Surface modification of ceramic powders by titanate coupling agent for injection molding using partially water soluble binder system

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Abstract

In the conventional process of ceramic injection molding (CIM), wax-based binders could only be removed by thermal or organic solvent debinding. Recently, water solvent debinding, with its high efficiency and environmental acceptability, has appeared as a good alternative. In this study, zirconia powder modified by titanate coupling agent was applied in partially water soluble binder system for injection molding. In contrast to previous researches about titanate modification mainly focusing on rheological behavior and modification mechanism, investigations on the sintering behavior and densification process were also made in this study. Experimental results reveal that titanate modified powder exhibits densification temperature almost 100 °C lower than that required for the pure, original powder, giving rise to finer microstructure and therefore hopefully improved mechanically properties. It suggests a novel modification route to fabricate injection molded ceramic components using partially water soluble binder system.

1. Introduction

Ceramic injection molding (CIM) has attracted much attention for its capability of producing complex-shaped and precise ceramic components at low cost.[1] Suspensions used for CIM are primarily composed of ceramic powders and organic vehicles, together with a relatively minor amount of dispersants.[2] The surfactant dominates the suspension properties to a significant extent. In the past few decades, a large number of literatures about the modification mechanism and effect on rheological property using various types of surfactants have been reported.[2–8] The surfactants applied in CIM could be roughly divided into two categories: one is fatty acids (SA, OA, HSA) adsorbed on ceramic powder surface by hydrogen bonding through a Lewis acid-base reaction,[9] and the other is coupling agent (silanes, titanates) coated onto ceramic powder by covalent bonding.[5,7] Each of them could serve as

a bridge between the molten polymer and ceramic powder, improving the dispersion of ceramic powders in the binders against agglomeration, enhancing the compatibility between binder components and reducing the viscosity of the system.[4,9] However, previous researches on titanate coupling modification in ceramic injection molding are quite limited. Hunt et al. reported that titanate coupling agent could reduce the viscosity of the zirconia-polypropylene suspensions and serve as a flow modifier which is more efficient than dibutyl phthalate (DBP).[10] Takahashi et al. investigated the effect of the aluminate, silane and titanate coupling agents on the rheology of zirconia-polypropylene compounds and found that silane was the most effective agent for torque and viscosity reduction in compounds with 2% addition.[11] Liao et al. used mineral oil as a model solvent to examine the effect of titanate additions on the stability and rheology of AlN dispersions for the development of polyolefin-based ceramic injection molding formations.[8] It is apparent that the relevant researches on titanates only focused on the improvement of the rheological properties whereas the influence of the incorporated titanates on sintering behavior and densification process was missing. In addition, previous studies

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on the coupling agent are limited to wax-based binders system for CIM, and it has been widely acknowledged that binders of wax-based system could only be removed by thermal debinding or organic solvent debinding. For thermal debinding, the process is time-consuming because the debinding rate must be slow in order to avoid internal pressure buildup from decomposed gas, which causes cracking, blistering and exfoliation during debinding[12]; for organic solvent debinding, the organic solvents are mostly flammable, carcinogenic and not environmentally acceptable.[13] By contrast, partially water-debinding followed by rapid thermal pyrolysis, with its high efficiency and environmental acceptability, has appeared as a good alternative.[14] For this approach, water-soluble binder is firstly removed while the interconnected pore channels are formed from exterior to interior, leaving the insoluble binders in the contact region and the pore channels could serve as escape paths for decomposed gas during subsequent thermal debinding for insoluble binders.

In this study, zirconia powder modified by titanate coupling agent was applied in partially water soluble binder system for ceramic injection molding. In contrast to previous researches about titanate modification mainly focusing on rheological behavior and modification mechanism, investigations on the sintering behavior and densification process were also made in this study. Experimental results reveal that titanate modified powder exhibits densification temperature almost 100 °C lower than that required for the pure, original powder, giving rise to finer microstructure and therefore hopefully improved mechanically properties. It suggests a novel modification route to fabricate injection molded ceramic components using partially water soluble binder system and it could be believed that the current work would push forward the progress of ceramic injection molding using partially water soluble binder system.

