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Control of H_2O generated during the CO_2 hardening process in a casting mold

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Abstract

An additive reagent was introduced into a water glass binder system for enhancing the mechanical properties and dimension stability of a casting mold, and for improving the surface quality of a cast product. Two different processes with three different additive reagents were employed to investigate the relation between fracture strength of the mold and water (H_2O) existed in the mold. In processes I and II, the mold samples were coated with a water glass binder, and then dipped into different solutions with additive reagent after and before carbon dioxide (CO_2) hardening, respectively. The fracture strength of the mold was enhanced by reducing H_2O content in the mold, achieved by a hydrolysis reaction of additive reagents. In process I, the H_2O movement was restricted in the mold by the solid phase, converted from the water glass during CO_2 hardening. When employing process II, especially in the TEOS used as additive reagent, the fracture strength was significantly increased due to the effective reduction of H_2O content in the mold and the homogeneous generation of glass phase by a sol–gel reaction of the additives.

Keywords: Water glass; Additive reagent; Hydrolysis reaction; Fracture strength

1. Introduction

Typically, the inorganic and organic binders are included as additives in a casting mold to lend sufficient thermal and mechanical properties, and to increase the adhesive strength between starting particles [1–3]. When the molten metal is injected into the casting mold, the organic binder is thermally degraded. Therefore, the mechanical properties of the mold under a high temperature arise from the inorganic binder. Conventionally, the water glass based on metal silicate is used as an inorganic binder, and hardened by carbon dioxide (CO_2) gas in preparing the mold for a big cast product [4–8]. However, the casting mold prepared with the water glass exhibits a low fracture strength as a result of the remains of water (H_2O) generated in the mold, in spite of a drying process having been carried out, which is generated by the degradation of water glass. Furthermore, as molten metal is poured into the mold, the generated gas and the sodium carbonate crystal grown in the mold result in deterioration of the surface quality and mechanical properties of the cast product, inducing the requirement for an additional drying process [9].

In this study, an additive reagent was introduced into the conventional binder system based on the water glass for the elimination of H_2O created by a solidification reaction of water glass. The additive reagents were composed of silicate, metal alkoxide or their complex, being consequently converted into silica (SiO_2) or metal hydroxide of a solid phase by H_2O, generally called as sol-gel and hydrolysis reactions, respectively. In addition, two different processes were used to maximize the effects of additives on fracture strength: the mold sample dipped into the water glass binder was again dipped into the additive

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solutions after (process I) and before (process II) CO_2 hardening. The fracture strength of the molds prepared using new additive systems was compared with that of the mold prepared using the water glass binder only, using various analytical techniques. The relationship between the fracture strength of the mold and the preparation process was discussed, based on the microstructure observed.

2. Experimental Procedures

The new additive systems for preparing the mold with a high fracture strength were prepared using water glass (sodium silicate, $Na_2O \cdot SiO_2$, 53% hydrated H_2O; Sigma-Aldrich Korea, Yongin, Korea), and tetraethyl orthosilicate (TEOS; Sigma-Aldrich Korea) and/or sodium methoxide (NaOMe; Sigma-Aldrich Korea). The starting particle composed of SiO_2 and alumina was mixed with 7 wt% water glass, and then pressed with 60 MPa to form the mold sample with a cuboid shape of $10 \times 10 \times 50$ mm^3. The mold sample was hardened for 1 min under a CO_2 atmosphere and then dried at 200 °C for 17 h. Two different processes (processes I and II) were employed to determine the additive reagent species and to optimize the process, as shown in Fig. 1. In processes I and II, the water glass-coated mold samples were dipped into additive solutions, consisted of the TEOS, NaOMe, or TEOS+NaOMe, after and before CO_2 hardening, respectively. The coating ratio of starting particle to additive reagent in the mold sample was 10:1 by volume. The basic formulations used to prepare the mold samples using the new additive systems are shown in Table 1.

The microstructure of the mold samples prepared was observed using a scanning electron microscope (SEM, Model JSM-5610; JEOL, Tokyo, Japan). The fracture strength of the mold samples after the drying process at 200 °C was measured using a universal testing machine (Instron 5566; Instron Corp., Norwood, MA, USA) in the 4-point bending mode, at a rate of 0.5 mm min^{-1}. Tests were carried out at room temperature, and 10 runs were performed to determine the standard deviation of fracture strength according to ASTM C 1661-02C [10]. The support spans of the low and upper noses were 2.5 cm and 1.0 cm, respectively. The thermal stability of the mold before the drying process was analyzed using a thermogravimetric analyzer (TGA Q50; TA Instruments, Crawley, West Sussex, UK). A sample of about 10 mg was placed in a platinum crucible and heated over a temperature range from 80 to 500 °C, at 5 °C min^{-1}, under a N_2 atmosphere, using a flow rate of 40–60 mL min^{-1}, to investigate thermal decomposition behavior.

