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Rheological behavior of titania ink and mechanical properties of titania ceramic structures by 3D direct ink writing using high solid loading titania ceramic ink

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ABSTRACT

In this paper, high solid loading titania ceramic ink containing sodium hexametaphosphate and sodium alginate had been successfully prepared at room temperature. Rheological behaviors of titania ceramic ink with different solid content were investigated. The rheological results indicated that high solid loading (72 wt%) titania ceramic ink whose shear elastic modulus reached approximately 10^6 Pa in the linear viscoelastic region was the optimal ceramic ink for direct ink writing, due to its good shear thinning and viscoelastic behavior. High solid loading (72 wt%) titania ceramic ink was utilized to fabricate three dimensional titania ceramic parts, and a series of test methods were employed to examine the related properties of titania ceramics sintered at different temperatures including the volumetric shrinkage, porosity, density, microstructures, compressive strength and elastic modulus. The results showed that the volumetric shrinkage and density increased when increasing the sintering temperatures, and the opposite phenomenon was found in porosity of titania ceramic. When the sintering temperature was 1300 °C, the compressive strength was about 125.00 MPa. The elastic modulus of titania ceramics sintered at different temperatures (from 1000 °C to 1400 °C) was between 1.22 GPa and 6.87 GPa.

1. Introduction

Ceramic materials play an important role in industrial production and daily life because of their high strength, high hardness, high temperature capability, wear resistance, corrosion resistance, etc [1–3]. However, it is difficult to generate ceramic parts with arbitrary geometries through conventional ceramic manufacturing processes, additive manufacturing provides a promising opportunity to meet this need and opens a new market for ceramic components [4,5]. Direct ink writing, as an effective kind of additive manufacturing methods, has attracted a great attention in a range of practical applications in recent years, e.g., magnetic structures, electrochemical storage devices, biomedical components, photonic crystal patterns, nanocrystal aerogel structures, etc. [6–11]. It is also capable of producing more complex ceramic components than traditional manufacturing due to its mold-free and computer-aided manufacturing [12–14]. Ceramic components fabricated by direct ink writing can achieve dense or porous structures, which is determined by the required properties, and it is more economical and simple than other additive manufacturing techniques for ceramics, including selective laser sintering, selective laser melting and stereo lithography apparatus [15–17].

Fabrication of ceramic components by direct ink writing is through filaments extruded from a fine nozzle assembling layer by layer, so it is understandable that direct ink writing also has some special requirements for ink used to generate ceramic components [10]. The ideal ink suitable for printing three dimensional ceramic parts has to meet related rheological properties requirements. On the one hand, the ink should have appropriate viscosity so that can be smoothly extruded through a nozzle without clogging, on the other hand, the ink must have the ability to avoid collapse and defective deformation during printing. So it is necessary for the ink

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to be with high elastic modulus and sufficient ceramic powder content to maintain shape after the ink squeezed out the fine nozzle, which means that coordinating the ratio of ceramic powder and organic additives is the key to success of direct ink writing [18,19]. In the previous studies on alumina, titania and other ceramics fabricated by direct ink writing, the solid content of ceramic ink was relatively low [13,20,21]. However, higher solid loading ceramic ink is more favorable for ceramic forming by direct ink writing, because it is beneficial to increase the supportability of ceramic green body and improve the mechanical properties of ceramics. Organic or inorganic additives act as rheology modifiers in ceramic ink for direct ink writing. There are many kinds of rheology modifiers for ceramic fabricated by direct ink writing, including PAA, PEG, PVP, etc [12,13,22]. The type and amount of organic or inorganic additives should be determined according to the actual situation.

Moreover, titania is a kind of functional inorganic material, its biocompatibility, bioactivity and stability contribute to integrating with bone safely and promoting direct contact between bone tissue and bone implant, so it is believed to be a promising biomaterial for bone implant [23–25]. Titania ceramic materials created by direct ink writing technology with gel-sol ink performed good biocompatibility and contributed to cell growth [26]. However, it is crucial for biomaterials that not only possess bioactivity and safety but appropriate mechanical properties [27]. Conventional biomaterials such as stainless steel, titanium alloy have been widely used as bone implants due to their biocompatibility and high mechanical strength [28,29]. However, high mechanical strength of these alloy materials can cause bone resorption and stress shielding between implants and surrounding bone tissue once implanted, these intractable problems will affect the rehabilitation effect of patients [30]. Titania as a bone implant material with prominent biomedical properties, which has huge potential application in bone implant and can be a competitive candidate in the field of biomaterials. So it is necessary to investigate mechanical properties of 3D printed titania ceramic parts to better match the surrounding bone tissue, then effectively reduce bone resorption and stress shielding phenomenon.

