

Free-polymer-induced Gelation of Non-aqueous Colloids for Direct Ink Writing

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Direct ink writing (DIW) facilitates the fabrication of three-dimensional (3D) green structures through the layer-by-layer deposition of colloidal gel-based inks. Several gel designs have been developed for aqueous systems. Here, we report a facile gelation method for a non-aqueous system: Y_2O_3 -stabilized ZrO_2 (YSZ) particles dispersed in ethanol. First, fluidic and concentrated YSZ colloids were prepared using polyethyleneimine (PEI) as a dispersant. Then, a fluid-to-gel transition was triggered by adding polyvinyl butyral (PVB) as a free polymer. The resulting colloidal gels had a viscoelastic response adequate for DIW. Further analysis revealed that the depletion flocculation mechanism plays an important role on this gelation. Moreover, using the non-aqueous colloidal gel, a helical coil structure of $\sim 100\ \mu\text{m}$ diameter was patterned via the deposition of a continuous filament extrusion through a cylindrical nozzle in a water reservoir. During the deposition, a PVB film was formed *in situ* on the surface of the filament because of the poor solubility of PVB in water, which was used to avoid variations in the ink rheology owing to unexpected ethanol evaporation. The present methodology may be a useful route for the engineering of 3D green structures.

Keywords: Direct-ink-writing, Non-aqueous system, Gelation, Rheology, Depletion flocculation.

1. Introduction

Additive manufacturing (AM) allows for the manufacturing of ceramics without molds. Recently, this technique has rapidly grown [1,2]. Direct ink writing (DIW), which is a type of low-cost AM, offers the materials flexibility and allows for the fabrication of three-dimensional (3D) colloidal structures of green bodies via the layer-by-layer deposition of a continuous filament that is extruded through a cylindrical deposition nozzle [3-6]. The diameter of this filament is typically 100-250 μm [3,6]. These structures would be useful for a great number of applications as assembled nanomaterials [7], composite soft materials [8], and tissue engineering scaffolds [9].

Aqueous concentrated colloidal gels have been widely used as inks for DIW [3-6], because their rheological behavior, shear thinning with a large yield stress, is suitable for easy filament-flow during extrusion while holding their shape after deposition. Additionally, concentrated colloidal gels minimize the drying-induced shrinkage. 3D colloidal periodic structures and scaffolds have been successfully fabricated using aqueous gels such as DIW inks. The gels are prepared by the two-step control of interparticle forces in water [3]: first, colloidal particles are dispersed well through repulsive interactions (electrostatic and steric repulsion forces). Then, their destabilization for gelation is triggered via charge neutralization by adding inorganic salts [10], polymer electrolytes [11], or inducing pH changes [12], which promote the

physical bonding of colloidal particles. Aqueous gelling agents, such as Pluronic F-127 [4, 6] and bile salts [13], have also been used for the gelation of aqueous systems for DIW.

However, there has been considerably less attention paid to colloidal gels for non-aqueous systems, although ethanol and cyclohexane are used as solvents in ceramics colloidal processing [14, 15]. There are some circumstances where non-aqueous systems are preferable, especially when aqueous system of certain ceramics materials leads to particle oxidation and aggregation [15]. Previous studies have focused on the preparation of low viscous and fluidic concentrated slurries, aiming for applications in slip [16] and tape casting [17]. Since the charge stabilization is usually not as significant in non-aqueous systems as it is in aqueous ones, the abovementioned destabilization approach cannot be applied for non-aqueous systems.