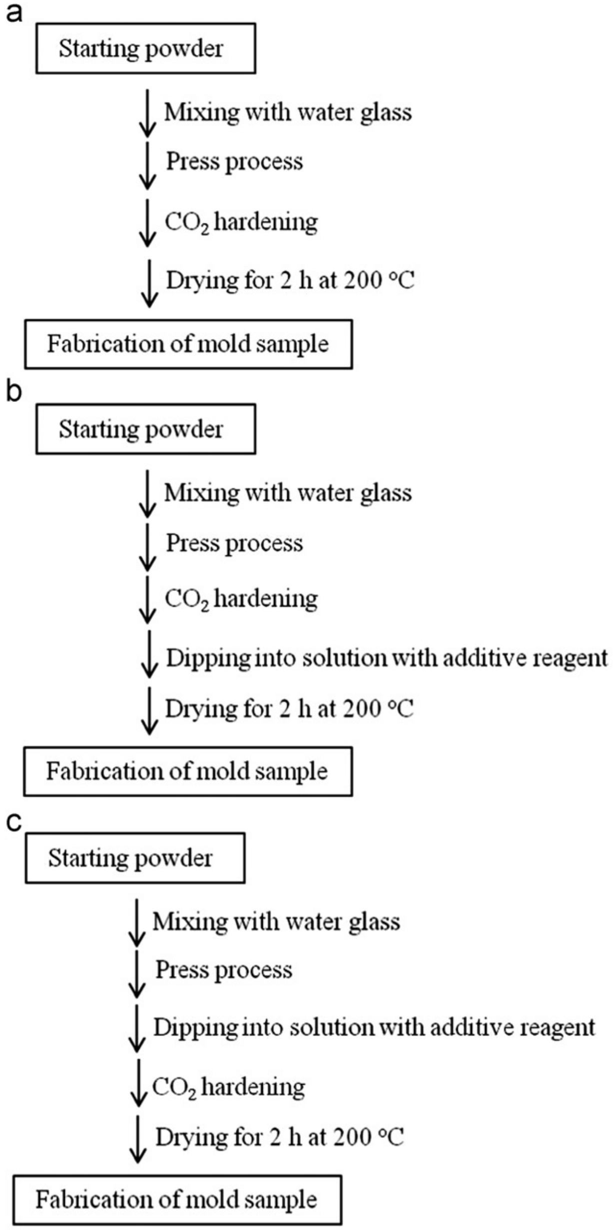

Fig. 1. Schematic diagram for preparing mold samples using (a) the conventional additive system, and the new additive systems by (b) process I and (c) process II.

3. Results and discussion

The water glass (sodium silicate) used in the conventional binder system is solidified by the following reactions during hardening and drying processes:

$$Na_2O \cdot mSiO_2 \cdot nH_2O + CO_2 \rightarrow mSiO_2 \cdot nH_2O + Na_2CO_3 \quad (1)$$

$$Na_2O \cdot mSiO_2 \cdot nH_2O \rightarrow Na_2O \cdot mSiO_2 \cdot (n-1)H_2O + H_2O \quad (2)$$

The water glass decomposes to sodium carbonate and hydrated silica, in the presence of CO_2 (see Eq. (1)): this is known as "CO_2 hardening". Then the H_2O present in the water glass escapes from the resulting hydrated water glass, which is consequently converted to an anhydrous

Table 1
Formulations and conditions for preparing mold samples in this study.

Run number	Inorganic binder	Additive reagent	Process	Drying condition
1	Water glass	–		72 h, 200 °C
2-1	(sodium	TEOS	I	
2-2	silicate)	NaOMe		
2-3		TEOS+NaOMe		
3-1		TEOS	II	
3-2		NaOMe		
3-3		TEOS+NaOMe		

silicate. The mechanical properties of the casting mold are induced from solidification reactions of Eqs. (1) and (2). When the generated H_2O remains in the mold, the mold shows a poor strength. Therefore, in this study, an additive reagent with the hydrolysis reaction was applied to decrease the content of H_2O that was retained in the mold.