Research on related mechanical properties of titania ceramic parts fabricated through 3D printing is still insufficient, and it is worthy to pay more attention. In this work, an additive manufacturing way of titania ceramic was reported, the rheological properties of different ceramic inks were studied, the related mechanical properties and micrographs of titania ceramic structures generated by 3D printing were investigated. The elastic modulus of titania ceramics was between 1.22 GPa and 6.87 GPa, which was close to the elastic modulus of high density cancellous bone that was in a range of 0.28 GPa and 1.86 GPa, and this was important for bone implant materials [31].

2. Experimental

2.1. Materials

Commercially available rutile titania powder with an average particle size of 0.36 μm (high purity 99.9%) was purchased from Ningbo Xinfu Titanium Dioxide Co. Ltd., China. The detailed physical properties of titania powder were illustrated in Fig. S1, Fig. S2 and Fig. S3. Sodium hexametaphosphate (SHMP, CP) and sodium alginate (SA, CP) were available from the Sinopharm Chemical Reagent Company (Shanghai, China). Deionized (DI) water from a Millipore-Q purification system (Millipore, USA) with a resistivity of 18.2 MΩ cm was utilized during this work.

2.2. Preparation of titania ceramic ink

Titania powder should be fully dried in the drying oven before use to ensure accuracy during the weighing process. Titania ceramic ink used to fabricate titania ceramic parts by direct ink writing was prepared by mixing uniformly an appropriate amount of titania powder, deionized water, sodium hexametaphosphate and sodium alginate. Sodium alginate and deionized water were used as binder and solvent, respectively. Sodium hexametaphosphate was used as dispersant, which could reduce particle agglomeration and contribute to improving ceramic powders content. It was necessary to completely dissolve sodium alginate and sodium hexametaphosphate in deionized water first during the experiment, which was beneficial to the better mixing of ceramic powders in the subsequent experimental steps. In order to obtain homogeneous and stable titania ceramic ink, the mixture should be stirred thoroughly at room temperature for 6 h using mechanical stirrer. Finally, the titania ceramic ink consisting of sodium hexametaphosphate and sodium alginate was vibrated for 30 min and followed by sonication. The composition of ceramic ink with different content was shown in Table 1.

2.3. Direct ink writing

Titania ceramic structures were fabricated with ceramic inks of optimized rheological behavior by a computer-aid design and computer-aid manufacturing device. The titania ceramic ink was filled in a 500 ml plastic syringe and passed through the nozzle at room temperature under the conditions of room temperature and normal pressure, three dimensional titania ceramic parts were created by continuous filaments via layer-by-layer deposition process, as shown in Fig. 1. During the printing process, the ceramic inks flow rate was controlled by a stepper motor, the nozzle with a diameter of 1 mm or 2 mm was used to fabricate three dimensional titania ceramic parts at the printing speed of 5 mm s^{-1}. The nozzle was incrementally moved along the Z axis direction once the underlying layer was finished and this process was repeated until the desired 3D titania ceramic structures were completed. According to ASTM D695 [32], samples used for compression tests were printed as a cylindrical shape of height H = 40 mm and diameter D = 20 mm. All specimens were printed with a layer thickness of 2 mm, which was equal to the nozzle diameter (2 mm).

All the printed titania ceramic samples were dried in the drying oven at 50 °C for 24 h in order to be fully dried. Before this, the size of simples should be measured with vernier caliper to prepare for the subsequent calculation of the shrinkage of the samples. Then the printed samples were sintered in an electric tube furnace (GSL-

Table 1
Composition of titania ceramic ink.

Titania/g	Deionized Water/ml	SHMP/g	SA/g	Content/%
59.50	27.65	0	0.05	0%(SHMP)
59.50	27.65	0.26	0.05	0.30%
59.50	27.65	0.53	0.05	0.60%
59.50	27.65	0.79	0.05	0.90%
59.50	27.65	1.06	0.05	1.20%
59.50	27.65	0.30	0	0%(SA)
59.50	27.65	0.30	0.44	0.50%
59.50	27.65	0.30	0.88	1.00%
59.50	27.65	0.30	1.33	1.50%
59.50	27.65	0.30	1.78	2.00%
35.64	27.65	0.30	0.05	56.00%(titania)
42.00	27.65	0.30	0.05	60.00%
49.78	27.65	0.30	0.05	64.00%
59.50	27.65	0.30	0.05	68.00%
72.00	27.65	0.30	0.05	72.00%

Fig. 1. Schematic diagram of direct ink writing.

