Thermoreversible colloidal gelation for direct-assembly of nanoparticles†

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1. Introduction

Direct ink writing (DIW) techniques offer the ability to produce ceramic components on-demand with complex structures. These techniques can be attractive routes for advanced ceramics, sensors, composites, tissue engineering scaffolds and photonic materials[1],[2]. Several approaches such as robocasting [3],[4], fused deposition [2],[5], and micropen writing [6] have been introduced and have demonstrated solid freeforming of 2D and 3D colloidal structures via a layer-by-layer deposition of particle based inks. In each approach, ink is continuously extruded through a micro-nozzle to create a filamentary element.

Nanoparticle suspensions for filament-based direct writing techniques must satisfy two important criteria [4]. First, they should exhibit a well-controlled viscoelastic response, i.e., they flow through the deposition nozzle and then set immediately to facilitate shape retention of the deposited features. Secondly, they should contain a high volume fraction of powder to minimize drying-induced shrinkage after assembly is complete, i.e., the particle network must be able to resist compressive stresses arising from capillary tension. The developed nanoparticle ink was an aqueous colloidal gel comprised of poly(acrylic acid)(PAA)-coated $BaTiO_3$ nanoparticles, whose interactions were carefully modulated by changing ionic strength through the addition of monovalent or divalent salt species [7]. However, there is a large risk that the rapid gelation induced by change of salt concentration or pH may result in large inhomogeneities in the dense suspension.

In this study, we have newly developed thermoreversible viscoelastic slurries which may provide homogeneous gel state for DIW. Its thermoreversible property increases reliability on the preparation of homogenous gel and allows easy operation on the processes of DIW including ink charge and nozzle cleaning. The slurry of ceramic nanoparticles was prepared with addition of poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers [8],[9] and then applied for DIW. The PEO-PPO-PEO aqueous solution with enough concentration shows nearly Newtonian behavior (sol state) at cooled temperatures (5°C) and thickened (gel state) at room temperature (25°C) or above 25-70°C. These states were reversible with the temperature change. The reversible sol-gel transition can be appeared by physical cross-linking of the triblock copolymer due to temperature-induced hydrophobic interactions.

2. Experimental

(Material)

Alumina powder (TM-DAR,Taimei Kagaku, Japan) was used for the model particles. The specific surface area of the powder, measured by nitrogen adsorption, was approximately $13m^2/g$ yielding an equivalent spherical diameter of 120nm. A poly(acrylic acid)(PAA) type dispersant (CELNA D305, Chukyo-yushi, Japan) was used. A high affinity of PAA on oxide surfaces can promote the colloidal stabilization of oxide particles in aqueous system. Poly(propylene oxide) - poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers (Lutrol F127, MW~12,000, BASF, Germany) as a gelling agent. Deionized water was used as solvent.

(Preperation of colloidal ink)

The solid volume fraction of alumina in the aqueous suspension was set at 15vol%. The amount of PAA added was 1.0mass% of the solid. The suspension was milled in a laboratory scale ball mill for 24h using alumina milling media. Then, F127 was mixed and dissolved under cooling below 10°C. The total amount of F127 added was 29mass% of the solid.

(Rheological Measurements)

The rheological measurements of the colloidal inks were conducted using a rheology meter (HAAKE Rheostress RS600, Thermo fisher scientific Inc., USA). As sensor attachments, cone-plate type sensors with 20 and 35mm diameters were employed. To avoid undesired influence from different mechanical histories, samples were homogenized by shearing at an identical rate of $20s^{-1}$ for 10s and left standing for an additional 10s prior to measurement. Flow curves were automatically recorded via a built-in program. The measurements were performed with the following input conditions: the shear rate increased logarithmically from $0.1s^{-1}$ to $100s^{-1}$, over the time period of 2min. The measurement temperatures were 5 and 30°C.

(Direct Ink Writing)

A robocasting system with a micro-pen was employed. The colloidal ink was housed in a syringe and warmed at 30°C to induce sol-gel transition. And then the resultant

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colloidal gel pushed out as a filament through a tapered nozzle (diameter, D=100μm) by a pneumatic system. The filament was deposited on a plate or deposited layers while the position of the nozzle was moving with a CAD system control. The deposition was carried out in air, and the plate for deposition was warmed at 60°C. The deposited colloidal gel was dried with keeping the assembled shape.
The CAD program was designed to form the 3D-woodpile structures. The width between lattices was set 500μm.
(Sintering)

After drying, the assembled specimen was burned to remove polymers at 500℃ for 5h and then sintered at 1450℃ for 2h.

