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Fabrication of 3D Printed Metal Structures by Use of High-Viscosity Cu Paste and a Screw Extruder

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Three-dimensional (3D) printing is an important, rapidly growing industry. However, traditional 3D printing technology has problems with some materials. To solve the problem of the limited number of 3D-printable materials, high-viscosity materials and a new method for 3D printing were investigated. As an example of a high-viscosity material, Cu paste was synthesized and a screw extruder printer was developed to print the paste. As a fundamental part of the research, the viscosity of the Cu paste was measured for different Cu content. The viscosity of the paste increased with increasing Cu content. To print high-viscosity Cu paste, printing conditions were optimized. 3D structures were printed, by use of an extruder and high-viscosity metal paste with appropriate printing conditions, and then heat treated. After sintering, however, approximately 75% shrinkage of the final product was observed. To achieve less shrinkage, the packing factor of the Cu paste was increased by adding more Cu particles. The shrinkage factor decreased as the packing factor increased, and the size of final product was 77% of that expected.

Key words: High-viscosity material, 3D printing technology, viscosity, Cu paste, screw extruder, shrinkage

INTRODUCTION

It has been suggested 3D printing is the third industrial revolution. A variety of 3D printing methods have been introduced and equipment is available commercially. Traditional 3D printing methods can only print specific materials, for example thermoplastics, ultraviolet (UV) light-curable ink, and metal powder.[1–4] Because of this limitation, the range of 3D-printable materials is the biggest problem in 3D printing technology. To apply 3D printing technology to other industries and fields of research, this limitation must be solved. To solve the problem, use of high-viscosity materials for 3D printing was investigated in this research. Because of the high viscosity of the materials, the printed structure is retained after printing. Because high-viscosity materials consist of powder and high-viscosity flux, if a ceramic or metal powder is used in the high-viscosity material, 3D printing can be used to print all these materials. Even if the high-viscosity material does not include a powdered material, it has the special property that it can be used as a 3D printable material for special purposes.

In this study, high-viscosity materials were prepared and printed to confirm the efficiency of the high-viscosity materials and to optimize the printing conditions. High-viscosity Cu paste was prepared and printed as one example of 3D printable materials because of its wide range of applications. Printing a metallic 3D structure is one aspect of additive manufacturing that has received substantial attention. Such processes as selective laser sintering (SLS) and electron beam melting (EBM) have been used to fabricate 3D metal structures.[1] These processes directly melt metal particles and produce 3D structures by stacking and sintering

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metal layers. However, these processes have problems which make them difficult to apply in industry. The cost of the printing equipment and of its maintenance are rather high, because of the advanced laser and electron beam system. Another disadvantage is that the printing equipment can only print metal. Cost and limited printability are disadvantages when critical mechanical properties are required. In addition, too much time is consumed completing a printed 3D structure.

To solve these problems, high-viscosity, low cost materials are used in current 3D printing processes. Traditional metal 3D printers use metal powders, only, as printing materials; in this research, high-viscosity materials comprising mixtures of particles and flux have been used as printable materials. Usually, high-viscosity materials are synthesized by mixing particles, high-viscosity flux, and additives.[5–12] Typically, high-viscosity flux is prepared by using an organic solvent and additives, so it is hard to handle and needs special caution. However, high-viscosity flux has been readily synthesized by use of a water-soluble polymer and additives. As the main printable material, Cu particles have been used to synthesize high-viscosity metal paste, because Cu is one of the least expensive metals and has many applications because of its high electrical conductivity.[13,14]

Traditional 3D printing methods, SLS,[15] fused deposition modeling (FDM),[16] and stereolithigraphy apparatus (SLA),[17] can only print specially prepared materials, not high-viscosity materials. Therefore, other printing methods are needed to overcome the limits of current technology. To extrude high-viscosity materials, another printing process involving a screw extruder was used in this research. After printing of the high-viscosity material, treatment is required because otherwise 3D structures printed with high-viscosity material do not harden. Therefore, such hardening processes as UV curing or chemical or heat treatment should be used to complete the manufacture of printed structures. In this study, Cu particles were used as the main printable material, so sintering was conducted to harden the printed metal structure. In addition, conditions for screw extrusion were optimized for printing of synthetic high-viscosity materials. The viscosity of the material is the most significant property because it determines the nature and conditions of the printing process. Therefore, as a fundamental part of this research, the amount of Cu particles in the paste was varied and the effect on the viscosity of the material was studied.