1700X, Hefei Kejing Materials Technology Co. Ltd.) at an air atmosphere. The sintering temperatures were set to 1000 °C, 1100 °C, 1200 °C, 1300 °C and 1400 °C, respectively. The sintering procedure was increased from room temperature to sintering temperature with a heating rate 10 °C min^{-1} and held at sintering temperature for three hours. After the sintering process was finished, the titania ceramic parts fabricated by direct ink writing were cooled to room temperature at an air atmosphere in the furnace and then the size of samples should be measured.

2.4. Physical and mechanical characterization

The rheological properties of titania ceramic ink were measured using a rotational rheometer (Haake RS6000, Thermofisher Co. Ltd., Germany) equipped with a parallel plate geometry (PP15ER, diameter of 15 mm, and gap of 1 mm). Steady state flow and the oscillatory mode were employed during rheological measurements. Viscosity and shear stress were measured as a function of steady shear rate increasing from 0.1 s^{-1}–1000 s^{-1} using steady state flow mode. Shear elastic modulus (G′) was measured as a function of stress amplitude range of 1 Pa to 1000 Pa through oscillatory logarithmic stress sweep mode at the frequency of 1 Hz and a fixed strain of 0.4%. All tests were performed at room temperature.

The shrinkage of samples was calculated based on the difference in size of before and after sintering. The porosity and bulk density were measured using the Archimedes method. X-ray diffraction (XRD) (D8 Advance, Bruker, Germany) was used to identify the phases present in the sintered samples, using Cu Kα radiation ($\lambda = 0.15406$ nm) at a scanning rate of 0.19° s^{-1} in the 2θ range 20–80°. Field emission scanning electron microscopy (SEM, Hitachi S-4800, Japan) was utilized to observe microstructures of titania ceramic parts generated by direct ink writing. The mechanical properties of the printed titania ceramic rod samples were tested by a universal testing machine (CMT-5105, Shenzhen MTS Company). The test specimens were sanded by sandpapers to ensure that the two tested ends were flat and parallel. Finally, in order to ensure reliability of compressive strengths, five samples at each sintering temperature were tested.

3. Results and discussion

3.1. Rheological properties of titania ceramic ink

The rheological properties of the titania ceramic ink with different component content were illustrated in Fig. 2. Sodium alginate (SA) acted as a binder in this paper, which was a type of gelling polysaccharide most isolated from brown kelp, and it could be dissolved in water at room temperature to form a viscous liquid [33]. Its bonding property was used to effectively bond titania inorganic powder, which was beneficial to the molding of ceramic materials. Sodium hexametaphosphate (SHMP) was used as an anionic dispersant, whose main dispersion mechanism was improving the repulsion of inorganic particles [34]. As shown in Fig. 2(a) and (b), SHMP dispersant significantly reduced the viscosities and shear elastic modulus of titania ceramic ink. It was obvious that the viscosities and shear elastic modulus of titania ceramic ink gradually increased with the increase of SA binder, as shown in Fig. 2(c) and (d). The ratio of dispersant and binder should be decided based on these rheological results. The rheological properties of the titania ceramic ink were also closely related to the content of titania ceramic powder, as shown in Fig. 2(e) and (f). Titania ceramic ink with different solid content all showed obvious shear thinning behavior with increasing shear rate, and the viscosities decreased sharply. When the shear rate was too small or at rest, the particles in the ceramic ink were intertwined with each other and have a large viscosity. However, the particles in the ceramic ink were subjected to the shear stress during different flow layers when increasing the shear rate, which weakened entanglement of particles and caused shear thinning behavior [35,36]. For example, the viscosity of high solid loading (72 wt%) titania ceramic ink decreased from about 4000 Pa s to 60 Pa s when shear rate increased from 0.1 s^{-1} to 21.0 s^{-1}. The rheological behavior of ceramic ink shear thinning was vital for direct ink writing, which could ensure that the ceramic ink pass through the pipe and the nozzle smoothly without clogging under certain external force. Viscosities of high solid loading titania ceramic ink were higher than low solid loading ceramic ink at same shear rates. For example, viscosity of ceramic ink with 56 wt% titania powder content were approximately 180 Pa s at shear rate of 0.1 s^{-1}. However, for ceramic ink with a solid content of 72 wt%, the viscosity reached about

