Rapid Prototyping of Fine Ceramics
-Slurry Casting Using Silicon Rubber Mold-

by
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1. Introduction

Layered manufacturing is a rapid prototyping method which is drawing attention for being able to produce real models directly from three-dimensional CAD data. The most commonly used rapid prototyping is the laser stereolithography method using photopolymer resins. Recently, models made by the method can be converted to metal by the lost investment casting. For ceramics parts, layered manufacturing using powder as the material was considered as an ideal method, but due to the low density of the R/P model, at the moment, slurry casting is the only method which can be applied to manufacture these parts from the practical view point.

In this study, the method of producing green powder parts by copying models using highly practical slurry casting shown in Fig.1 was investigated. Generally, plastic molds are used as the molds for copying in slurry casting, but in terms of separability from the mold, disassembly
of the mold, and wear of mold, the use of silicon rubber molds should prove to be more advantageous. Similar method has been reported to have been successful in the production of Si₃N₄ turbo chargers by using metal molds and a special binder and heating. Nothing is known about this method yet. Experiments to find a binder for slurry casting in room temperatures using rubber molds without water absorbability showed that there is an extremely promising binder made of water soluble phenol developed as a sand mold for casting. As a result of using this binder, a rapid prototyping method for ceramics with a high level of practical use was developed.

2. Forming Method

Fig. 2 shows the forming process applied in this experiment. First, the laser stereolithography model is copied onto silicon rubber to make the rubber mold, ceramics slurry containing water and binder is poured into this rubber mold, and the forming process is carried out. Because the rubber mold has good copiability but is not water-permeable, excessive binder content will cause the green part to collapse after debinding even if the slurry had solidified. For this reason, it is necessary to keep the binder content as low as possible in the process. In this experiment, two types of green parts were made—a simple venus status (using type A slurry) and a complicated turbo fan (using type B slurry).

First, the percentage of alumina powder making up the green part was set at 48% for type A and 47% for type B. Investigations were also carried out on the percentage of mixing the binder, hardener, dispersion agent, defoaming agent, and water in slurries containing 52% and 53% binder to make slurry with good liquidity. This slurry was poured into the rubber mold to produce the green parts. After the slurry hardened, the green parts were removed from the rubber mold, after which vacuum drying, debinding, and sintering were performed.
3. Experiment results

(1) Making the slurry

Taking into consideration the sintering characteristics of alumina ceramics, the binder content making up the slurry was set at 52 vol% for type A and 53 vol% for type B. The problem with these binder contents was how to make a slurry that can be poured easily, has low viscosity, and will produce green parts with appropriate strength. The results of preliminary experiments showed that the slurry viscosity is affected by the content of the binder considerably. Therefore for type A, the binder content was decreased to the level the green part did not collapse when separated from the rubber mold. Table 1 shows the mixing ratios of the type A and type B slurries used in this experiment.

It was also found that the order of mixing the materials is important for making low viscosity slurry. To make the slurry, first appropriate amounts of water and dispersion agent are mixed (too much dispersion agent will on the other hand cause the slurry viscosity to increase). Alumina powder is mixed with this mixture little by little at a high speed using a mixer to disperse the alumina powder agglomerate into primary particles. Next, the binder is added, followed by the hardener, and defoaming agent. This process was found to produce a low viscosity slurry.

(2) Slurry viscosity

Fig. 3 shows the relation between time and slurry viscosity when the hardener is added to the type A and B slurries used in the experiment. The horizontal axis indicates the time from the mixing of hardener into the slurry. The hardener was mixed for 15 seconds. Measurement results showed that the more the binder, the higher the slurry viscosity, and the quicker the hardening speed. In this experiment, the amount of

Table 1 Mixing ratio of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Mixing ratio (vol%)</th>
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<tr>
<td></td>
<td>Type A</td>
</tr>
<tr>
<td>Alumina powder, Average size: 0.5 μm</td>
<td>48.0</td>
</tr>
<tr>
<td>Main binder (water soluble phenol)</td>
<td>8.5</td>
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<tr>
<td>Hardener</td>
<td>1.9</td>
</tr>
<tr>
<td>Dispersion agent</td>
<td>0.6</td>
</tr>
<tr>
<td>Water</td>
<td>41.0</td>
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<tr>
<td>Defoaming agent</td>
<td>≤0.0001</td>
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Fig. 3 Relation between time and viscosity
hardener added was 20 wt% of the binder. The speed at which the slurry hardens can be investigated using the amount of hardener mixed and the type of hardener used. When the amount of hardener added is reduced, the hardening speed slows down but the demerit is it takes a long time for the green part to reach the strength at which it can be removed from the rubber mold. On the other hand, when the hardener amount is increased, it reduces the time taken for the green part to reach the strength at which it can be removed from the rubber mold, but the demerit is the slurry viscosity increases rapidly, and this decreases the time the pourable low viscosity slurry state is retained. The higher the viscosity of the slurry, the more the bubbles produced during pouring will not escape.