2. Experimental

The ceramic powder used was a commercial zirconia (3 mol% Y_2O_3) with average particle size (d_{50}) of 0.16 μm and Brunauer–Emmett–Teller specific area of 8.2 m^2/g (grade YSZ-F-DM-3.0, Farmeiya Advanced Materials Co. Ltd., Jiujiang, China). The titanate coupling agent TC-201 was obtained from Anhui Taichang Chemical Co. Ltd. (Chuzhou, China). The process of the powder being modified by titanate coupling agent is as follows: the powder after drying was first dispersed in ethanol under ultrasonic treatment for 30 min to limit particle agglomeration, then the titanate was stirred in the suspension for about 2 h. The coupling agent was adsorbed on the particle surfaces.[7] The suspension was then dried in an oven to remove ethanol and the modified powder was obtained after pulverizing and sieving.

Afterwards, the powders were mixed with the binders in a twin screw kneader (SK-160, Shanghai Rubber Machinery, Shanghai, China) at 150–170 °C until homogenous feedstock was obtained. The used organic vehicles (binders) in the experiments were polymethyl methacrylate (PMMA, Plexiglas-8n, Degussa Co. Ltd, Beijing, China), polyethylene glycol (PEG) (Sinopharm Chemical Reagent Beijing Co. Ltd.,

Table 1
The organic binders used.

Components	PEG	PMMA	SA	DBP	Phenothiazine
Weight percentage (%)	66	20	8.5	5	0.5

Beijing, China), stearic acid (SA, Shantou Xilong Chemical Factory Guangdong, China), dibutyl phthalate (DBP, Beijing Modern Eastern Fine Chemical) and phenothiazine (Sinopharm Chemical Reagent Beijing Co. Ltd., China) with the compositions shown in Table 1. It should be noted that phenothiazine was used here as an antioxidant, for PEG is quite easy to be oxidized in air when the temperature is higher than 120 °C. The chemical stability could be promoted if a small amount of antioxidant is added.[15] The solid loading of the system was 57 vol%. Specimens with the dimensions of were fabricated on an injection molding machine (JPH30C/E, Qinchuan Hengyi Plastics Machinery Co. Ltd, China) and the dimension of the molded specimens was 4.5 mm × 6.0 mm × 42.0 mm. Debinding was performed in two steps: water leaching to remove the PEG and thermal pyrolysis to remove residual binders. The green (as-molded) specimens were immersed in distilled water of 40–60 °C to remove most of the PEG. The second stage involved a thermal treatment. Because the pore nets formed in the first stage, heating rate of the second stage could be quite fast. The grown bodies after debinding were then sintered at different temperatures (1300 °C, 1350 °C, 1400 °C, 1450 °C, 1500 °C, 1550 °C) in air to study the sintering process. The sintering was done in a chamber furnace (LHT04/17, Nabertherm, Germany).

The BET surface area was analyzed by Specific surface area analyzer (Quadrasorb SI-MP, Quantachrome Instruments, USA). The measurement range is 0.005–5000 m^2/g and the error estimates are less than ±1.5%. The viscosity of the suspension was measured by the Modular Compact Rheometer (Physica MCR300, Anton Paar, Austria). The particle size distribution was obtained using a laser particle size analyzer (Master Sizer 2000, Malvern Instruments Ltd., Malvern, Britain). The chemical information of the powders was measured by means of Fourier Transformation Infrared Spectrometer (FTIR-6700, Nicolet, USA). The morphology, structure and composition were characterized using field emission scanning electron microscopy (FESEM, LEO1530, Germany) and transmission electron microscopy (TEM, H-800, Hitachi, Japan). The shrinkage curves of the injection molded compacts were obtained by thermo dilatometer (DIL402PC, Netzsch, Germany) operated at a heating rate of 10 °C/min up to 1550 °C in ambient atmosphere. The bulk densities of the sintered specimens were measured by the Archimedes method.