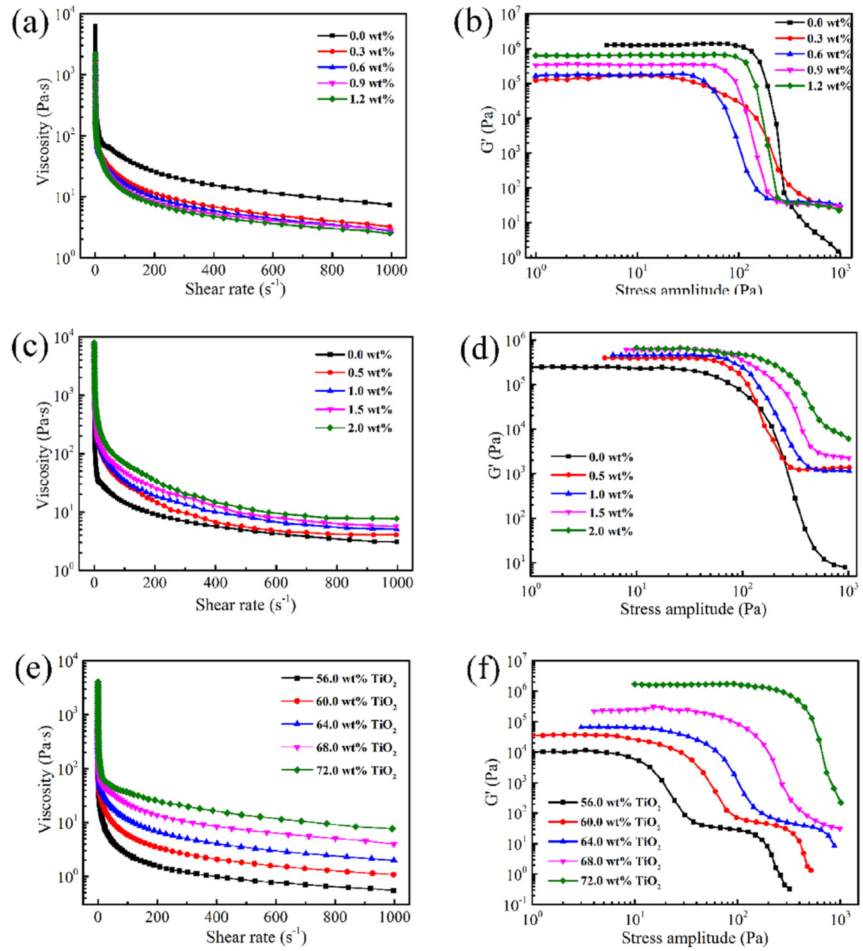

Fig. 2. The viscosity of the titania ceramic ink vs. shear rate, (a) different content of SHMP dispersant, (c) different content of SA binder, (e) different content of titania; The elastic modulus (G′) of titania ceramic ink vs. stress amplitude, (b) different content of SHMP dispersant, (d) different content of SA binder, (f) different content of titania.

4000 Pa s when the shear rate was 0.1 s^{-1}. Above results indicated that titania powder content played an important role in effectively adjusting the viscosity of ceramic ink, high solid loading titania ceramic ink was more viscous and needed a larger stress to make it flow. To make the ceramic ink perform shear thinning behavior, the yield stress (τ_y) must be overcome, which can be described by Herschel-Bulkey [37] equation:

$$\tau = \tau_y + k\dot{\gamma}^n \tag{1}$$

Here, τ is the shear stress, n is the shear thinning exponent (<1), k is the viscosity parameter, and $\dot{\gamma}$ is the shear rate. When stress is beyond yield stress, titania ceramic inks exhibit shear thinning phenomenon due to attrition between ceramic particles and additives. It can be understood that yield stress is the shear stress when shear rate is close to zero, and it is a critical point to push ceramic inks flow. According to Herschel-Bulkey equation, shear stress performs an increasing trend and then approximately reaches a relative stable platform. The relationship between shear stress and shear rate which is in line with the general trend of Equation (1) is can be understood with the help of Fig. 2(e).

An appropriate elastic modulus is important for the ceramic ink to maintain its shape after the ceramic ink is extruded from the nozzle. According to the past research on colloidal ink for direct ink writing, whether the elastic modulus of ceramic ink is suitable for direct ink writing can be evaluated by the equation [38,39]:

$$y = k\left(\frac{\varnothing}{\varnothing_{gel}} - 1\right)^x \tag{2}$$

where y is the elastic property of interest (shear yield stress (τ_y) or elastic modulus (G′)), k is a constant, x is the scaling exponent (~2.5), $\varnothing_{gel}$ is a critical volume fraction which is known as the gel point, $\varnothing$ is the colloid volume fraction. The elastic properties of colloidal ink are mainly determined by two parameters: $\varnothing$, which is proportional to bond density, and $\varnothing_{gel}$, which is inversely proportional to bond strength. Here, we can also use this model to evaluate whether titania ceramic ink is suitable for direct ink writing. As illustrated in Fig. 3, ceramic green body fabricated by ceramic ink with 56 wt% titania or 60 wt% titania collapsed and deformed greatly. When titania content of ceramic ink reached 64 wt% or above this value, a complete ceramic green body could be formed by direct ink writing. We could regard 64 wt% titania of ceramic ink as a critical mass fraction. In order to match better with the model for evaluating the suitability of titania ceramic ink, we converted the mass fraction of titania ceramic ink into volume fraction. The corresponding titania volume fraction of the ceramic ink with 64 wt% titania, 68 wt% and 72 wt% titania was 29.59 vol%, 33.44 vol% and 37.80 vol%, respectively. According to rheological results in Fig. 2(f), the elastic modulus of ceramic ink with 68 wt% titania and 72 wt% titania was approximately 1.65×10^6 Pa, 2.50×10^5 Pa, respectively. We regarded 29.59 vol% as a critical