EXPERIMENTAL

Materials

Cu particles were used to synthesize high-viscosity metal pastes; 106 μm (Acros Organics, 99%, powder) and 25 μm (Sigma Aldrich, 99%, powder) Cu particles were used. Polyvinyl carboxy polymer (MakingCosmetics) and poly(vinyl alcohol) (PVA; Fisher Science Education) were used as viscosity enhancement reagents in the high-viscosity flux.

Synthesis of High-Viscosity Metal Paste

To prepare the high-viscosity material, the viscosity enhancement reagent, 7 wt.% polyvinyl carboxy polymer, was dissolved in water. The pH of the solution was adjusted to 7 by addition of sodium hydroxide solution and then the solution was stirred until it was transformed into a gel. PVA was then dissolved in water to furnish a 7 wt.% PVA solution. The polyvinyl carboxy polymer gel and the PVA solution were then mixed in the ratio 95:5 polyvinyl carboxy polymer–PVA to prepare a high-viscosity flux. When the two polymers had been completely mixed, Cu powder was added to the flux. The Cu content was 50, 55, 60, or 65 wt.%. The Cu particles and the high-viscosity material were thoroughly mixed then the Cu paste was protected from any further contact with air.

Viscosity Measurement

The prepared high-viscosity metal paste was printed by use of an extruder type 3D printing machine. By use of this equipment the viscosity of the metal paste could be obtained by use of the Hagen–Poiseuille equation (Eq. 1)[18]:

$$Q = \frac{\pi r^4 \Delta P}{8 \mu L} \tag{1}$$

where Q is the volumetric flow rate, L is the length of the tip, r is the radius of the tip, ΔP is the difference between the pressure at the end and the top of the tip, and μ is the viscosity of material. In this experiment volumetric flow rate was measured every minute for a total of 5 min and the measured volumetric flow was plotted as a function of time. The slope was determined by the volumetric flow rate. The radius (1 mm) and the length (13 mm) of the tip were both fixed. ΔP was calculated by use of a material of known viscosity (viscosity range: 3,700,000–3,800,000 cP).

3D Printing Process and Heat Treatment

To print the high-viscosity metal paste and construct metal 3D structures, an extruder type of printing machine was developed and a FDM 3D printer (Opencreators, NP-mendel) was modified and connected to the extruder. A schematic diagram of the 3D printing equipment is shown in Fig. 1. Printing conditions were optimized according to the viscosity. All of the printed metal 3D structures were dried in air at room temperature then heat treated with charcoal by use of a box furnace (Box furnace, Lindberg/Blue M) at 950°C for 2 h.

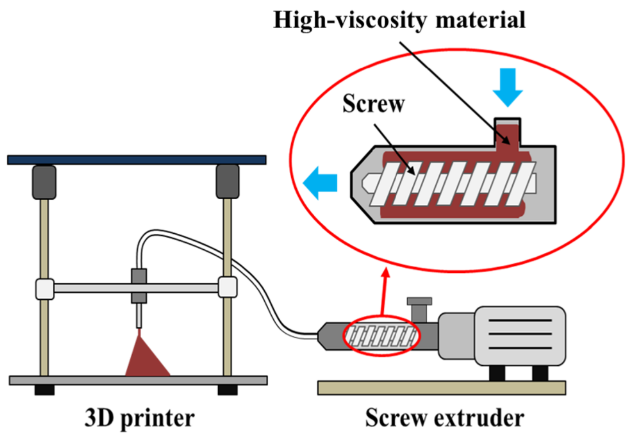

Fig. 1. Schematic diagram of a 3D printer for high-viscosity materials.