When the content of the hardener was increased for the type B slurry during one process performed, it was found that the pouring time was short (90 seconds), but the turbine-shaped green part could be removed in one hour. In this case, however, it was difficult to perform vacuum defoaming of the slurry after the hardener was added.

The slurries used in this experiment were also found to undergo thixotropy when the binder was added. For this reason, the viscosity increases according to the amount of binder added. For slurries not added with the hardener, it was possible to maintain low viscosity at a uniform level by adding vibrations. Even when the hardener was added, the vibrations added helped to slow down the speed at which the viscosity increased.

The slurry is poured while placing the rubber mold on vibration table and vibrating it. Because this pouring process is performed in air, a slight amount of bubbles were found in some of the complex shaped green parts. But it should be possible to produce bubbles-free green parts by carrying out the pouring process in vacuum.

To compare the viscosity of the slurry containing binder and that not containing, a slurry containing alumina powder, water, and deflocculant and having a powder density of 48 vol% was made and its viscosity was measured. The results showed that slurry that does not contain binder has a very low viscosity of 0.6 dPa-sec, indicating that the binder amount affects the viscosity of the slurry to a great extent.

(3) Strength of green part

The green part must have sufficient strength to be removed from the rubber mold after the slurry solidifies. The strength is determined by the amount of binder contained and the amount of binder hardened. In this experiment, two types of rubber molds with different shapes were used. The statue (Venus)-shaped green part was easy to remove from its rubber mold due to its simple shape. The green part strength is sufficient if it does not collapse when held by the hand. The strength of the turbo fan-shaped green part on the other hand has to be increased because the contact area between the rubber mold and green part is large and the wing part is thin. The compressive strength before and after drying was studied for the type A and type B slurries used in this experiment.
Table 2 shows the results. The compressive strength of the green part when removed from the mold was 5 kgf/cm² for type A and 76 kgf/cm² for type B. After vacuum drying these green parts for one hour at 100°C, the compressive strengths increased for both types, to 85 kgf/cm² for type A and 300 kgf/cm² for type B. The reasons for the increase are: the green part shrinks when dried and causes the strength to increase, and the heating of the green part causes the unhardened parts of the phenol resin (the binder) to harden and this increases the strength.

One method of increasing the green part strength quickly is to heat the rubber mold after pouring in the slurry. But in this case, it is essential to seal the mouth of the rubber mold for pouring in the slurry to prevent the moisture in the slurry from evaporating. If evaporation takes place, the green part may shrink and crack. As the green part will not shrink as long as there is no evaporation, cracking will not occur even if the green part is removed after a long time.

(4) Drying, debinding, and sintering of green part

Due to the good liquidity of the slurry used, vacuum defoaming was also carried out satisfactorily. The green part was found to contain a high amount of water after hardening and this was removed by vacuum drying quickly. After drying, air channels made up of holes from the water escaped out were formed in the green part. The presence of these air channels enabled the high speed debinding. Because the phenol resins used as the binder is a thermosetting resin, the green part did not deform easily even when heated during debinding. The normal sintering was performed after debinding. Fig. 4 shows the effects of the sintering temperature and retention time on the density.

<table>
<thead>
<tr>
<th>Table 2 Compressive strength of green parts</th>
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<tbody>
<tr>
<td>Compressive strength (kgf/cm²)</td>
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<tr>
<td>Before drying</td>
</tr>
<tr>
<td>Type A</td>
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<td>Type B</td>
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Fig. 4 Effects of sintering temperature and retention time on density
density, and Fig. 5 shows the laser stereolithography model, the rubber mold and the sintered product.

Fig. 5  Laser stereolithography model, rubber mold and sintered product
4. Conclusion

In this study, a rapid method of producing ceramic parts was developed. In the method, slurry is poured into a rubber mold copied from a laser stereolithography model made by layered manufacturing to obtain the green part. For the type A slurry, the weight of the sintered part was 100g and the porosity was 6%. For type B, because the weight of the sintered part was heavy (700g), and the sintering temperature and time were insufficient, the porosity was 12%, but this could be improved.

When the slurry had a certain level of viscosity and thixotropy, the binder and powder did not separate after pouring and forming, and the density of the green part was even. In addition, because this method produces air channels in the green part, debinding is good, which makes the method applicable to large ceramic green parts. Moreover, as the silicon rubber mold can be used repeatedly, the method can be applied not only to trial productions but small-lot production as well. The good copiability of the slurry also enables ceramic green parts copied with detailed patterns to be produced.

These above results indicates that this method may become one of the main methods of manufacturing ceramic parts using layer manufacturing. At present, studies are being carried out on a slurry casting method using metal powder as an attempt to apply this method to molds.

Acknowledgement

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Reference

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