In this work, we developed a facile gelation protocol of non-aqueous colloids for DIW. First, a concentrated and fluidic colloid was prepared in a non-aqueous solvent using a polymeric dispersant. Then, fluid-to-gel transition was triggered by adding free (non-adsorbed) polymers. The free polymers cause colloidal flocculation (depletion flocculation) [18]. The process was performed using a model system comprising polyethyleneimine (PEI)-adsorbed, Y_2O_3 -stabilized ZrO_2 (YSZ) particles in the presence of polyvinyl butyral (PVB) using ethanol as solvent. PEI and PVB were the dispersant and free polymer. The presence of a small amount of PVB (3 mass%) efficiently induced colloidal gelation for the YSZ colloids with particle concentrations exceeding 20 vol%. The resulting gels had a viscoelastic response adequate for DIW. In the DIW experiment, the deposition process was carried out in a water reservoir to prevent the variation of ink rheology owing to ethanol evaporation. The results indicate that a PVB film was formed *in situ* on the surface of the filament. The colloidal structures were removed from the water after the deposition was complete, dried under ambient conditions, and finally processed

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at 500 °C for 5 h for removing the organic additives and at 1400 °C for 2 h for sintering.

2. Experimental

The chemicals used in this study are summarized in Table 1. 8mol% Y_2O_3 -stabilized ZrO_2 (YSZ) powder (TZ-8Y, Tosoh, Japan) was used. Its specific surface area was approximately 13.2 m²/g, yielding an equivalent spherical diameter of 77 nm. Branched polyethylenimine (PEI, MW~10,000 g/mol, Nippon Shokubai, Japan), which has been reported as a good dispersant for ZrO_2 [19], was used. It is worth noting that the high affinity of PEI on oxide surfaces may promote the colloidal stabilization of oxide particles in an ethanol system [20]. Polyvinyl butyral (PVB, MW~63,000g/mol, #3000K, Denka, Japan) was used as a thickening agent, although it is conventionally used as a binder. Dibutyl phthalate was the plasticizer (DBP, 278.34 g/mol, Wako Pure Chemical, Japan). Ethanol (purity 99.5%, Wako Pure Chemical, Japan) was the solvent. PEI, PVB, and DBP are all soluble in ethanol.

Concentrated YSZ colloids were prepared by adding an adequate amount of PEI (1.5 mass% respect to YSZ powder) into ethanol and milling for 24 h with ZrO_2 milling media. The amount of PEI to be used was experimentally determined (section 3.1). PVB (3 mass% respect to YSZ powder) was then gradually mixed with the concentrated YSZ colloids using a conventional stirrer. DBP (2.4 mass%) was also mixed. Afterwards, the YSZ colloids were transferred into containers and left overnight at room temperature. The rheological measurements of the colloidal inks were conducted at 20 °C using a viscometer (HAAKE VT-550, Thermo Fisher Scientific Inc., USA). An NV sensor with an annular-type cylinder and an SV-DIN sensor with a rod-pin type cylinder were employed. To prevent undesirable effects from different mechanical conditions, samples were homogenized by shearing at 100 s⁻¹ for 60 s and left standing for an additional 60 s prior to measurement. A robocasting system with a micro-pen was employed (SHOT mini-200α, Musashi Engineering, Japan). The concentrated YSZ colloidal gel ink was placed in a syringe and deposited through a tapered nozzle (diameter, D = 100 μm) using a pneumatic system in water. The direct-assembled colloidal structures were removed from the water after the deposition was complete and dried under ambient conditions. They were heated at 1 °C/min from room temperature to 500 °C and hold for 5 h in air to remove the organic additives, and then heated at 5 °C/min to 1400 °C and hold for 2 h in air for sintering.

3. Results and discussion

3.1. Optimization of the dispersant for the concentrated YSZ colloids

Fig. 1 shows the apparent viscosity as a function of PEI concentration for YSZ colloids with a 30 vol% particle concentration. The apparent viscosity initially decreased, reaching a minimum at 1.5 mass% PEI, and then increased with PEI. The minimum viscosity indicates that colloidal stabilization was achieved, i.e., the dispersant polymer is adsorbed in a monolayer onto the surface of the particles [4,21,22]. This PEI concentration (1.5 mass%) facilitated the loading of at least 38 vol% of the YSZ particles in ethanol.

When the PEI concentration is too low to provide complete surface coverage (<1.5 mass%), the dispersant molecules could form bridges between surfaces, causing flocculation, i.e., increasing the apparent viscosity [18]. Then, when the PEI concentration exceeds the saturation adsorption limit (>1.5 mass%), the

Table 1. Chemical reagents used in this study.