Alkyl silicate and metal alkoxide undergo the sol-gel and hydrolysis reactions, respectively, as shown below [11–13]:

$$(RO)_3Si[O-Si(OR)_2]_nOR+(n+2)H_2O \rightarrow (n+1)SiO_2+2(n+2)ROH \quad (3)$$

$$NaOR+H_2O\rightarrow ROH+NaOH \quad (4)$$

where $(RO)_3Si[O-Si(OR)_2]_nOR$, SiO_2, NaOR, ROH, and NaOH denote alkyl silicate, and silica, sodium alkoxide, alcohol, and sodium hydroxide, respectively. Alkyl silicate is degraded to form silanol and alcohol through the hydrolysis reaction (by Eq. (3)), and silica is consecutively formed by the condensation reaction between silanol molecules (by Eq. (2)). The series of reactions are usually called the sol–gel reaction. Sodium alkoxide is hydrolyzed to form sodium hydroxide (by Eq. (4)). In addition, silica forms a continuous solid layer by the sol–gel reaction of silicate, whereas NaOH generated just by the hydrolysis reaction has a solid particle [14–16]. Therefore, the H_2O generated in the reaction (by Eq. (2)) is used in the hydrolysis reaction of alkyl silicate and sodium alkoxide, thus reducing the content of H_2O in the mold.

Fig. 2 shows SEM morphologies at the interface and surface of particles in the mold samples prepared using the conventional additive system and the new additive systems after the drying process. These additive systems changed into a solid phase through various gelation reactions, as shown in Eqs. (1)–(4). Therefore, the green shape of the mold was well maintained after the drying process, irrespective of the preparation process used. In the case of the molds prepared by process II, the surface of particles became smooth and even, compared to that by process I. In addition, the solid phase in process II was homogeneously covered on the surface of particles and located at the interface between particles (denoted by the black dotted arrows in Fig. 2(c)). These results mean that the hydrolysis reaction of additive reagents with the residual H_2O satisfactorily proceeds. However, in the particles prepared by the conventional additive system, the solid phase between particles was not observed (opposite to the case when the new additive systems are employed). In process I, the use of H_2O in the hydrolysis reaction was restricted by the solid phase formed from the water glass by CO_2 hardening, resulting in the unnoticeable reduction of H_2O content generated in the mold. Therefore, the gelation of additive reagents was conducted by the H_2O in air, leading to the insufficient conversion of the additives into the solid phase. Therefore, in process I, the phase converted from additive reagents aggregated on the surface of particles (denoted by the white solid arrows in Fig. 2(b)). It implies that the H_2O has an effect on the hydrolysis reaction of the additives, and subsequently has a decisive effect on the fracture strength of the mold.

The fracture strengths of the molds prepared by each process were measured at room temperature, and the results are shown in Fig. 3. The processes with new additive systems (introduced in this work) were designed to decrease H_2O content existed in the mold by the hardening process of water glass. Therefore, the fracture strength of the mold samples prepared by process II was significantly increased, compared with the mold sample prepared using the conventional binder system. However, the fracture strength of the mold samples prepared by process I was not much enhanced, independent of additives. This is because the use of H_2O in the hydrolysis reaction was restricted by the solid phase generated from the water glass during the CO_2 hardening process, as already addressed in Fig. 2. In addition, in process II, the addition of NaOMe deteriorated the fracture strength. In this work, NaOH generated solid particles after the hydrolysis reaction while TEOS was converted to a continuous layer of solid phase, proven in our previous work [16]. Therefore, by contrast to the TEOS, the addition of NaOMe did not have an effect on the fracture strength of the mold. Consequently, the new additive system used in process II, especially in the TEOS, could be applied for the fabrication of molds with a high fracture strength.

The TGA results of mold samples before the drying process are presented in Fig. 4. In process II, the fracture strength showed the most excellent value when the TEOS was used as additive reagent (Fig. 3). Therefore, only TGA results for the mold prepared with the TEOS among additive reagents are shown in Fig. 4, including the TGA result of the conventional additive system as reference data. In the cases of the conventional additive system and of process I, the weight of the mold decreased consistently, indicating that the variation level of weight according to temperature was constant. However, the weight of the mold prepared by process II sharply decreased at the relatively lower temperature, <100 °C, due to the reduction of H_2O content caused by the sol–gel reaction of TEOS. It is verified that the addition of TEOS strongly affects the content of H_2O in the mold.

