Molding and Mold Properties of Spherical Artificial Sand Coated with Inorganic Binder

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In recent years, molds made by additive manufacturing (AM) are increasingly applied to build prototypes and small-quantity casting products. Technological development aiming to use mass-produced castings is advancing with the emergence of high speed AM molding technology. Mass production is expected to improve the potential of the entire casting product, such as the realization of complicated internal structures, thinness, and weight reduction by the improvement of cavity accuracy.

Regarding binders applied to AM sand molding technology, so far organic self-hardening systems are mainly applied and their use is spreading. On the hand, in the case of aluminum alloy castings, the application of hardening system with is required from the viewpoint of the clean working environment. The purpose of this study is to develop an AM sand molding technology utilizing a hardening system with an inorganic binder and artificial sand. The developed hardening system is composed of sand coated with an inorganic binder and inkjettable hardening catalyst. First, the hardening characteristics of the developed hardening system were evaluated using hand molded test pieces, and it was found that it is effective for increasing the initial hardening rate compared with conventional methods. Next, the ability to mold with this hardening system was tested using a binder jetting AM molding apparatus. The gas component generated by heating was measured and the coefficient of linear expansion of the molded test pieces was tested to evaluate the characteristics of the molded test. It was confirmed that harmful gas can be reduced and the mold has low thermal expansion. [doi:10.2320/matertrans.F-M2020802]

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1. Introduction

In recent years, casting molds made by additive manufacturing (AM) are increasingly applied being used to build prototypes and small quantity casting products. Technological development aiming to use mass-produced castings is advancing with the emergence of sophisticated AM techniques. Mass production is expected to improve castings in various ways, such as realizing more complicated internal structures, thinness, and weight reduction by the improvement of cavity accuracy.

Additive manufacturing technique for sand mold (hereafter referred to as 3D AM technique), is a type of AM technique which is increasingly applied in industry to build molds by recoating wet sand with liquid catalyst and refractory particles, and printing this with inkjet binder made of mainly furfuryl alcohol. With molds made by this method, the hardened material is decomposed by the heat produced during pouring and harmful gases are generated as a result, leading to a poor working environment. There are also concerns of casting defects caused by hydrocarbon gas generated by the decomposition of the hardened material.¹

Moreover, in the above 3D AM method uses silica sand with wide surface area and irregular shape is mainly used. Spherical artificial sand with small surface is rarely used because it cannot be recoated due to the tendency for the sand particles to clump together as a result of the surface tension of the water used as the solvent to make the liquid catalyst. This clumping tendency between refractory particles can be reduced only by using sintered artificial sand having a spherical surface with irregularities, and only a small amount of liquid catalyst.

Crystal structure of artificial spherical sand is alumina or mullite particle. Artificial spherical sand has a small coefficient of linear expansion and high fire resistance, and can be used for high precision castings due to almost no volume expansion by heat during pouring.²

In contrast, silica sand undergoes a phase transition at 573°C due to heat during pouring, which causes its volume expansion.³ At this time, microcracking occur in the mold, which easily leads to veining defects caused by the penetration of molten metal into the mold.

From the viewpoint of casting quality, it is preferable to use artificial spherical sand. However, the tendency for clumping together of artificial sands because of the spherical shape and small surface area of the sand particles. The clumping tendency due to high surface tension of water is the greatest issue concerning AM process for using artificial sand.

Moreover, to realize a clean working environment, there is a need to develop a sand 3D AM technique with a hardening system made of inorganic binder instead of the conventional organic self-hardeners mainly used for aluminum alloy castings.

In the aim to develop a sand 3D AM technique employing a hardening system made of inorganic binder and artificial sand, in this study, a hardening system composed of artificial sand coated with an inorganic binder and hardening catalyst which can be ejected by ink-jet printing was developed. For enhance the casting mold strength expression by increasing the hardening rate the characteristics of the hardening system were first evaluated using a wooden test mold.