3. Results and discussion

A simplified model system, based on paraffin oil as solvent, was used to investigate the influence of the agent amount on the rheological property and determine the optimal amount. The mixture was composed of zirconia and paraffin oil in the mass ratio of 5:3. The shear viscosity of model system versus
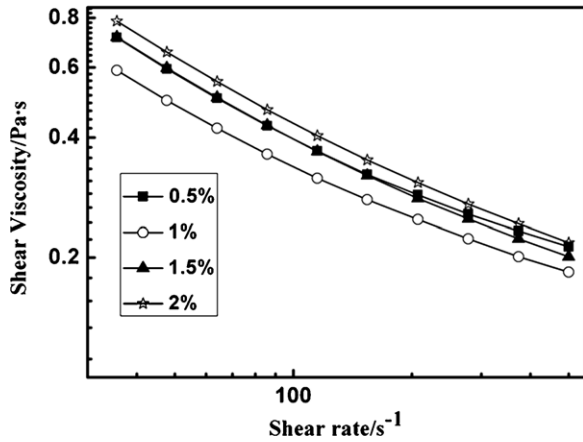
Fig. 1. The shear viscosity of the model system versus varying shear rates for different additions of titanate at room temperature.

Fig. 3. Typical TEM images of the modified powder.

varying shear rates for different additions of titanate at room temperature on a log–log plot is shown in Fig. 1. The suspensions exhibit a pseudoplastic flow over the shear rate range employed and a similarity is presented in their viscosity dependence. It suggests that the viscosity does not decrease monotonously with the increment of the amount of the titanate. The viscosity achieves the lowest value with 1 wt% addition of the titanate and rises again with further increment of the titanate content. Therefore, we could suppose that the optimum amount of the titanate addition is ~1 wt%. The possible cause may be that monolayer titanate coating forms around the particle with 1 wt% addition, in which case the best modification effect could be achieved. If the amount of the addition exceeds its saturated adsorption quantity, redundant coupling agent would adsorb on the first layer and polarity would exhibit again, leading to the increase of the mixture viscosity.[6]

The size distribution of the original zirconia powder and that of the modified powder are shown in Fig. 2 respectively. It indicates that the average particle size of the modified powder is smaller than that of the original one and the size distribution after modification is narrower because agglomerations of the
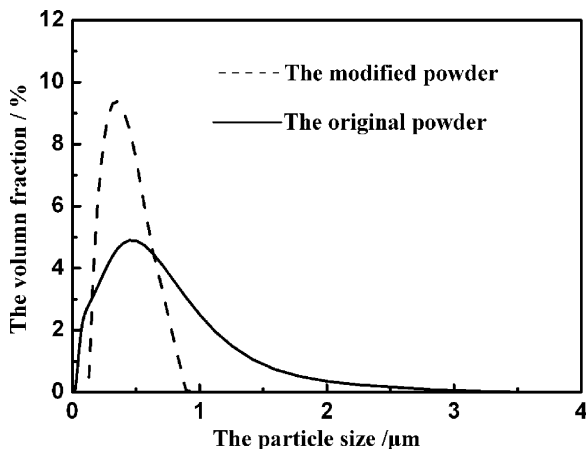
particles decrease or disappear. Typical TEM image of the modified powder is shown in Fig. 3 and the powder is well dispersed.

Fig. 4(a) is the infrared absorption spectrum of pure zirconia. $3415\,cm^{-1}$ is defined as the vibration peak of hydroxy(–OH), which proves that the surface of zirconia powder is rich in hydroxyl group and provides the possibility of reaction with the titanate. Fig. 4(b) is the infrared absorption spectrum of the modified zirconia powder and the modified powder was treated in ethanol bath under ultrasound to extract the physically coated titanate. The intensity of the vibration peak of hydroxy weakens, implying there is a reaction between hydroxy and the titanate. New peaks appear at $1469\,cm^{-1}$ and $1385\,cm^{-1}$ as compared with Fig. 4(a), which originate from the $1461\,cm^{-1}$ and $1381\,cm^{-1}$ of the titanate coupling agent (Fig. 4(c)) respectively. As the physically coated titanate coupling agent was extracted from the modified zirconia powder before its infrared spectrum was analyzed, it is reasonably believed that those new peaks of the modified powder were caused by the titanate coupling agent

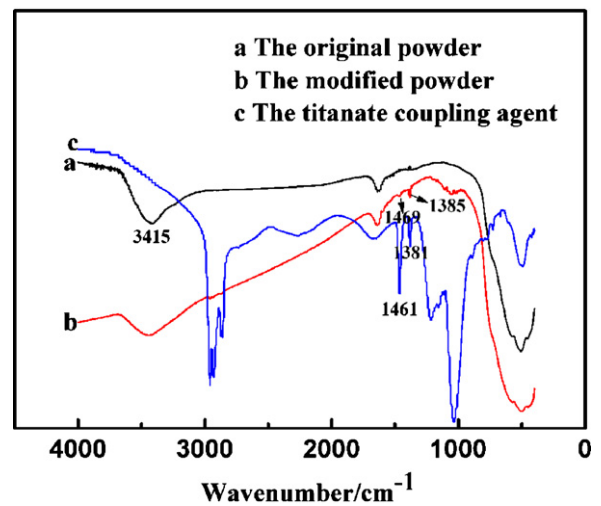Fig. 2. The respective size distribution of the original zirconia powder and the modified powder.