Fig. 5 shows photographs with real size (10 mm × 10 mm × 50 mm) of the mold samples prepared using the conventional additive system and the new additive systems

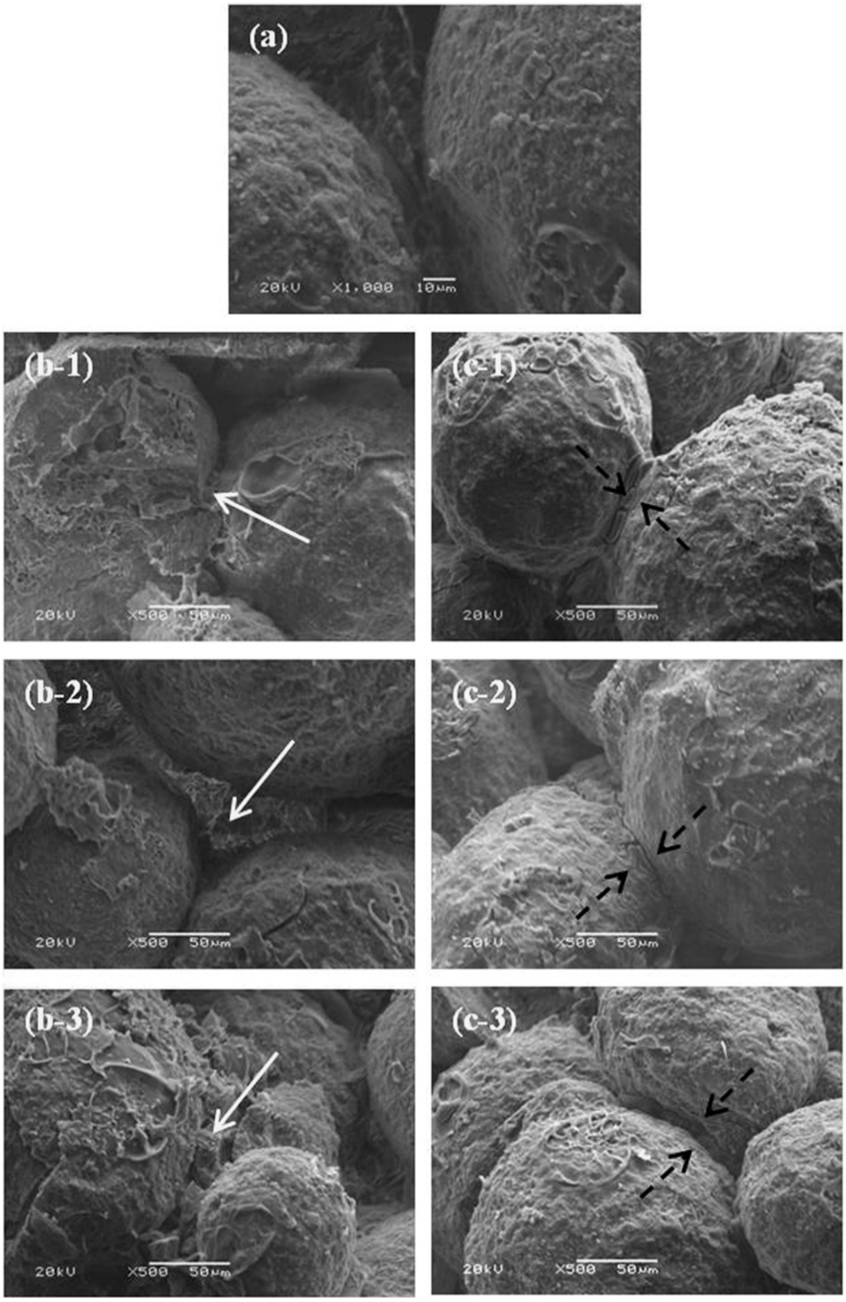

Fig. 2. SEM morphologies at the surface and interface of particles in mold samples prepared using different processes: (a) the conventional additive system and the new additive systems by (b) process I and (c) process II, after the drying process. Each number denotes samples used TEOS, NaOMe, and TEOS+NaOMe as additive reagents, respectively. The white solid and black dotted arrows indicate solid phases generated by processes I and II, respectively.

in process II given reasonable properties, after the drying process. Any contortion of shape was not observed in the mold samples prepared through the conventional additive system and the new additive system.