Trade name	Formulation	Feature	Particle size or molecular weight	Supplier
TZ-8Y	8 mol% Y_2O_3 -stabilized ZrO_2 (YSZ)	Powder	77nm*	Tosoh
SP-200	Branched polyethylenimine (PEI)	Dispersant	$M_w \sim 10,000$	Nippon Shokubai
#3000K	Polyvinyl butyral (PVB)	Binder	$M_w \sim 63,000$	Denka
DBP	Dibutyl Phthalate	Plasticizer	278.34g/mol	Wako Pure Chemical
Ethanol	Purity 99.6%	Solvent	-	Wako Pure Chemical

* equivalent diameter of specific surface area

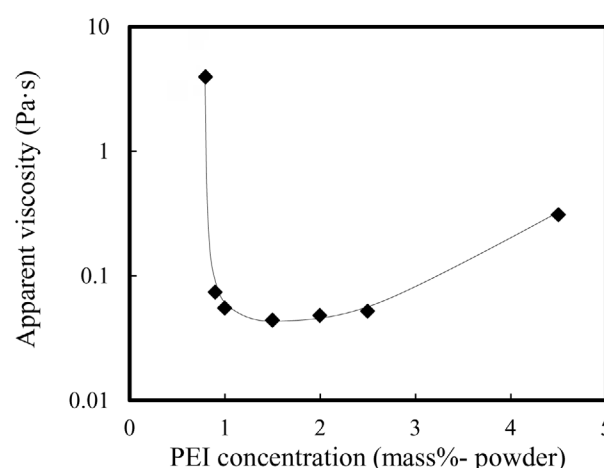


Figure 1. Relationship between PEI concentration and apparent viscosity of the 30 vol% YSZ colloid (shear rate = 100 s⁻¹).

non-adsorbed dispersant molecules exist as free polymers. In a colloidal system that contains free polymers, the interparticle gap may become so small that polymer molecules are unable to fill all of the spaces between colloidal particles. Thus, some depletion zones comprising only solvent develop. This causes depletion flocculation via osmotic gradients [18], thereby increasing the apparent viscosity.

In the following experiment, PVB was added as a free polymer into the PEI-stabilized YSZ colloids (1.5 mass%) to induce gelation; its effect on the rheological properties was examined. It is worth noting that as expected from their molecular weights (Table 1), the PVB polymer was much larger than PEI.

3.2. Gelation of concentrated YSZ colloids

First, a well-dispersed YSZ colloid was generated using PEI to facilitate high solid loading, then it was followed by a fluid-to-gel transition by adding PVB. In this study, after adding PVB (3 mass%) to the well-dispersed YSZ colloid with a 38 vol% particle concentration, the colloid became solid-like when stationary. Fig. 2 shows the typical flow curves for the colloids ($\phi = 38$ vol%) with and without PVB. The flow behaviors of the colloid with PVB displayed shear-thinning characteristics with a large shear yield stress. Additionally, compared with the colloid without PVB, a significant increase of almost two orders of magnitude was observed for the shear stress as well as the apparent viscosity. The shear yield stresses were calculated using the Casson model. Equation (1) is often used to describe the flow curve of a system containing flocculated particles [22].