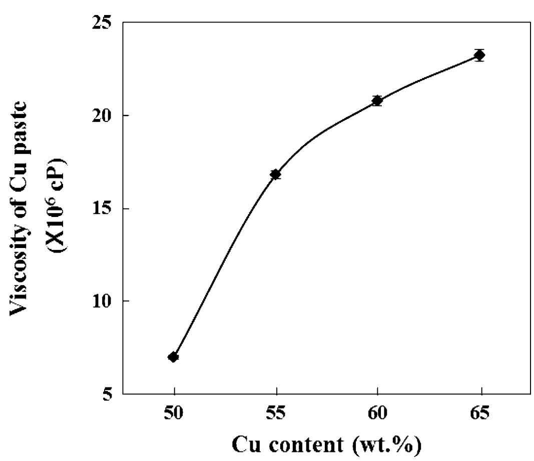

Fig. 2. Viscosity of paste with different Cu content.

RESULTS AND DISCUSSION

Viscosity of Metallic Paste Containing Different Amounts of Metal Particles

The viscosity of the paste was measured by use of the Hagen–Poiseuille equation. The results are shown in Fig. 2.

The viscosity of the Cu paste increased as the Cu content increased. The viscosity increased substantially from 50 to 55 wt.% Cu. The viscosity of the highest condition (65 wt.%) was approximately 2.3×10^7 cP. The difference between the lowest and highest Cu content was 15 wt.% whereas the viscosity for the 65 wt.% Cu content was approximately 3.3 times that for the 50 wt.% Cu content. The packing ratio between the flux and the particles changed because of addition of Cu particles. As the metal content increased, the fluidity of the paste decreased. The fluidity of paste can directly affect printing speed. Figure 3 shows the effect of Cu content on the volumetric flow rate of the paste.

The volumetric flow rate dropped substantially from 50 to 55 wt.% Cu, then decreased sharply.

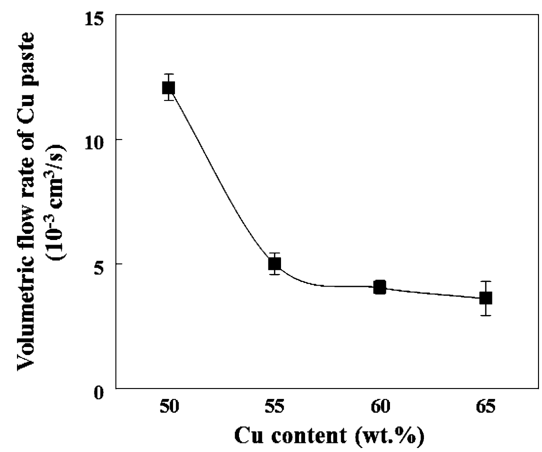

Fig. 3. Volumetric flow rate of Cu paste for different Cu content.

Table I. Printing conditions

Printing condition	Value
Tip size	500 μm
Printing head speed	2–10 mm/s
Layer height	0.4 mm
Fill density	50–90%
rpm (ΔP, screw extruder)	45 rpm

The volumetric flow rate of the Cu paste decreased as the metal content increased. This means that when the viscosity of the paste is high the volumetric flow rate is low, which reduces the printing speed. To increase the printing speed, the viscosity of the paste should be reduced. However, the viscosity of Cu paste was determined by the Cu particle content and because the maximum Cu powder content was 65 wt.% in this work, the highest Cu content only was used to print and fabricate the 3D structure.

Printing Process and Conditions for 3D Metal Structure

3D metal structures were printed by use of the high-viscosity Cu paste and a 3D printer with a screw extruder. To obtain a fine 3D metal structure, the printing conditions list in Table I were used.

To control the quantity of paste printed the speed of rotation of the screw extruder was fixed and the printing head speed, only, was changed. Because fill density can affect the quality of the final structure, this was also changed in this work. These conditions are very important for printing high-viscosity materials because, unlike traditional 3D printing processes, for example FDM, the printed material does not solidify quickly. Therefore, if the printing speed is too fast, the printed layers might not be connected. In addition, if the fill density is too low, the printed layers cannot be stacked properly (or the printed layers would collapse) and the final printed structure might not be the same as the 3D model generated by computer-aided design (CAD). If the fill density is too high, the printed layers can overlap, compromising integrity. When patterns overlap, excess printed material will remain in the printed layer and will push outward from each other. These excess materials can cause expansion of each printed layer. Thus, if the fill density and the printing speed are not optimized, fine products cannot be fabricated by use of high-viscosity materials. Examples of these problems are shown in Fig. 4.