4. Conclusions

A new additive reagent was used for the preparation of a casting mold to enhance the mechanical properties and dimension stability, and to improve the surface quality. An additive reagent with the hydrolysis reaction was introduced into the conventional additive system based on the water glass in an effort to the decrease in the content of H_2O generated by the hardening reaction of water glass under CO_2 gas. In the mold prepared by process II, the solid phase was well and uniformly formed at the interface between particles and covered on the surface of particles. However, the solid phase generated through process I was aggregated on the surface of particles in the mold, resulting from the insufficient gelation of additives by the CO_2

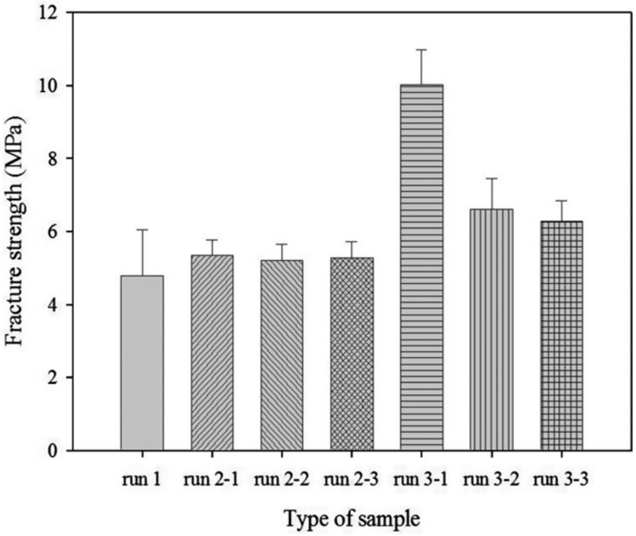

Fig. 3. Fracture strengths of mold samples prepared using different processes.

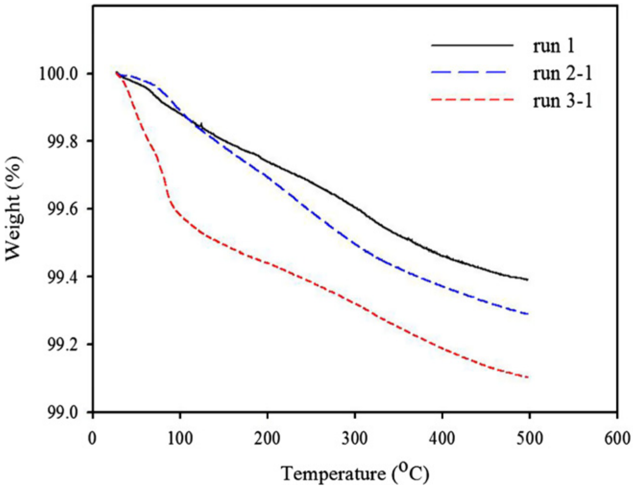

Fig. 4. TGA analysis results of mold samples prepared by the conventional additive system (run 1) and the new additive systems (run 2-1 and run 3-1).

hardening process. Especially, in the process II, when TEOS was used as additive reagent, the fracture strength of the mold was significantly improved by continuous amorphous state of silica, compared to NaOMe with solid particle after the hydrolysis reaction. This indicates that high strength mold can be prepared by using the new additive system in process II.

Acknowledgments

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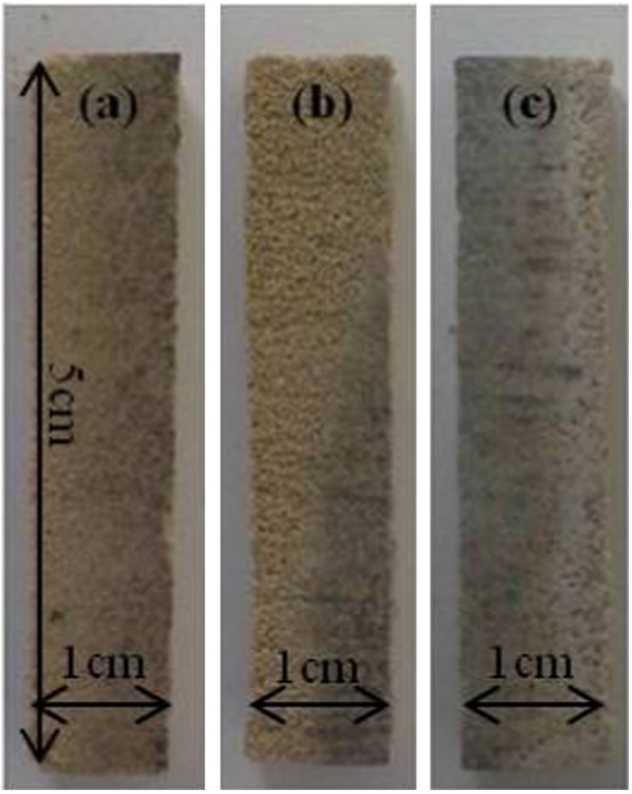

Fig. 5. Photographs of mold samples prepared using different processes: (a) run-1 by the conventional additive system, (b) run 3-1, and (c) run 3-2 by the new additive systems in process II, after the drying process.

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