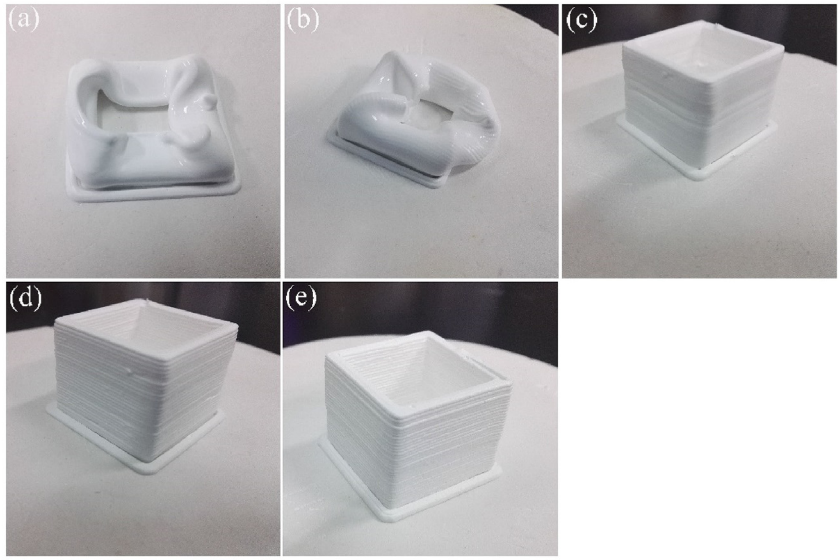

Fig. 3. Direct ink writing of ceramic ink with different titania content. (a) 56 wt%, (b) 60 wt%, (c) 64 wt%, (d) 68 wt%, (e) 72 wt%.

volume fraction, taking the ceramic ink volume fraction 33.44 vol%, 37.80 vol% into the equation for evaluation. Here, k was a constant, x was the scaling exponent (~2.5). After calculation, we obtained that k was about 4×10^7. This indicated that the capabilities of titania ceramic ink could also be evaluated by this model. In order to obtain a good printing effect, the elastic modulus of the ceramic ink should reach about 10^5 Pa. The titania volume fraction in ceramic ink evaluated by this model was approximately 32.28 vol% when the elastic modulus of the ceramic ink reached 10^5 Pa. This has a certain instructional significance for the direct ink writing of titania ceramic ink.

Elastic modulus (G') of ceramic ink with different titania content was illustrated in Fig. 2 (f). It was observed that titania ceramic ink with different solid content all had a plateau of elastic modulus when the shear stress was lower than the shear yield stress (τ_y), which represented linear viscoelastic properties. In the linear viscoelastic region, the elastic modulus of titania ceramic ink nearly remained constant as the shear stress increased. However, the shear elastic modulus decreased sharply from the shear yield stress, which represented the beginning of irreversible plastic deformation. Among the prepared titania ceramic ink, the ink containing 72 wt% titania had the highest equilibrium elastic modulus of approximately 1.65×10^6 Pa and shear yield stress of about 310 Pa. The elastic modulus of titania ceramic ink in the linear viscoelastic region were in the magnitude range of 10^4 Pa and 10^6 Pa. As illustrated in Fig. 2 (f), the shear yield stress of titania ceramic inks were approximately 10 Pa, 20 Pa, 50 Pa, 100 Pa and 310 Pa, respectively. The shear elastic modulus and shear yield stress of titania ceramic ink all increased with the content of titania powder, which was helpful to fabricate titania ceramic parts via direct ink writing. However, it didn't mean that the higher the shear elastic modulus was, the better the direct ink writing was. In actual experiment process, titania ceramic ink with beyond 72 wt% titania powder content was not fit for direct ink writing due to nozzle clogging during printing. The ceramic ink with low titania content (56 wt% and 60 wt%) was also not suitable due to lower elastic modulus, large deformation and collapse defects were observed during printing process. High titania loading ceramic ink (64 wt%, 68 wt% and 72 wt%) all could be utilized to print titania ceramic structures by 3D direct ink writing. The actual printing effect of ceramic ink with different titania content was illustrated in Fig. 3. At the same time, it was also an effective way to directly evaluate the capabilities for direct ink writing of ceramic ink. The supporting capabilities of ceramic ink and the printing effect were gradually improved with the increase of titania content. When titania content reached 64 wt%, 68 wt% and 72 wt%, it was obvious that the ceramic ink could be completely formed through direct ink writing without defects such as collapse and large deformation. In this paper, ceramic ink containing 72 wt% titania content was used to generate three dimensional ceramic structures by the nozzle of 1 mm in this kind of additive manufacturing method, as shown in Fig. 4. When printing the lattice truss structures, a high elastic modulus is especially important to maintain the shape after the ink passes through the nozzle, which can also reduce effectively the midspan deflection of a suspended strut for a desired span length [40].