To print the prepared Cu paste, printing conditions were optimized. Printing head speed was controlled at 6–8 mm/s and fill density was controlled between 75 and 85%; these conditions were suitable for printing fine 3D structures. 3D structures printed by use of high-viscosity Cu paste are shown in Fig. 5.

After printing, the 3D structures were heat treated. Because of the heat treatment, the surface of the sintered 3D metal structure was not clean and the size of final product shrank. To measure the shrinkage of the final product, cylindrical structures were printed and heat treated. After this process,

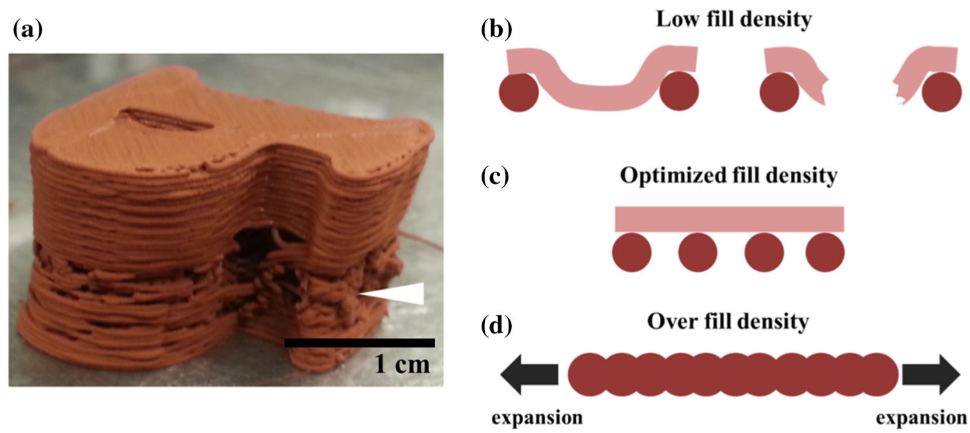

Fig. 4. Problems during printing high-viscosity material without optimization of printing conditions: (a) The result from printing of high-viscosity material without optimization of printing head speed and ΔP, and schematic diagram of high-viscosity material printing with: (b) low fill density, (c) optimized fill density, and (d) over fill density.

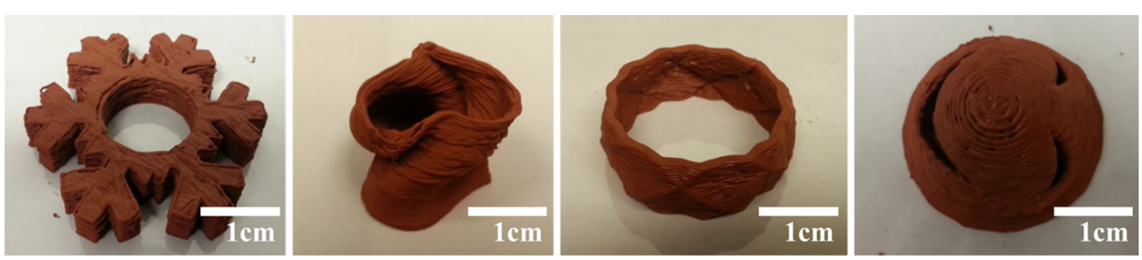

Fig. 5. 3D structures printed by use of Cu paste (106 μm, 65 wt.%) and screw extruder 3D printer.

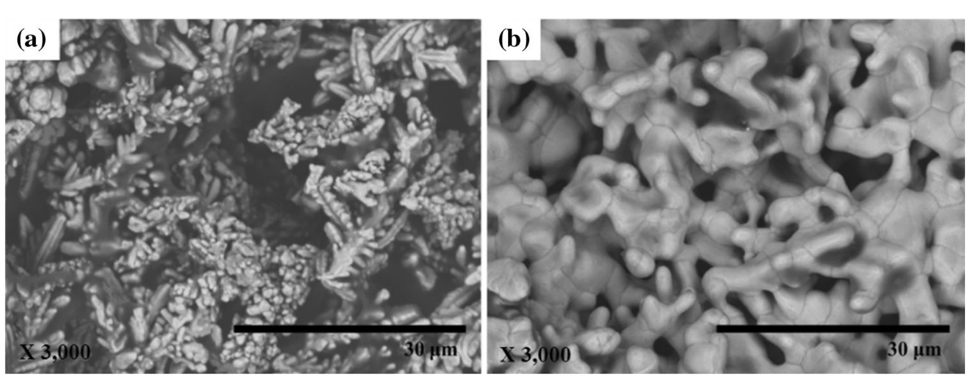

Fig. 6. SEM images of surface of a 3D metal structure: (a) before sintering; (b) after sintering.