In addition, a 3D AM process based on the binder jetting method using the developed hardening system was carried out, and moldability was verified. For evaluating the properties of the mold, gas components generated at high temperatures during pouring and the linear expansion...
Table 1 Refractory granular material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Refractoriness(K)</th>
<th>Thermal expansion coefficient at 1000°C(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica sand</td>
<td>SiO$_2$</td>
<td>2003</td>
<td>1.5</td>
</tr>
<tr>
<td>Artificial sand (Sintering method)</td>
<td>Al$_2$O$_3$·SiO$_2$</td>
<td>2098</td>
<td>-0.03</td>
</tr>
</tbody>
</table>

2. Experimental Method

2.1 Evaluation of inorganic hardener coated with sintered artificial sand and its characteristics

2.1.1 Inorganic hardener using binder-coated sand

Binder-coated sand is sintered artificial sand coated with sodium silicate as the inorganic binder. 50% triethylene glycol diacetate aqueous solution was used as the ink-jet catalyst for hardening.

Examples of refractory particles used for making the mold include sintered artificial sand and general silica sand. Table 1 shows the characteristics of both types of sand. Silica sand has a high expansion coefficient, and is easily affected by the heat from molten metal at high temperatures, so the mold cracks due to expansion. Moreover, when molten metal flows into the casting mold, veining defects can also occur. On the other hand, since sintered artificial sand has the mullite structure of silica and alumina, its expansion coefficient is small and veining defects are unlikely to occur.

Sodium silicate is generally represented by the molar formula Na$_2$O·nSiO$_2$·mH$_2$O, and the coefficient of SiO$_2$/Na$_2$O is called the molar ratio. The relationship between the weight ratio of SiO$_2$ and the Na$_2$O and is shown by the following formula:

$$\text{Molar ratio} = \frac{\text{weight ratio (SiO}_2\text%/Na}_2\text{O%)} \times \text{Na}_2\text{O molecular weight/SiO}_2\text{ molecular weight}}{\text{weight ratio (SiO}_2\text%/Na}_2\text{O%)} \times 1.032$$

The physical properties and applications of sodium silicate differ depending on the molar ratio, and it is industrially produced in the range of $n = 0.5$ to 4.0 approximately. That with $n$ below 1 is called crystalline sodium silicate, while that with $n$ greater than 1 is amorphous. The molar ratio of the amorphous type can be changed continuously, and it is commercialized as an aqueous solution or powder. The sodium silicate of the binder-coated sand has a molar ratio of 2.5.

Triethylene glycol diacetate [CH$_3$COO(C$_2$H$_4$O)$_2$OCCH$_3$] is an organic ester which has a high boiling point (286°C) and can be dissolved in water. It can be applied by ink-jet printing by mixing with water, and it can also be used for making molds by combining with binder-coated sand.

When ink-jet printing is performed by binder jetting, water in the aqueous solution elutes the sodium silicate coated on the binder-coated sand. At the same time, hydrolysis of triethylene glycol diacetate in the aqueous solution occurs. The silica content in the sodium silicate increases with the formation of salt and triethylene glycol, causing the refractory particles to bond together. Among these products, triethylene glycol volatilizes and salts remain.

2.1.2 Preparation of binder-coated sand by coating artificial sand with inorganic binder

Table 2 shows the test and the comparative materials. To prepare the test material, inorganic binder (liquid state at room temperature) was added to spherical sintered artificial sand heated to about 120°C, with stirring, and cooled to room temperature while volatilizing the water as the solvent.

Sintered artificial sand (average particle diameter 106 µm) was used as the laminated sand. After heating this sand to about 120°C, sodium silicate (molar ratio 2.5 (SiO$_2$/Na$_2$O): 50 baume[20°C]) was added to the sand by 0.3 mass%, and cooled down to 25°C after stirring for 10 min. The binder-coated sand was then removed.

As for the comparative materials, a conventional furan-based organic self-hardening binder for molds built by AM binder jetting technique was prepared by adding a solution consisting of 90 mass% furfuryl alcohol and 10 mass% resorcinol with N-(2-aminoethyl) 3-aminopropylmethyldimethoxysilane by 0.3 mass% to improve adhesion with coated sand. A 60 mass% metaxylene sulfonic acid aqueous solution was used as the hardening catalyst. Sintered artificial sand (average particle size 106 µm) and silica sand (average particle size 106 µm) were used as comparative materials.