$$\tau^{0.5} = k_1 + k_2 \gamma^{0.5} \quad (1)$$

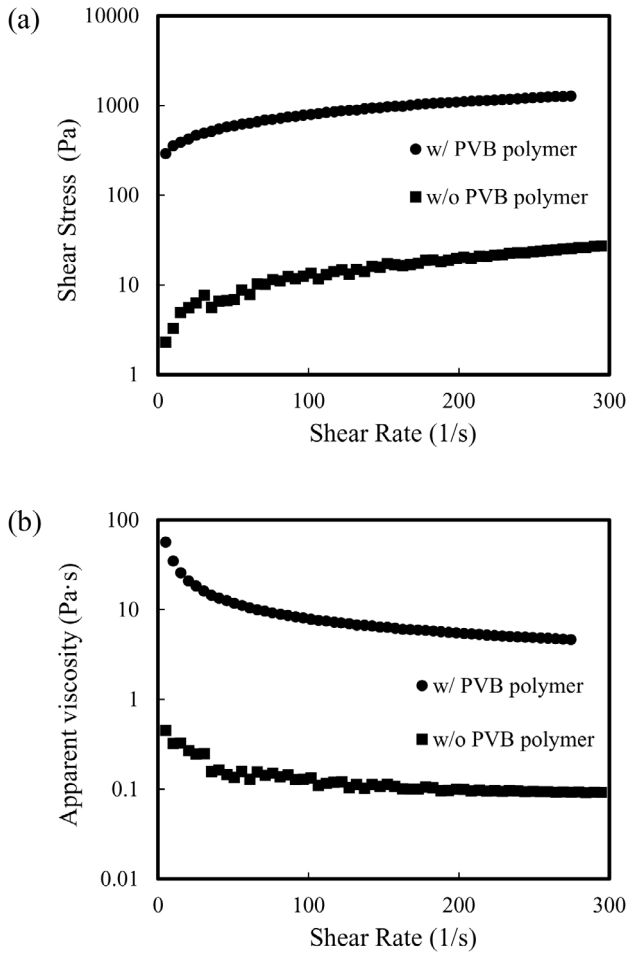


Figure 2. Flow curves of PEI-adsorbed YSZ colloids ($\phi = 38\%$) with and without PVB. (a) Shear stress and (b) Apparent viscosity as a function of shear rate.

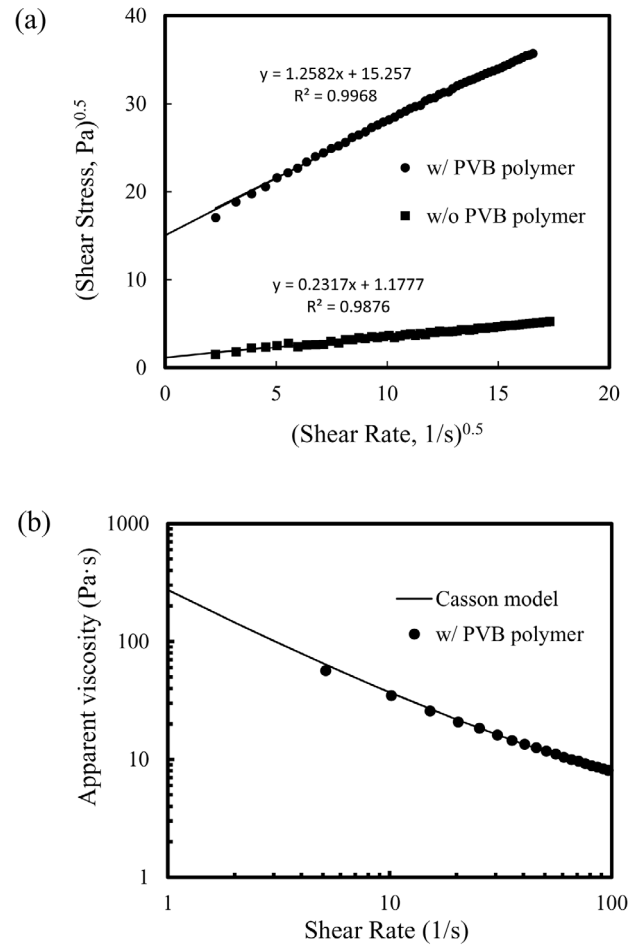


Figure 3. (a) Casson plots corresponding to the flow curves shown in Fig. 2(a). The square of the intercept represents the yield stress. (b) Apparent shear viscosity curve fitting using the Casson model. Solid circles represent experimental data for YSZ colloids ($\phi = 38\%$) with PVB.