the volume of the printed cylinder was measured. The volume of the final structure was reduced to 25% of its original volume. During the heat treatment process, evaporation of the high-viscosity flux and binder occur, which creates many void spaces between the layers and metal particles. In addition, the distance between the metal particles decreased because metal particles melted and formed necks. Metal particles can connect but, because of the empty spaces resulting from the large amount of flux in the paste, the size of final structure was reduced. Scanning electron microscopy (SEM) images of the surface of a 3D structure are shown in Fig. 6.

In Fig. 6a there is a large amount of empty space, but the structure can maintain its shape because of high-viscosity flux and binder in the paste. In Fig. 6b, the surface of the 3D structure has less empty space than in Fig. 6a and the particles in Fig. 6b are well connected to each other. Therefore, during the sintering process, metal particles fill the empty space. For this reason, the size of the final product reduced. After heat treatment, some samples had cracks on the surface as a result of the rapid shrinkage that occurred during the heat treatment process. To reduce the defects and shrinkage of the final product, less flux should be used and the metal content should increase.

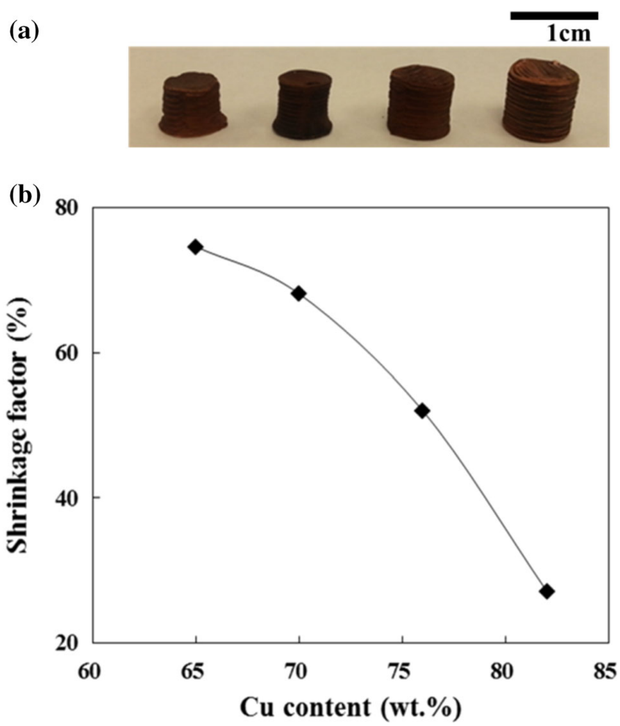

Fig. 7. Shrinkage factor for the paste and comparison of final structure size for different Cu content: (a) shrunken samples with different Cu content after heat treatment; and (b) plot of shrinkage factor as a function of Cu content.

Effect of Packing Factor on Fabrication of Metal 3D Structures

To prevent formation of defects and the effect of shrinkage, high-metal-content Cu paste was prepared. Cu particles of diameter 25 μm were mixed with high-viscosity flux. A maximum 86 wt.% Cu particles could be mixed with the flux. However, 86 wt.% Cu paste was too thick and its adhesion was too weak, so 82 wt.% Cu paste was printed by use of the screw extruder. In this part of the experiment, the packing factor of the Cu paste was changed by use of different particle sizes. To confirm the effect of packing factor on shrinkage of the final product, 106 μm and 25 μm Cu were mixed at different ratios (106 μm:25 μm = 7:3 and 3:7). Four types of Cu paste were synthesized and printed. In addition, the same printing conditions were applied and adjusted for printing of the Cu paste. The sintering process was also conducted under the same conditions. After heat treatment, the volume of the final structure was measured. The volume of the final product was approximately between 25% and 77% of its original 3D modeling size. By reducing the size of the Cu particles and increasing the proportion of small particles in the paste, the Cu content can be increased from 65 wt.% to 82 wt.% which, in turn, reduces shrinkage of the final product. The measured shrinkage factor for different Cu content is shown in Fig. 7.