Furfuryl alcohol [C$_5$H$_6$O$_2$] has a high boiling point of 171°C, and a low surface tension of 38.0 mN/m, and is easily polymerized by an acid solid catalyst. Resorcinol [C$_6$H$_4$O$_2$] is a benzenediol with two hydroxyl groups in the benzene ring, and promotes the hardening reaction of furfuryl alcohol. N-(2-Aminomethyl) 3-aminopropylmethyldimethoxysilane [H$_2$NC$_6$H$_4$NHCH$_2$CH$_2$(OCH$_3$)$_2$] is a silane coupling agent, which induces chemical bonding between the sand and hardened material, which is effective for improving the mold strength.

Metaxylene sulfonic acid [(CH$_3$)$_2$(C$_6$H$_5$)SO$_3$H] is a catalyst which can harden furfuryl alcohol-based binder at room temperature. It has a melting point of 64°C and contains solid properties at room temperature of 20°C.

2.1.3 Fluidity evaluation of binder-coated sand

The fluidity of the sand was evaluated using a slump cone.
First, a cup called slump cone (size: 50 mm in opening \times 80 mm in height \times 40 mm in bottom) shown in Fig. 1 was filled with sand, a plate was placed over the opening of the cup and turned over, and the slump cone was pulled up vertically from the plate. Next, the spread diameter (D) of the test sand was measured, and the ratio of this diameter to that of the slump cone was calculated. The clumping state of the sand was observed.

The comparative materials, silica sand before coating, and silica sand kneaded with 0.2 mass% organic furan self-hardener, were evaluated.

### 2.1.4 Mold strength expression test

In order to evaluate the strength expression rate of the mold, test and comparative molds were prepared. The test mold, for preparing a specimen of 50 mm \times 50 mm, was made by placing kneading sand into a wooden pattern at the room temperature of 25°C in relative humidity of 50%. The compressive strength of the mold cured for 1 h, 2 h, 3 h, and 12 h after placing the sand in the wooden pattern was measured according to JACT (Japan Association of Casting Technology) test method HM-1 (compression strength test method).\(^7\)

The test material (sand) used for the test mold was prepared by adding hardening catalyst to binder-coated sand by 3.6 mass% at the room temperature 25°C in humidity of 50%, by kneading with a mixer. Two comparative materials (sands) were prepared. For comparative material 1, hardening catalyst was added to 100 mass% silica sand with average particle diameter of 106 µm by 0.2 mass%.

For comparative material 2, triethylene glycol diacetate was added to silica sand with an average particle diameter of 106 µm by 0.2 mass%, and then with sodium silicate by 3.0 mass% (molar ratio 2.5 (SiO\(_2\)/Na\(_2\)O)).

### 2.2 Evaluation of characteristics of 3D AM mold

#### 2.2.1 Moldability and expansion rate test

3D additive manufacturing of a cylindrical test mold (30φ × 50 mm) was performed by the binder ink-jet printing the binder at a pitch of 280 µm in the X, Y, and Z axis directions, respectively. The moldability of the test mold was investigated, and the thermal expansion coefficient was measured for 5 min at the temperature of 1000°C, using the M-2 JACT test method M-2 (rapid thermal expansion measurement method).\(^8\)

The test material was prepared by adding hardening catalyst to the binder-coated sand by 3.6 mass% by ink-jet printing. On the other hand, the comparative material was prepared by adding hardening catalyst to silica sand with an average particle diameter of 106 µm by 0.2 mass%, and this was added with binder by 2.0 mass% by ink-jet printing to laminate the silica sand.

#### 2.2.2 Gas generation evaluation

Qualitative analysis of the gas components of the molds made by AM process using the above test material and comparative materials was carried out at 350°C by GC/MS (gas chromatography, Q1000-GCMS manufactured by Nippon Denshi Co., Ltd.).