3.2. Shrinkage and density

During the experiment, ceramic ink containing 72 wt% titania solid content with good rheological properties was selected for direct ink writing. The sizes of the printed samples were larger than that designed, which indicated that the printed sample has a certain degree of deformation and spreading. After the sintering process, there was obvious volumetric shrinkage occurred in sintered samples. Fig. 5(a) illustrated the volumetric shrinkages of samples sintered at different sintered temperatures, it was observed that there was significant difference compared to green body. The volumetric shrinkage of the sample increased as the sintering temperature increased from 1000 °C to 1400 °C, it was about 12.0%, 24.8%, 46.3%, 50.9% and 52.6%, respectively. It indicated that titania ceramic parts became more dense as sintering temperatures increased. The porosity and density of titania sintered at different temperatures were shown in Fig. 5(b), the sintering process of titania ceramics was the physicochemical process of pores expelled, density increased and grain growth. As illustrated in Fig. 5(b), density of titania ceramic at 1400 °C reached 91.5% of the theoretical density, and this value just reached 43.4% when sintering temperature was 1000 °C. When it came to the term of porosity, it was observed that the porosity of titania ceramic samples had an obvious drop when the sintering temperature

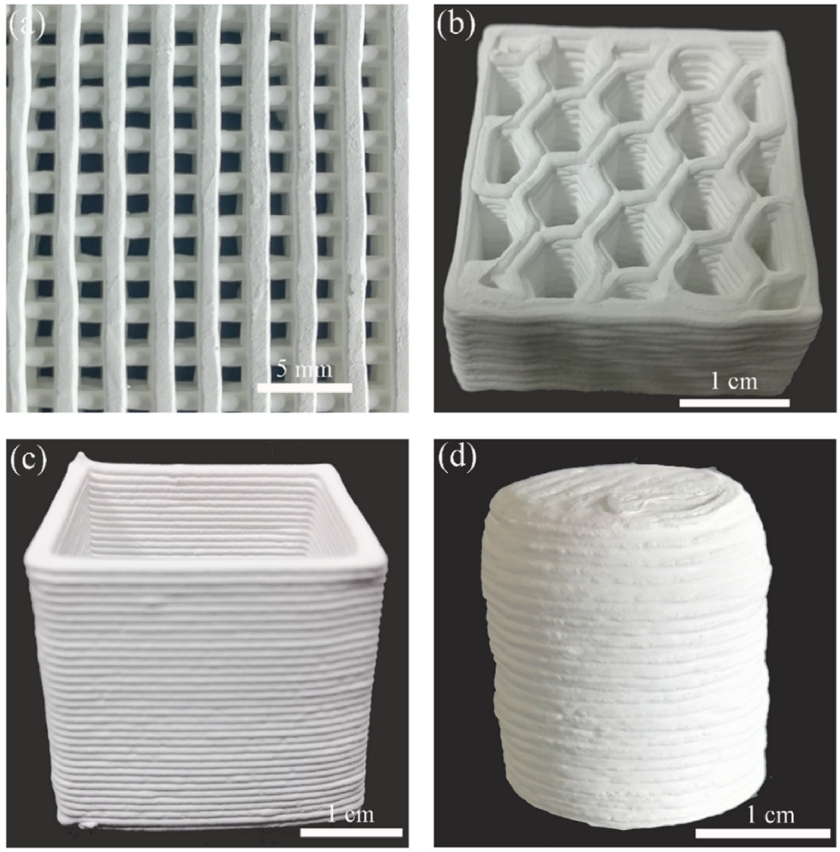

Fig. 4. Titania ceramic parts printed by 3D direct ink writing using titania ceramic ink.