Figure 7 shows how the shrinkage factor decreased as the Cu content of the paste was increased. Increasing the Cu content causes an increase of the packing factor of the Cu paste. Cu paste with a high packing factor should be used to reduce shrinkage of the final product. By applying

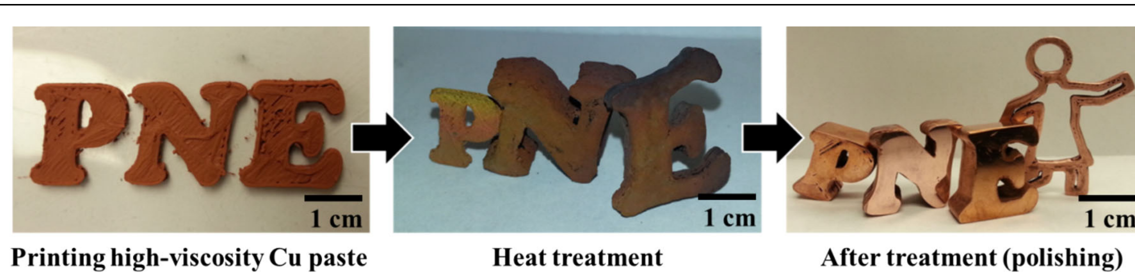

Fig. 8. Complete process for fabrication of 3D metal structures from high-viscosity Cu paste.

the information from this result, shrinkage of final structure can be prevented or reduced.

Even with an increase in Cu content, small cracks were observed for some samples after sintering. The whole process for fabricating metal 3D structures required both the extruder printing process and the sintering process, to obtain a fine product free from small cracks or defects. As one treatment method, simple polishing was performed. After finishing, the rough surface of the product was properly cleaned. The complete fabrication process for 3D metal structures is illustrated in Fig. 8.

CONCLUSION

In this research, high-viscosity Cu paste was synthesized then printed by use of a 3D printer with a screw extruder. A fundamental aspect of this research was measurement of the viscosity of the Cu paste by use of our equipment and the Hagen–Poiseuille equation, because the viscosity of 3D printable high-viscosity materials is hard to measure by use of conventional methods. As the Cu content was increased, the viscosity of the Cu paste also increased; the viscosity of the printed paste containing 65 wt.% Cu was 2.3×10^7 cP. The viscosity of materials with extremely high viscosity can be measured by use of this method. In addition, to obtain a satisfactory 3D structure, printing conditions for high-viscosity Cu paste must also be optimized for pastes of different viscosity. In this work a suitable printing speed was 6–8 mm/s and the fill density was 75–85%.

Sintering was used as a method of treatment. After sintering, shrinkage of the final product was observed. The shrinkage factor decreased as the Cu particle content was increased. In this study, a shrinkage factor of 23% was obtained for the paste with the highest Cu content. It was also confirmed that as particle size was reduced, the maximum Cu content of the paste was increased. Also, when 106 μm and 25 μm Cu particles were mixed to modify the packing factor of the Cu paste and increase Cu content, the Cu content of the paste increased as the proportion of smaller particles in the paste was increased. Therefore, to prevent shrinkage of the final product, the packing factor of the Cu paste should be increased and the proportion of flux in the metal paste should be reduced.

After sintering, polishing, a common method of surface treatment, was performed to remove the cracks. Depending on the printed material, this final step can be changed. Therefore, after treatment, methods suitable for the specific materials should be developed to improve quality of the final 3D structure obtained by printing high-viscosity materials.

Printing processes and conditions can change as a result of changes of viscosity, and the quality of the 3D structure might also change. The viscosity can be affected by several factors including packing factor, particle size, shape, and high-viscosity flux composition. The viscosity of materials and the factors affecting viscosity are significant aspects of 3D printing with high-viscosity materials. Therefore, for further research to improve and apply these materials and processes effectively, the relationship between viscosity and factors affecting the viscosity of materials should be analyzed and studied thoroughly. A prototype 3D printer with a screw extruder for high-viscosity materials was used in this research to produce the printed products. To improve the quality and accuracy of the final products, printing equipment with optimum printing conditions should be developed.

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