Preparation of Three Dimensionally Electroconductive Pattern of Si₃N₄–TiN System by Ink Jet Printing

Hisanori YOKOYAMA, Seizo OBATA, Nobuhisa KATO, Tadashi HOTTA*, Hiroya ABE**, Makio NAITO** and Shin-ichi HIRANO***

Gifu Prefectural Ceramics Research Institute, 3–11, Hoshigadai, Tajimi-shi, Gifu 507–0811, Japan
*Japan Fine Ceramics Center, 2–4–1, Mutsuno, Atsu-kku, Nagoya-shi 456–8587, Japan
**Joining and Welding Research Institute, Osaka University, 11–1, Mihogaoka, Ibaraki-shi, Osaka 567–0047, Japan
***Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya-shi 464–8503, Japan

Three-dimensional electroconduction pattern of Si₃N₄–TiN system was prepared using the ink jet printing method. Two kinds of 20 vol% ink were prepared by milling insulating powder (Si₃N₄) and electroconductive powder (TiN), of which the viscosity and the dispersibility were carefully adjusted. The droplet formation process and the compact characters were examined, and the effect of the ink characters on both printing and forming behaviors was studied. It was revealed that the viscosity and the structure of the ink influenced the printing behavior and the compact characters. The laminated body was processed by patterning on a compact of Si₃N₄ followed by firing for 3 h at 1750°C in N₂. The sintered body showed an interesting structure with three-dimensional electroconduction pattern.

[Received August 5, 2003; Accepted December 11, 2003]

Key-words: Ink jet printing, Three-dimensional electroconduction pattern, TiN, Si₃N₄ ink characters, Printing behavior, Compact characters

1. Introduction

The ink jet printing system becomes an attractive technique for producing the materials in a wide variety of applications, such as personal color printing, bar code printing, flat-panel displays manufacturing and rapid prototyping. Advantages offered by this method include low-cost process, rapid manufacture and flexible production, because of printing directly by the computer control.

Currently, solid free forming methods of ceramics using ink jet printing system have been developed. These methods were proposed as three dimensional printing (3DP) and direct ceramic ink jet printing (DCIJIP).

The 3DP is the method by which components are built by printing of a binder onto the thin layer of spreading dry powders or slurry. Enokiyo achieved the fine conductive line formation with Ag by the 3DP system. The DCIJP is the system where ceramic ink is deposited with droplets through a nozzle. A new DCIJP method for printing by wax based ink in the hot melt was also proposed.

There are two types of ink jet printer which are classified into continuous type and drop on demand (DoD) type. The DoD printer can be employed the fine patterning in comparison with the continuous printer, because the capability of the distance between a nozzle and a substrate is smaller. In addition, using multiple nozzle, the components with a composite architecture or graded composition can be fabricated.

The authors have already succeeded the fabrication of functional gradient materials of Si₃N₄–TiN system by the DoD ink jet printing.

Ceramic ink for the ink jet printing has to be adjusted viscosity and stability, in order to prevent the blockage of the nozzle and the hard sediment. It is also important to make clear the feature of droplet formation mechanism and the lamination character for the fabrication of fine components. The effect of ink character on both printing and forming behaviors has to be extensively examined in detail.

This study was carried out to understand the effect of the TiN ink character on the droplet formation process and the compact character, and then produce the three-dimensional conduction pattern of Si₃N₄–TiN system using the ink jet printing.

2. Experimental

2.1 Preparation and characters of ceramic inks

The starting materials were TiN (TiN-01, Japan New Metals Co.) and Si₃N₄ (E-10, Ube Industries Ltd.) with 5 mass% Y₂O₃ (NRN, Daichi Kigenso Kagaku Kogyo Co.) and 5 mass% Al₂O₃ (AKP-30, Sumitomo Chemical Ltd.). Mean particle size of TiN, Si₃N₄, Al₂O₃ and Y₂O₃ powers was 1.8, 0.45, 0.34 and 0.33 μm, respectively. TiN slurry (40 vol%) and Si₃N₄ slurry (40 vol%) were prepared with ion exchanged water by ball-milling for 24 h. Both slurries were prepared at pH over 9.5 with NH₄OH. TiN ink and Si₃N₄ ink were then diluted at 20 vol% by polyethylene glycol and water. The solvent ratio was adjusted to be water: polyethylene glycol = 8:2. Microcrystalline cellulose (MC) was added to prevent sedimentation of the ink by adjusting the viscosity. The effect of the TiN ink character on both printing and forming behaviors was studied. The amount of MC in the TiN inks is shown in Table 1.

The apparent viscosity of the ink was measured from 100 s⁻¹ to 3600 s⁻¹ shear rate after 60 s at 25°C, using a viscometer (VT550, HAAKE) with a double gap cylinder sensor. The ink of 100 × 10⁻⁶ m² was poured into a 100 × 10⁻⁶ m² graduate cylinder and left for 24 h in order to estimate the stability and the dispersion of the ink. The sedimentation velocity of the TiN ink was measured by the change of the sediment volume with time.