where k_1 and k_2 are structure-dependent constants for the system, τ is the shear stress, and γ the shear rate. The plot of $\gamma^{0.5}$ as a function of $\tau^{0.5}$ follows the Casson model, and the square of the intercept (k_1) is the shear yield stress. As shown in Fig. 3 (a), both colloids, with and without PVB, agree with the Casson model (correlation factor, $R \sim 0.99$). The calculated shear yield stress was 233 Pa for the YSZ colloid with PVB, which is comparable with that of aqueous inks used for DIW [4,10,23]. The shear thinning behavior was also well fitted for the YSZ colloid with PVB as shown in Fig. 3 (b), which is similar to those reported for DIW inks [4,11]. When stressed beyond this yield point, the colloid begins to behave like a fluid because of the attrition of particle-particle physical bonds within the gel. Contrastingly, it was only 1.4 Pa for the colloid without PVB, which is too low for gelation.

The sharp rise in the elasticity followed the PVB addition. The resulting colloidal gel had a viscoelastic response useful for DIW. This enhanced flocculation may be attributed to a depletion flocculation mechanism due to the introduction of PVB.

To further understand this gelation process, the effect of the YSZ particle concentration was investigated. As shown in Fig. 4, the shear yield stress significantly increased for the YSZ colloids with PVB when exceeding 20 vol%. As the particle concentration increased, the gap between the surfaces of neighboring particles decreased. If PVB polymer was larger than the gap, it would be excluded from the gap, and depletion zones would develop. Therefore, PVB polymer would lead to an efficient depletion flocculation. The average gap h between first-neighboring YSZ particles can be calculated from the following Woodcock equation [24]:

$$h = d \left[\left(\frac{1}{3\pi\phi} + \frac{5}{6} \right)^{0.5} - 1 \right] \quad (2)$$

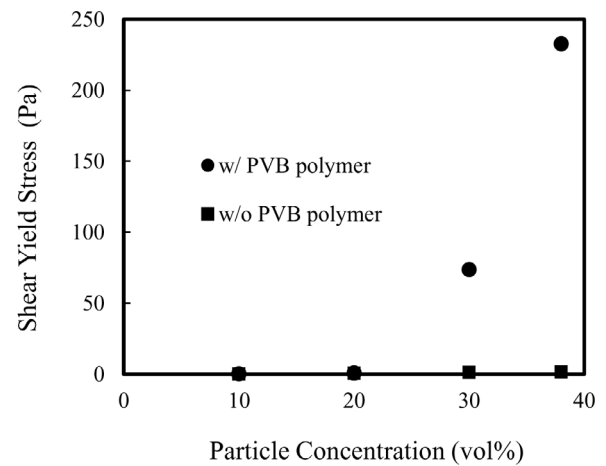


Figure 4. Relationship between particle concentration and shear yield stress for PEI-adsorbed YSZ colloids with and without PVB.

where d is the particle size and ϕ is the volume fraction. The calculated average gap of the 10, 20, 30, and 38 vol% well-dispersed YSZ colloids ($d = 77$ nm) were 29, 13, 6.9, and 4.2 nm, respectively. The average size of the dissolved PVB in ethanol, ~ 10 nm, was measured through the dynamic light scattering method, as shown in Fig. 5. This was larger than the gaps for the 30 and 38 vol% colloids; thus, the depletion flocculation would be dominant for these concentrations (beyond 20 vol%). Although the thickness of the PEI adsorbed on YSZ particles was

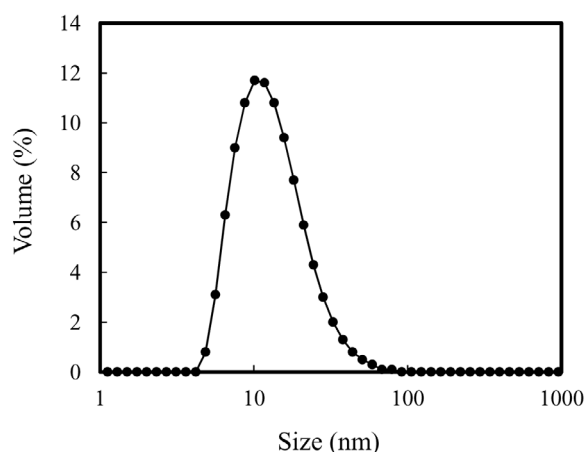


Figure 5. Typical dynamic light scattering profile for PVB in ethanol (PVB concentration 1 mass%).