Fig. 4. (a) The infrared absorption spectrum of pure zirconia; (b) the infrared absorption spectrum of the modified zirconia powder; and (c) the infrared absorption spectrum of the titanate coupling agent.
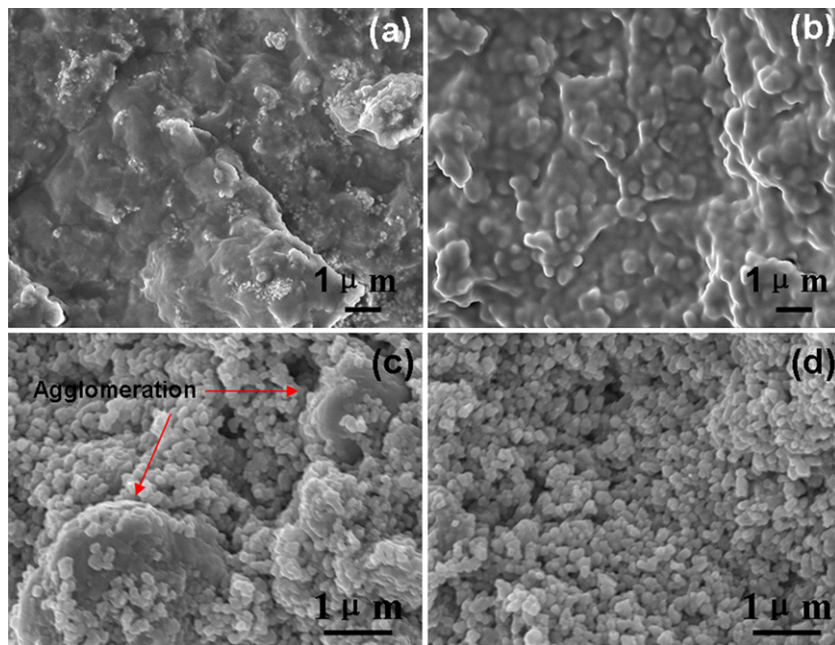
Fig. 5. (a and b) Respective SEM images from the fracture surface of the injection molded compacts of the original powder and the modified powder; (c and d) respective SEM images of the PMMA/PEG system after debinding in water solvent of the original powder and the modified powder.

chemically bonded with the zirconia powder. The reaction could be expressed as follows[16]:

$$R'-O-Ti(OR)_3 \ + \ ZrO_2\text{-}OH \ \longrightarrow \ ZrO_2-O-Ti(OR)_3 \ + \ R'OH$$

$$R' = \ -HC\begin{matrix}CH_3\\CH_3\end{matrix}, \quad R = \ -\overset{\displaystyle O}{\underset{\displaystyle OH}{P}}-O-\overset{\displaystyle O}{P}\begin{matrix}OC_8H_{17}\\OC_8H_{17}\end{matrix}$$
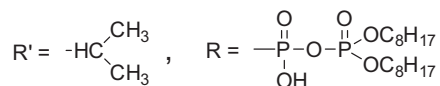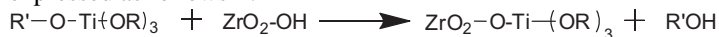
Fig. 5(a) and (b) are the SEM images of the fracture surface, respectively from the injection molded compacts of the original and modified powder. The modified powder could be homogeneously dispersed in organic binders while the original compact shows a significant agglomeration. Fig. 5(c) and (d) respond to the respective SEM images of the PMMA/PEG system after debinding in water solvent. Significant agglomerations still stay (as indicated by the red arrow) in the original PEG-removed compact while the modified system shows an ordered stacking structure.