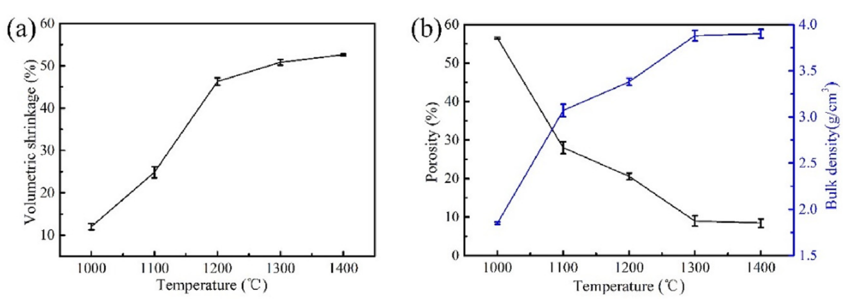

Fig. 5. (a) Volumetric shrinkage, (b) Porosity and bulk density of titania ceramic parts sintered at different temperatures.

increased. The value of porosity decreased from 56.5% to 8.4% when the sintering temperature increased from 1000 °C to 1400 °C, which was also corresponding to the experimental results of volumetric shrinkage and density. It was beneficial to exhaust pores, reduce the shrinkage and improve density of titania ceramic body when increasing the sintering temperature.

3.3. Microstructure and mechanical properties

The microstructure of the samples was characterized by scanning electron microscopy (SEM). Fig. 6 showed microstructure of titania ceramic sintered at different temperatures, which indicated that the increase of sintering temperature promoted the growth of titania grains. However, the growth of titania grains was not obvious at sintering temperatures of 1000 °C and 1100 °C, and the degree of sintering was relatively insufficient. The process of grain growth of titania during sintering was also accompanied by pore discharge and volume shrinkage in the ceramic body, so a well-crystallized rutile titania ceramic was obtained through high temperature sintering. It was found that the grain morphology changed with the sintering temperature, the grains of titania ceramics were rod-shaped at lower sintering temperature, and when the sintering temperature increased, the grains grew and gradually transformed into polygons. The size and morphology of the grains had an important influence on the mechanical properties of the titania ceramics, which would be discussed in mechanical properties.

The specimens used to test the compressive strength were printed into a cylinder of 20 mm in diameter and 40 mm in height at the printing speed of 5 mm s^{-1}. However, the sample size after printing was about 26.9 mm in diameter and 40.2 mm in height. It was obvious that the lateral deformation is more severe than the longitudinal direction. And sintered specimens were polished by

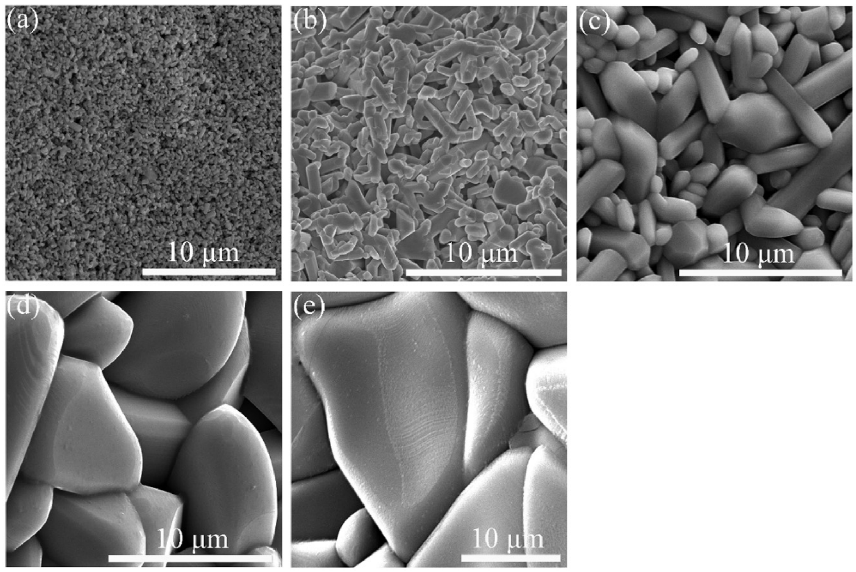

Fig. 6. SEM images of the samples sintered at different temperatures, (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, (d) 1300 °C, (e) 1400 °C.

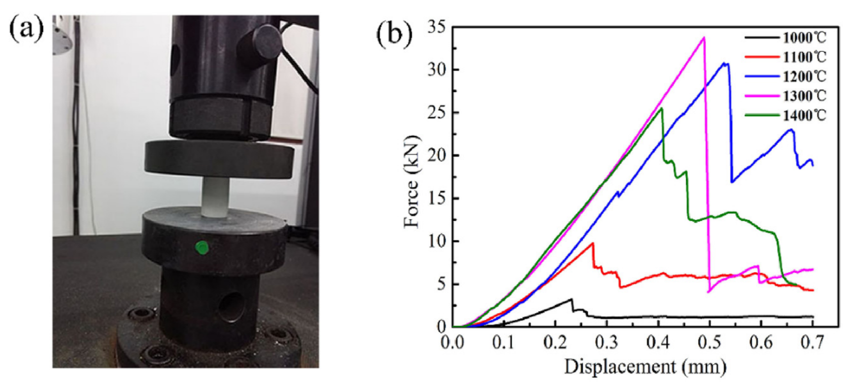

Fig. 7. (a) Mechanical compression test machine, (b) Compressive force-displacement responses for samples fabricated via 3D printing with different sintering temperatures.