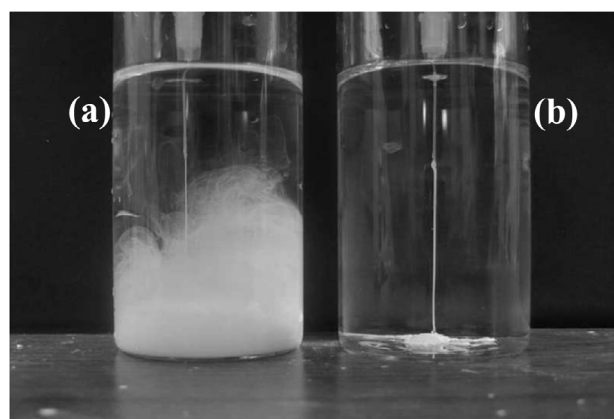


Figure 6. Photograph of the YSZ colloids in water, (a) without PVB, and (b) with PVB.

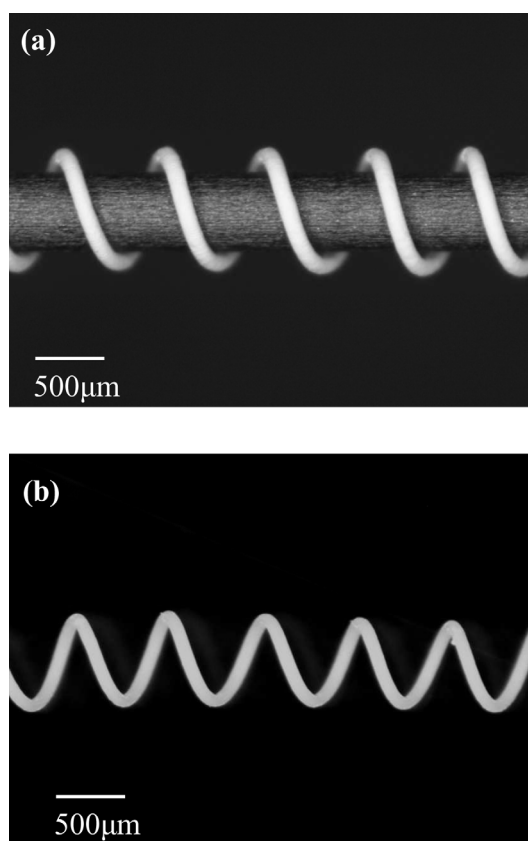


Figure 7. Optical micrographs of (a) the green helical coil structure fabricated by DIW using the YSZ gel, and (b) the sintered helical coil structure.

not considered, this could qualitatively explain the significant increase in yield stress with particle concentration assuming that depletion interactions occur within the gel.

Decreasing the polymer concentration is known to weaken the depletion flocculation [18, 25,28]. In this work, the colloidal gelation was not fully induced when adding 0.1 mass% PVB to the 30 vol% colloid; a 3 mass% PVB was necessary for the gelation. This binder concentration is lower than those used in ceramics forming methods such as tape casting [17,29] and injection molding [30]. Such low concentrations are useful for the development of novel ceramic-processing methods, such as DIW, because they facilitate fast burnout and high densities during sintering.

To the best of our knowledge, the present study is the first to show free-polymer-induced strong gelation for a non-aqueous system. The flocculation and rheological behaviors of ceramics suspensions in the presence of free polymers have been studied primarily for aqueous systems [25,26]. In these reports, binder materials were typically used as free polymers. Further, the sharp increase in elastic properties has been observed with increasing particle concentration [25]. To explain this rheological behavior, a depletion flocculation mechanism has been suggested. However, further analysis is required to identify the exact interparticle interactions of the highly loaded ceramic particles in which free-polymer species dramatically alter the rheological response.