Abe et al. have reported that the powder agglomerate structure of a slurry was observable directly by setting the slurry in the thin glass cell. The packed structure of the TiN particles in the ink was observed in the 10 μm thickness of glass cell with the optical transmission microscope (ECLIPSE E600, NIKON). In this apparatus, the solvent part in the slurry showed white color by the light transmission through the slurry, and some parts of particles packing structure showed black or gray color because the particles in the slurry intercepted the light transmittance.
2.2 Ink jet printing and printing characters
 Printing was conducted using the DoD ink jet printer (Michelangelo, LAC Corp.) with a nozzle of the valve system. Figure 1 shows a scheme of the printing system. The nozzle of 0.1 mm diameter is opened or closed by operating the needle, which is controlled with applied current to the solenoid coil. When the nozzle is opened, the droplet is ejected by high air pressure (0.15 MPa) introduced to the ink reservoir. The ink is circulated by the pump in order to prevent the sedimentation of particle. The resolution of this ink jet printer was 80 dpi. This resolution was not enough, but this printer could be used for the higher viscosity ink, which made it possible to increase the solids loading in the ink. The other ink jet printer systems required the viscosity of ink of less 10 mPa·s and the solids loading of ink of less 10 vol%.

The formation process of droplets during the ink jet printing was characterized with a monitoring system (HS-4540, NAC), which made it possible to observe the jetting behavior of the droplet in 0.22 ms interval. Mean ejection velocity was determined from the relationship between distance and time.

2.3 Compact characters
 The compact body was fabricated by multi-layer printing on the porous substrate. The printed compacts were calcined at 1200°C for 1 h in N₂ atmosphere. The apparent density and the apparent porosity of the calcined body were measured by the Archimedes method. The pore size distribution of the calcined bodies was measured by a mercury porosimeter (AutoPore III 9429, Micromeritics).

2.4 Preparation of three-dimensional electroconduction pattern of Si₃N₄-TiN system
 The compact body of silicon nitride formed by slip casting was used as a substrate for printing. The three-dimensional electroconduction pattern was fabricated by multi-layer printing of each pattern as shown in Fig. 2. The compact bodies were finally fired in 0.7 MPa N₂ atmosphere at 1750°C for 3 h. The cross section of the sintered body which fabricated by alternately multi-layer printing was observed by a scanning electron microscope (S-2400, Hitachi Ltd.).

3. Results and discussion
3.1 Characters of ink
 In the ink jet printing, it is important to control the stability of the ink. Figure 3 shows the result of sedimentation test of the TiN ink. The sediment volume of TN-1 ink without MC decreased rapidly compared with other inks, and became about 40 × 10⁻⁶ m³ after 24 h. The sediment volume of TN-2 and TN-3 inks decreased almost linearly with time.

Figure 4 shows the apparent viscosity at shear rate 100 s⁻¹ and the sedimentation velocity as a function of the amount of MC. The sedimentation velocity was calculated from the initial gradient of the sedimentation test. As the amount of MC increases, the apparent viscosity also increases, but the sedimentation velocity decreases. Especially, the sedimentation velocity decreases extremely much by adding over 0.1 mass% MC to the ink. It was confirmed that the addition of MC was effective in the control of the sedimentation behavior. All inks showed the pseudoplastic flow, and the relationship between the apparent viscosity and the amount of MC tended to be same regardless of shear rate, as reported.¹⁵

The photographs of the powder agglomeration structure of TiN ink are shown in Fig. 5. In TN-1 ink without MC, the solven area which shows white color was very small and uniformly dispersed in the ink. The inks with MC have rather large solvent area, which became more remarkable in TN-2 ink. It was supposed that the solvent area expanded due to the

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<th>Table 1. Characters of TiN Ink and Printing Properties</th>
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<td>TN-1</td>
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<td>TN-2</td>
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<td>TN-3</td>
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Re : Reynolds number

- Fig. 1. Schematic diagram of ink jet printing system.
- Fig. 2. Pattern of multi-layer printing.
White area: Si₃N₄ and black dot and line: TiN.
net-work agglomeration of the particles in the ink. The addition of MC accelerated the agglomeration of particles in ink. It was found that the apparent viscosity increased with MC and the sedimentation velocity decreased with MC.

3.2 Effect of ink characters on ink jet printing

The formation process of droplets during ink jet printing was characterized by monitoring a single jet ejection. Figure 6 shows the behavior of TiN droplets ejected from a nozzle. The droplets of TN-1 and TN-2 ink were ejected like fiber, and the length of TN-1 droplet was longer than that of TN-2. The droplet of TN-3 ink shows different behavior from that of other inks. The ejection velocity measured from this jetting behavior is shown in Table 2. The ejection velocity decreases as the amount of MC increases. In particular, the velocity of TN-3 ink with 0.2 mass\%MC is relatively low. In a nozzle of thermal system, it was reported that the ejection velocity and the droplet volume decreased as the ink viscosity increased.\textsuperscript{17} The same behavior was observed in this printing system, since the viscosity increased as the amount of MC increased (Fig. 4).