The agglomeration of the original powder can be attributed to the nature of the ceramic powder surface, the polarity (hydrophilicity) of which leads to the poor affinity between the ceramic powders and organic binders. Consequently, the bonding strength between ceramic particles and organic binders decreases, causing ceramic particles and organic binders to separate easily during the process of high-speed and high-pressure injection molding. However, when the titanate coupling agent is added to the ceramic powder in binders, the monohydrolyzable group on the titanate molecule can react with the surface hydroxyl groups of the powder, bonding the organotitanate on the particle surfaces while allowing the tails to extend into the binders, as proved by the above FTIR analysis.[8] Thus, the surface of the powder changes from hydrophilicity to hydrophobicity

whereby the particles of the titanate modified powder could enhance the bonding between ceramic particles and organic binders, resulting in the fabrication of the compacts without agglomeration.[17]

The thermal expansion curves of the injection molded compacts made from the original and modified powder are shown in Fig. 6 respectively. It illustrates that the shrinkage rate of the modified compact is higher than that of the original compact. The modified compact shrinks continuously until $\sim$1450 °C while
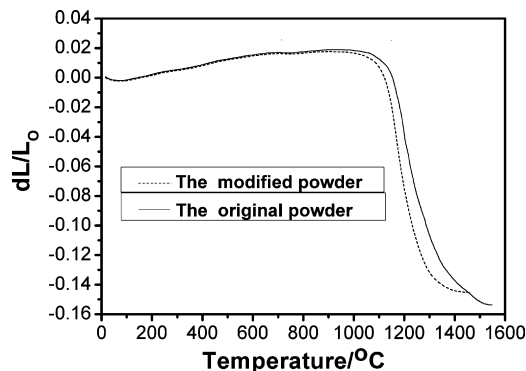

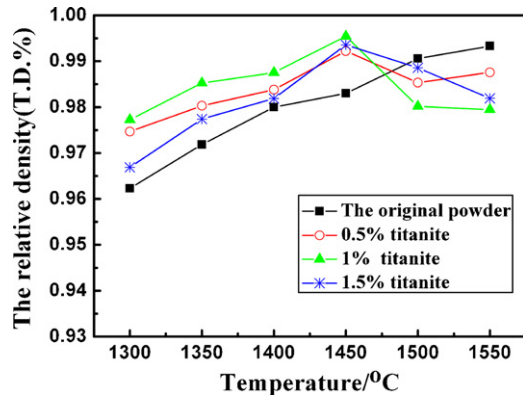Fig. 6. The respective thermal expansion curves of the injection molded compacts made from the original and modified powder.

Fig. 7. The relationship between the relative density (T. D.) and sintering temperature for various powders.

the original compact until ~1550 °C (100 °C higher than the modified one), it is probably because the modification promotes the dispersibility of the powder and homogeneity of the compact, leading to the improvement of sintering activity and the reduction of sintering temperature.[18]

Fig. 7 responds to the relationship between the relative density (T. D. %) and sintering temperature for various powders. It demonstrates that the relative density increases with the increment of temperature in the range from 1300 °C to 1550 °C for the original powder. By contrast, the modified powders with different amount of titanate coupling agent show a completely different densification behavior. The relative densities achieve the peak values at 1450 °C and gradually decline with further increment of temperature above 1450 °C, which further proves the fact that the modified powder could promote sintering activity. The density close to theoretical value could be obtained at lower temperature for the modified powder, which is significant for energy saving, especially for industrial production. It is worth noting that when the sintering temperature is above 1450 °C, the density decline of the modified powders indicates the possibility of the occurrence of oversintering. In addition, the densification rate and relative density are of the highest degree for the modified powder with 1 wt% addition of the titanate coupling agent, which agrees well with the above analysis about the optimum amount of addition.