3.3. DIW in water

The ink rheology must be stable during DIW deposition, but unexpected solvent evaporation often results in rheological changes. In the present ink design, solvent evaporation may be prevented by depositing our non-aqueous gels in water.

As shown in Fig. 6, when the YSZ colloid with PVB was extruded into water from a cylindrical nozzle, the extruded filament maintained its shape in water over several hours. However, the YSZ colloid without PVB was unstable, and the particles were randomly diffused in water. This can be explained by the fact that ethanol is a good solvent for PVB, unlike water. Thus, the PVB, which existed as a free-polymer in ethanol, precipitated in water owing to its poor solubility. Additionally, a shell-like PVB film may be homogeneously formed *in situ* on the surface of the filament to maintain the shape of the filament in water.

Since the *in situ* formed PVB film would prevent changes in the ink rheology owing to unexpected ethanol evaporation, it was possible to perform the DIW experiment. The PVB-induced YSZ colloidal gel ($\phi = 30$ vol%) was utilized as an ink. A helical, green structure was patterned via the deposition of a continuous filament extrusion through a cylindrical nozzle in a water reservoir as shown in Fig. 7 (a). The ink was first extruded into the water reservoir; then, it was rolled up on a cylindrical graphite fiber ($\phi = 500$ μm). The ink flowed through the nozzle at a volumetric flow rate to maintain a constant deposition speed of 60 mm/s. The extruded filament had an almost uniform diameter ($d = 140$ μm), indicating that the ink rheology was constant during deposition. Fig. 7 (a) illustrates a cylindrical rod-like feature, which was preserved using a smooth exterior surface during the extrusion and drying processes. PVB should have homogeneously precipitated around the filament.

The dried helical coil structure was burnt in air at 500 $^{\circ}\text{C}$ for 5 h to eliminate PEI and PVB, followed by firing at 1400 $^{\circ}\text{C}$ for 2 h for sintering. Fig. 7 (b) shows the sintered helical coil ($d = 110$ μm) with $\sim 20\%$ linear shrinkage in the diameter. As shown in Figs. 7 (a) and (b), the sample exhibited nearly isotropic sintering shrinkage, which probably occurred because of the homogenous packing of YSZ particles in the green structure. Fig. 8 shows the typical surface of the as-sintered sample. A relatively dense and

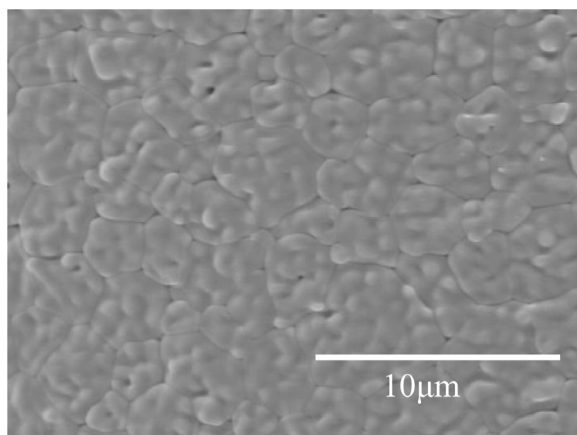


Figure 8. SEM image of the surface of the sintered helical coil structure.

smooth structure was observed. The precipitated PVB did not significantly influence the surface of the sintered body. Detailed examinations of the green and sintered samples are in progress and will be reported in a future work.

4. Conclusions

We have demonstrated the free-polymer induced gelation of non-aqueous colloids for DIW. The gel can be produced from any colloidal material provided the interparticle force is tailored to the desired viscoelastic response by controlling the particle concentration. Using the colloidal gel as an ink, a helical coil structure with diameter sizes of $\sim 100\ \mu\text{m}$ can directly be patterned through the DIW technique in a water reservoir. The approach presented in this work opens a new route for engineering 3D green structures of oxide, non-oxide ceramics, and metals.

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