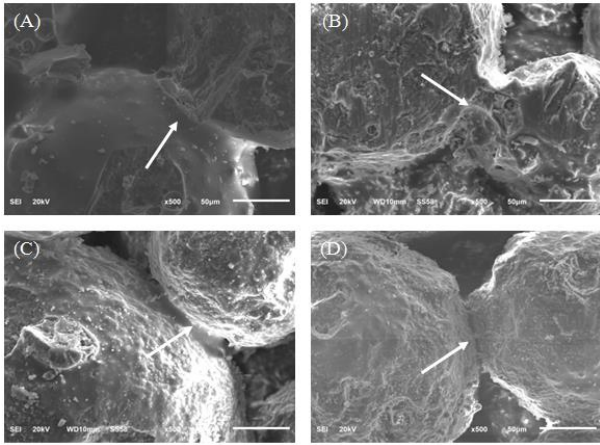


Fig. 7. Interface microstructure of particles in the molds prepared with various mole ratio in the ternary-phase system of TEOS, NaOMe, and  $\text{Al}(\text{OH})_3$  after a heat treatment at  $1000\text{ }^\circ\text{C}$  as the first heat treatment in the dual-heating process: (A) Run 1-1, (B) Run 2-1, (C) Run 3-1, and (D) Run 4-1. Arrows indicate the interface of particles and glass phase.

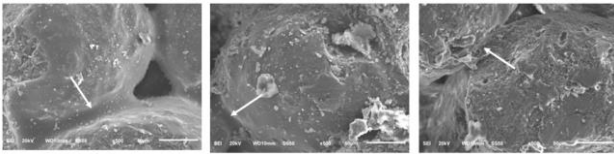


Fig. 8. Interface microstructure of particles in the molds prepared with various mole ratio in the ternary-phase system of TEOS, NaOMe, and  $\text{Al}(\text{OH})_3$  after a heat treatment at  $1200\text{ }^\circ\text{C}$  as the first heat treatment in the dual-heating process: (A) Run 2-2, (B) Run 3-2, and (C) Run 4-2. Arrows indicate the interface of particles and glass phase.

#### IV. CONCLUSIONS

Use The ternary-phase system of TEOS,  $\text{Na}_2\text{O}$ , and  $\text{Al}(\text{OH})_3$  was introduced and combined with the binary-phase system of TEOS and NaOMe to fabricate a mold with enough strength for the casting of large and/or thin products. The mold samples were dual-coated with the ternary- and binary-phase systems to improve the efficiency of glassification and to synthesize a new glass phase, which enhanced the mold strength. In the ternary-phase system, sodium aluminosilicate (nepheline,  $\text{NaAlSi}_3\text{O}_8$ ) and cristobalite ( $\text{TEOS}/\text{NaOMe}/\text{Al}(\text{OH})_3 = 5/1/1$  in mole ratio) were generated by a reaction of TEOS, NaOMe, and  $\text{Al}(\text{OH})_3$  under a heat treatment of  $1000\text{ }^\circ\text{C}$ . However, only  $\text{NaAlSi}_3\text{O}_8$  was synthesized at  $1200\text{ }^\circ\text{C}$ . For this reason, the strength values of mold samples heat-treated at  $1200\text{ }^\circ\text{C}$  as the 1<sup>st</sup> heat treatment at  $1000\text{ }^\circ\text{C}$  as the 2<sup>nd</sup> heat treatment were significantly increased. The highest and reliable strength could be obtained for the mold sample prepared with the mole ratio of 2:1:1 in the ternary-phase system of  $\text{TEOS}/\text{NaOMe}/\text{Al}(\text{OH})_3$ , when the mold sample was heat-treated at  $1200\text{ }^\circ\text{C}$  as the 1<sup>st</sup> heat treatment in the dual-heating process. Therefore, the application of ternary-phase system as an inorganic binder in the fabrication of the mold could effectively enhance the mold strength with optimizing the precursor composition and heat treatment condition.

#### ACKNOWLEDGMENT

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