200-grit sandpaper to meet test requirements. The test machine used to test compressive strengths of titania ceramic parts was shown in Fig. 7(a). For the reliability of the experimental results, both ends of the specimen must be parallel to each other. There were five parallel specimens at each sintering temperature. In Fig. 7(b), compressive force-displacement responses were illustrated, it was observed that compressive force of samples sintered at 1300 °C was the highest among samples sintered at other temperatures. Based the compressive force-displacement responses and the sizes of titania ceramic parts used to stress test, the compressive strengths of titania ceramic sintered at different temperatures could be calculated. Then, the elastic modulus of the titania ceramic sample was obtained, according to the compressive strength and strain value. The mechanical properties results were shown in Fig. 8, including compressive strength and elastic modulus, it was apparent that there was a tendency to increase first

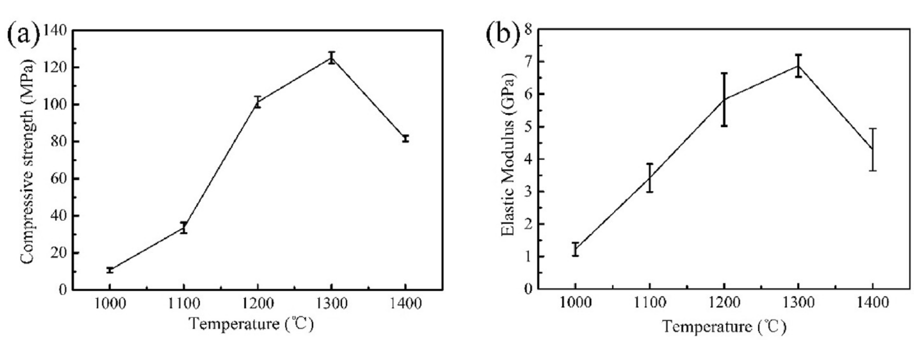

Fig. 8. (a) Compressive strengths, (b) Elastic modulus of titania ceramic samples sintered at different temperatures.

and then decreased both compressive strength and elastic modulus. Compressive strength of titania ceramic varied between about 10.60 MPa and 125.00 MPa, which had the highest value at sintering temperature of 1300 °C. This could be ascribed to that small porosity and titania grain stacked tightly, which was also corresponding to the test results of Fig. 5. As illustrated in Fig. 6, the grain size and morphology changed with sintering temperature, it was analyzed that titania ceramic parts with high compressive strength had appropriate grain size and polygonal grain shape. The compressive strengths of sintered samples from 1000 °C to 1200 °C was remarkably increased due to pores released continually and grain growth. However, the compressive strength of titania ceramic sintered at 1400 °C was lower than the samples sintered at 1300 °C, which indicated that it would adversely affect the compressive strength performance when the grain grew to a certain extent. The elastic modulus of titania ceramic sintered at different temperatures was in a range of 1.22 GPa and 6.87 GPa. It was close to the elastic modulus of human cancellous bone, which was in range of 0.28 GPa and 1.86 GPa [30]. It contributed to titania ceramic parts made by direct ink writing being a promising biomaterials for bone implants.

4. Conclusion

In this work, high solid loading (72 wt%) titania ceramic ink with favorable rheological behavior was prepared for direct ink writing, whose shear elastic modulus and shear yield stress were approximately 1.65×10^6 Pa and 310 Pa, respectively. Titania ceramic was obtained utilizing high solid loading titania ceramic ink by direct ink writing and sintered at high temperature. These samples occurred remarkably volumetric shrinkage from 12.0% to 52.6% at different temperatures. The value of porosity decreased from 56.5% to 8.4% when the sintering temperature increased from 1000 °C to 1400 °C. Titania ceramic's density reached 91.5% of the theoretical density when sintered at 1400 °C. Appropriate grain size was beneficial to improve the compressive strength, samples sintered at 1300 °C exhibited the highest compressive strength of 125.00 MPa. The elastic modulus of sintered samples was in a range of 1.22 GPa and 6.87 GPa, which was much lower than traditional metal biomaterials and close to the elastic modulus of human cancellous bone, this contributed to titania ceramic being a promising medical material.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jallcom.2018.12.334.

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