### 3. Experiment Results and Discussion

#### 3.1 Fluidity of sintered artificial sand coated with binder

Figure 2 and Table 3 show the results of the fluidity test.\(^9\)

The comparative material (wet type) was prepared by kneading the hardening catalyst with silica sand (conventional process). Fluidity test results showed that the ratio \((D/d)\) of the spreading diameter \((D)\) of the material to the diameter \((d)\) of the slump cone opening was 2.3. Clumping of the sand was also observed. On the other hand, in the case of sintered artificial sand, \(D/d\) was 3.3, and the fluidity was higher than that of silica sand. As for binder-coated sintered artificial sand, \(D/d\) was 3.1, and the fluidity was maintained as almost same as the fluidity of sintered artificial sand without coating and there was no clumping. These findings show that the binder-coated sand has excellent moldability and excellent fluidity, and can be well coated. Thus, it is expected to contribute to improved mold density and higher molding rate.
3.2 Casting mold strength expression

Figure 3 shows the results of the mold strength expression test. From comparison between the test material and the comparative materials, it is confirmed that the compressive strength of the test material remained high for 1 h, 2 h, and 3 h after mixing the sand, and the hardening rate also improved. Moreover, it was also found that the comparative material, which is an organic binder, collapses due to thermal decomposition at temperature 200°C or higher, whereas the test material (inorganic binder) softens between 550 and 670°C, and becomes liquid between 730 and 780°C. Since the thermal decomposition of the sand does not occur in the molding temperature range of the aluminum alloy, it is considered to have sufficient heat resistance for pouring aluminum alloy.

The hardening mechanism of sodium silicate involves the progress of the gelation of silica due to the generation of salt and triethylene glycol by the hardening effects of the triethylene glycol diacetate catalyst, and hydrolysis of triethylene glycol diacetate as shown in Fig. 4. Furthermore, in the binder-coated sand, most of the water contained in sodium silicate is removed in advance, and hardening reaction is performed only with water contained in triethylene glycol diacetate aqueous solution. Thus it is assumed that the hardening reaction can progress with little water and hardening is accelerated because less water is released.

3.3 Moldability and linear expansion of 3D laminated casting mold

Figure 5 shows a mold made using the developed hardening system. The mold was finished to a smooth mold surface with more or less no bumps on the surface. Table 4 shows the results of the thermal expansion coefficient measured with a test are mold made for the thermal expansion test. The results of this test confirmed that the thermal expansion coefficient is about 1/6 compared to the comparative material made of silica sand.

However, the linear expansion coefficient of the test material is larger than that of the comparative material, most likely because the artificial sand does not expand. However, due to the expansion of the sodium silicate binder, the linear expansion coefficient is larger than that of sand without binder.

3.4 Components of Gas generated from mold

Figure 6 and Table 5 show the results of qualitative analysis of the gas components at 350°C. Since in the comparative material uses with an organic material as the binder, the generation of methyl furan, ethylbenzene, xylene and sulfur dioxide were confirmed when the sand decomposed. On the other hand, when binder-coated sand was used, most of the gas generated from the test material was water, which is considered to be effective for improving the working environment and preventing casting mold gas defects caused by hydrocarbon gas.

4. Conclusion

The following results were obtained in this study.
(1) Binder-coated sand made by coating artificial sand with sodium silicate can be used for 3D AM technique with
ink-jet material of ester aqueous solution made by dissolving triethylene glycol diacetate in water. In particular, the water in the aqueous ester solution elutes the dry sodium silicate coated on the binder-coated sand, and the sodium silicate forms silica gel due to the actions of the ester. It was confirmed that this effect bonds the sand particles together and improves the hardening rate due to the improvement of mold strength expression. Consequently, improvement of the accuracy of the mold can be expected.

(2) By using sodium silicate as the binder, most of the gas generated at high temperature becomes water, and this is expected to improve the working environment and reduce casting gas defects caused by hydrocarbon.

(3) The expansion coefficient of the mold made by the 3D AM technique using sintered artificial sand was 0.2 to 0.3%. Veining defects caused by thermal expansion of the mold due to the heat during pouring are reduced, and high quality castings can be expected.

Acknowledgements

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REFERENCES

4) Fuji Chemical Co., Ltd.: Product Catalog, (Fuji Chemical Co., Ltd., 1995) p. 5.