The evolution of the microstructure during the densification process of the modified powder can be observed in Fig. 8, in which the as sintered surfaces of the sintered bodies for the 3Y-TZP modified by 1 wt% titanate coupling agent at different sintering temperatures (1300–1550 °C) are shown. The grains grow gradually with the increment of temperature from 1300 °C to 1550 °C. Homogeneous microstructure could be obtained at 1450 °C according to Fig. 8(d). The average grain size of the sintered body at 1450 °C is ~200 nm with no significant pores and abnormal grain growth observed (Fig. 8(d)). Non-uniform microstructures and abnormal growth of grains appear in some local region at the sintering temperature higher than 1450 °C due to oversintering, as indicated in Fig. 8 (e and f). Some grain
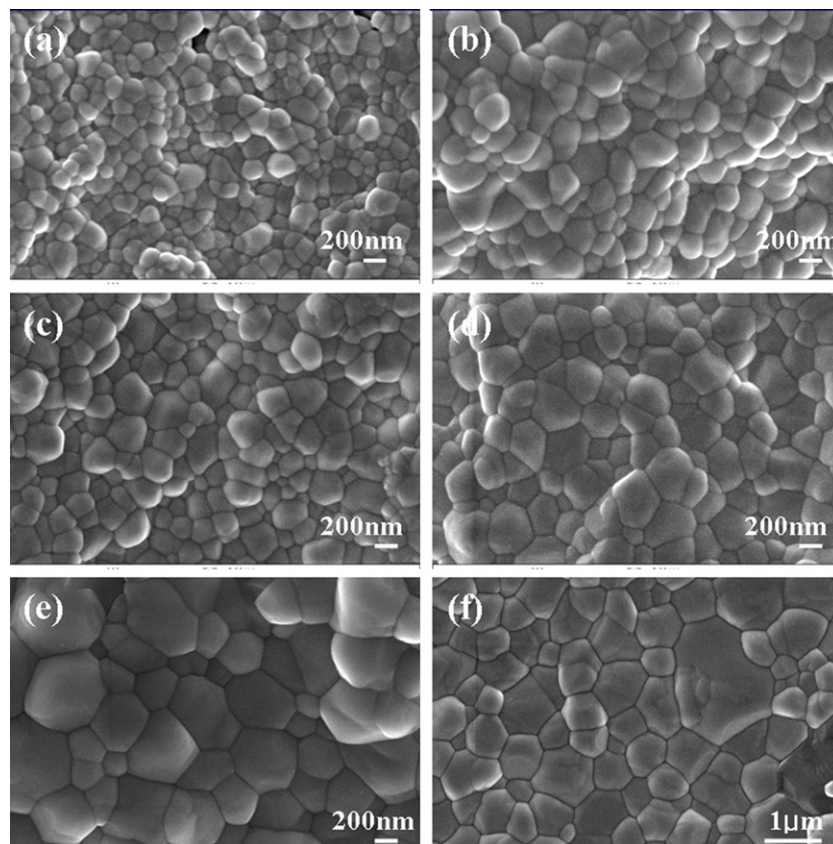

Fig. 8. The as sintered surfaces of the sintered bodies for the 3Y-TZP modified by 1 wt% titanate coupling agent at different sintering temperatures: (a) 1300 °C; (b) 1350 °C; (c) 1400 °C; (d) 1450 °C; (e) 1500 °C; and (f) 1550 °C.

grew up to the size of more than 2 μm at 1550°, which would be detrimental to the mechanical property of the zirconia ceramics. The above analyses suggest that the titanate coupling agent could effectively reduce the sintering temperature and lead to uniform microstructure with fine grain size (~200 nm), which would be beneficial to the mechanical property.

4. Conclusion

In summary, we have reported a surface modification strategy of titanate coupling agent in ceramic injection molding using water-based binders system. The optimum amount of the titanate addition is ~1 wt% based on the simplified model. The average particle size of the modified powder is smaller and the size distribution after modification is narrower because agglomerations of the particles decrease or disappear. The FTIR analysis indicates that the titanate coupling agent interacts with the zirconia powder by a chemical bonding. The modified powder could be homogeneously dispersed in organic binders while the original system shows a significant agglomeration in both the green compacts and the PEG-removed compacts. The relative densities of the sintered body for the modified powder achieve the highest values at 1450 °C, 100 °C lower than that in the case of the original powder, because the modified powder could promote sintering activity. The microstructure observation suggests that homogenous microstructure (sized in ~200 nm) with no significant pores and abnormal grain growth could be obtained at 1450 °C, which would be beneficial to the mechanical property. It is believed that the titanate coupling agent could not only reduce the viscosity and improve the homogeneity, but also promote densification and grain refinement of the water-based binders CIM system. It can be believed that current work would push forward the progress of ceramic injection molding using water-based binders system.

Acknowledgements

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