Rapid preparation and uniformity control of B_4C ceramic double-curvature shells: Aim to advance its applications as ICF capsules

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ABSTRACT

In this work, we report a rapid, simple and controllable approach to prepare B_4C ceramic double-curvature shells by dropping the coating slurry on a molybdenum (Mo) substrate. The B_4C slurry finally forms a nearly uniform spherical thin shell on the Mo substrates after drainage and curing process. We discovered that the uniformity and the wall thickness of the thin shell structure are controlled by the curing time and the viscosity of the slurry, respectively. This novel fabrication method not only provides an alternative way to prepare B_4C ceramic double-curvature shells for the potential application as an ICF capsule, but also sheds light on the uniformity control of other ceramic double-curvature thin shells.

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1. Introduction

Fusion energy has long been evaluated as a sustainable and clean energy, and research on inertial confinement fusion (ICF) is of great significance for the development of new energy. The preparation technology of ignition capsule is one of the key points of ICF [1–6], crucial for realizing the controlled nuclear fusion. According to the design requirements of the National Ignition Facility (NIF) [7], the diameter, wall thickness, sphericity, uniformity, surface roughness and so on are important indexes to evaluate the quality of capsules. Decade-long research in this area has revealed several low-Z materials as ideal ignition materials for national ignition device (NIF): Be-Cu, CH, diamond, and so on [8–10]. Particularly, B_4C is considered as one potential ignition material candidate because of its low density, nontoxicity, good heat resistance and stable chemical properties [11–13]. More importantly, unlike other

candidates, B_4C does not require doping. However, it is still a challenge to form B_4C ceramics with hollow microspheres [14,15], and there are only few reports on the successful preparation of B_4C ignition capsule. As early as 1997, Burnham et al. used magnetron sputtering technique to coat B_4C on polystyrene microspheres [16]. More recently, the poly(6-hexenyldecaborane) precursors are used to synthesize B_4C hollow microspheres by Wang et al. [17]. Unfortunately, both methods are time consuming with low thickness and uniformity. Therefore, exploring a new preparation approach should be invaluable for fabricating ICF-scale B_4C ignition capsule.

The double-curvature shells structure materials have received extensive attentions due to its wide application prospects [18,19]. Though currently available methods for preparing double-curvature shells, including the dip coating, rotational and injection methods [20–23], produce thin shells that are disqualified by the ICF design requirements. Besides, these methods are time consuming and small in size that is unsuitable for future industrial-scale production. Remarkably, Lee et al. reported the fabrication of hemispherical elastic shells by coating a polymer solution on a curved surface, which achieved a nearly uniform thin shell [24]. Inspired by this method, we study the preparation of the B_4C ceramic double-curvature shells by coating a curved surface with ceramic slurry, a novel approach for the fabrication of ignition

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capsules. The substrate needs to maintain its integrity during calcination while also be easily removed by acid. So metal Mo with a high melting point and relatively low thermal expansion coefficient was selected as the proper substrate in this study. In addition, Mo can be easily processed to a spherical shape and removed by aqua regia, also making it an ideal substrate material.

Here, we introduce a rapid and controllable method to fabricate B_4C ceramic double-curvature shells by dropping the coating slurry on a Mo substrate. Subsequently, the coating slurry through drainage and curing process forms a uniform thin shell. The effect of viscosity, drainage and curing time on the uniformity of as-prepared B_4C ceramic thin shell are investigated in details. The result shows that the formation of a uniform ceramic double-curvature shells structure depends strongly on the ability to maintain a relatively constant viscosity of the slurry during the drainage process. In addition, we found that the thickness of the thin shell can be controlled by adjusting the viscosity of the coating slurry. Finally, the dropping amount of the B_4C coating slurry will not affect the thickness of the B_4C thin shell.