One of the important factors for the droplet formation and jetting process is the Reynolds number which belongs to the hydrodynamic parameter.\textsuperscript{17} Reynolds number ($Re$) of the droplet ejection at a nozzle tip is shown as follows:

$$Re = \frac{V \cdot D \cdot \rho}{\eta}$$  \hspace{1cm} (1)

where $V$, $D$, $\rho$ and $\eta$ are the ejection velocity, the diameter of the nozzle, the ink’s density and the ink’s viscosity, respectively. The apparent viscosity at shear rate 3600 s\textsuperscript{-1} in this experiment was employed as $\eta$ due to the pseudoplastic flow of the ink. The values of $V$, $\rho$, $\eta$ and $Re$ calculated by equation (1) are shown in Table 1. $Re$ decreases as amount of MC increases. The Reynolds number shows the ratio between inertial

![Fig. 3. Sedimentation test of TiN ink.](image1)

![Fig. 4. Apparent viscosity and sedimentation velocity of TiN ink as a function of MC concentration.](image2)

![Fig. 6. Photographs of droplet formation process of TiN ink.](image3)

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<th>Table 2. Characters of TiN Calcined Body</th>
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![Fig. 5. Photographs of powder agglomeration structure of TiN ink in 10 $\mu$m glass cell.](image4)
force and viscous force in the pipe flow. In the pipe flow, \(Re\) under 200 becomes the laminar flow, and the unstable flow causes in \(200 < Re < 2300\). Besides, in \(Re\) above 2300, the turbulent flow causes. As a result of examining the dye ink using a nozzle of thermal system, \(Re\) was 20~90, and the droplet formation of ink with large \(Re\) was suitable for the printing.\(^{17}\) \(Re\) of the ceramic ink became a comparatively close value in comparison with that of the dye ink.

### 3.3 Effect of ink characters on formation of laminated body

Figure 7 shows the pore size distribution of TiN calcined body fabricated by multi-layer printing. In TN-1 ink without MC, the pore diameter of maximum pore volume frequency is 0.23 \(\mu m\). As the amount of MC increases, pore diameter increases. Table 2 shows the apparent density and the apparent porosity of TiN calcined body measured. As the amount of MC increased, the density decreased and the porosity increased. The density of the compact printed by TN-1 ink agreed with that of the compact formed by slip casting with the dispersion slurry.\(^{18}\)

The ink characters were found to influence strongly the compact character. It was indicated that the density of the compact decreased as the viscosity of ink increased. It was observed that the structure of laminated body was affected by ink agglomeraturn as shown Fig. 5. It was guessed that the net-work agglomeration structure of particle in the ink directly affected the structure of the compact. Therefore, the ink had to be prepared with controlling the viscosity and the net-work agglomeration structure.

### 3.4 Preparation of three-dimensional conduction pattern of \(Si_3N_4\)-TiN system

The ink characters affected the printing behavior and compact characters. The inks had to be prepared to have similar characters, when multi-layer printing was conducted by two kinds of ink, TiN ink and \(Si_3N_4\) ink. The TN-2 ink was selected as the TiN ink, because of low viscosity and high stability. The \(Si_3N_4\) ink was carefully prepared to adjust the same viscosity as that of the TiN ink. It was achieved by adding 0.1 mass\%MC in the \(Si_3N_4\) ink. The apparent viscosity at shear rate 3600 s \(^{-1}\) and the ejection velocity of \(Si_3N_4\) ink were 8.3 mPa\cdot s and 6.63 ms \(^{-1}\), respectively. The sediment of this ink was not occurred after 24 h.

Figure 8 shows a SEM photograph of the cross section of the laminated body sintered at 1750°C. Each green thickness of the TiN layer and the \(Si_3N_4\) layer was almost same. The sintered layer thickness is slightly different due to a difference of the shrinkage. In the TiN layer, some microcracks are observed as shown with arrow due to the differences in shrinkage and thermal expansion coefficient. Using two kinds of ink, the compact was prepared by laminating 6 layers shown in Fig. 2 on the \(Si_3N_4\) compact. Figure 9 shows the photograph of the multi-layer ceramic sintered at 1750°C. By adjusting the ink characters, this ink jet printing method can afford a promising system for producing the ceramics with three-dimensional patterns.

### 4. Conclusions

1. In the ink jet printing of the DoD system, the characters of ink, such as viscosity and powder agglomerate structure, had influence on the printing behavior and the compact characters.
2. The powder agglomerate structure of the ink was good agreement with the structure of the printing compact. As the agglomerate in the ink increased, the pore size of the compact increased and the density of the compact decreased.
3. The sintered body with the three-dimensional pattern could be formed by multi-layer printing using two kinds of ink with controlled the ink characters.

### References