3. Result and discussion

Figure 1 shows shear stress as a function of shear rate for the prepared colloidal ink at 5 and 30℃. Viscosity of the colloidal ink drastically increased with increase of temperature. The shear stress at the low shear rate ($0.1s^{-1}$) was about 100Pa (at 30℃). It was applicable for the DIW. Actually, the 3D wood-pile structure was successfully formed without any defects.

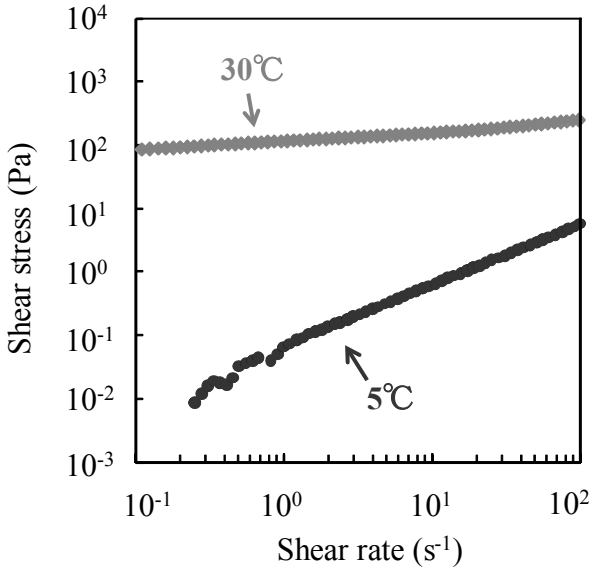

Fig. 1 Shear stress as a function of shear rate for the prepared colloidal inks

Figure 2 shows the photographs of the specimen assembled by the DIW. Fig.2(a) was taken by optical microscope. Fig.2(b) and Fig.2(c) were taken by scanning electron microscope (SEM). The wood-pile structure was formed according to the CAD program. The filament which was pushed out through the nozzle (diameter, D=100μm) swelled a little because of release from the pressure at the nozzle. After sintering, the diameter of the sintered filament was 125μm. The width between the lattices of the sintered specimen was about 380μm. The shrinkage with the sintering was about 20%.

4. Conclusions

In this study, we have newly developed thermoreversible viscoelastic slurries which may provide homogeneous colloidal gel states of nanoparticles for a direct writing technique. We used the PEO-PPO-PEO block co-polymer as a gelation agent. Using the present colloidal gel, the 3D wood-pile structure of alumina nanoparticles was directly formed.

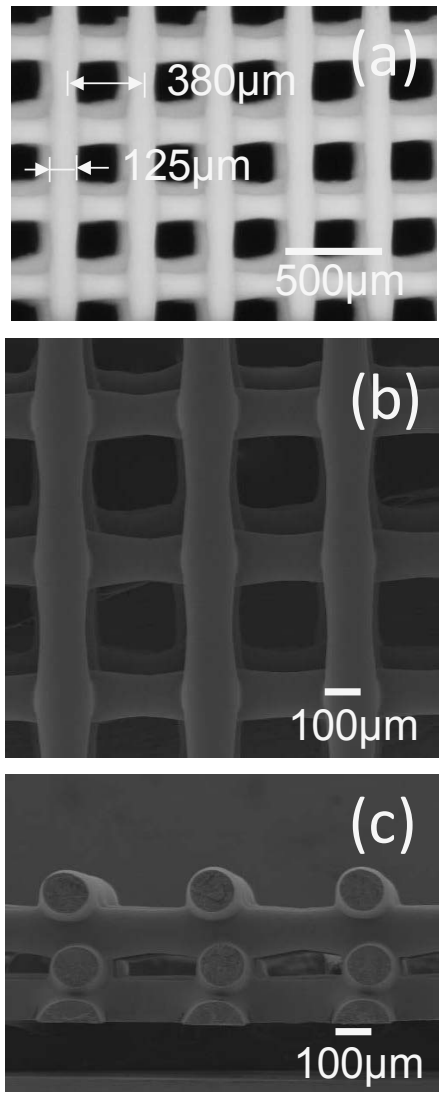

Fig. 2 Photographs of the assembled wood-pile structure after sintering at 1450°C
(a) optical microscope (b),(c) SEM

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