2. Experimental

In the experiments, the starting material is B_4C powder (1–3 μm, Aladdin, Shanghai, China). AM-MBAM and a water-soluble copolymer of isobutylene and maleic anhydride (ISOBAM-104, Kuraray Co., Ltd, Osaka, Japan) system were used to obtain the B_4C coating slurry for achieving a variety of rheological properties [25,26]. As for AM-MBAM system, 6.0 wt% acrylamide (AM, Aladdin, Shanghai, China) and 0.4 wt% N, N-methyl-enebisacrylamide (MBAM, Aladdin, Shanghai, China) were used as monomers and crosslinking agents, respectively. 0.5 wt% Poly-acrylic acid (PAA, Aladdin, Shanghai, China) was added as a dispersant, and 0.1–0.6 wt% ammonium persulphate (APS, Aladdin, Shanghai, China) was added as the initiator of polymerization. As for ISOBAM-104 system, 1.0 wt% ISOBAM-104 is acting as both dispersing and gelling agent. In the end, the B_4C slurries (AM-MBAM system) containing 30.00–42.66 vol% solid content was prepared by ball-milling the B_4C powder, AM, MBAM, PAA, APS and deionized water with agate balls for 10 h at a rotate speed of 200 r/min. The B_4C slurries (ISOBAM-104 system) containing 31.12–48.05 vol% solid content was prepared by ball-milling the B_4C powder, ISOBAM-104 and deionized water with agate balls for 10 h at a rotate speed of 250 r/min.

The fabrication procedure for the B_4C double-curvature shell is shown in Fig. 1. The molybdenum (Mo) ball with a diameter of
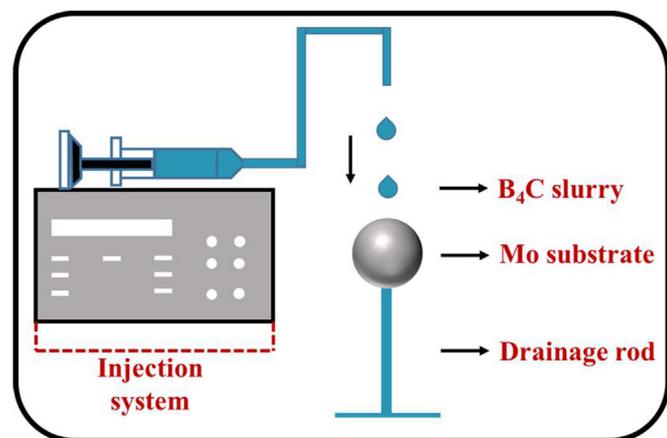
2 mm is used as the substrate, which is fixed on a drainage rod. The slurry from a certain height (50 ± 1 mm) is dropped on the Mo substrate to form a nearly uniform spherical shell, followed by further debinding and calcination to obtain the B_4C ceramic double-curvature shells.

The microstructure and wall thickness of the B_4C ceramic double-curvature shells were analysed by scanning electron microscopy (Model S-4800, Hitachi, Japan). The rheological properties of the B_4C slurries were evaluated using a rotary rheometer (HAAKE MARS III, USA) in shear rate range of $1-1000\,s^{-1}$ at room temperature. The phase constitution of the double-curvature shells was established by X-ray diffraction (DX-2700).

3. Results and discussion

The evolution process of the B_4C slurry on the substrate surface driven by gravity is illustrated by a schematic diagram in Fig. 2, where h represents the final wall thickness, μ is the viscosity of the slurry measured by shear rate of $100\,s^{-1}$, R is the radius of the substrate, g is the acceleration of gravity and θ is the azimuth angle. Generally, the viscosity value at a shear rate of $100\,s^{-1}$ can be used as a standard to evaluate the mechanical properties of B_4C slurry [27]. The surface tension is considered to be negligible. It can be observed from the schematic diagram that the B_4C slurry is drained along the substrate surface by gravity that eventually covers the whole substrate. Subsequently, the excess slurry is removed through the drainage rod at the bottom of the substrate. The slurry eventually cures in a limited time (t) and forms a nearly uniform double-curvature shells on the Mo substrate. Noted that the drainage process of the B_4C slurry takes only about 10–15 s (t_0) while $t \gg t_0$.

In a comparison study, we present the B_4C double-curvature shells prepared by AM-MBAM (36.45 vol%) and ISOBAM-104 (39.10 vol%) systems under the condition of the slurry viscosity of 0.3 Pa s, respectively, where Fig. 3(a–d) shows their outside surface morphology and cross-section of the shell. The cross-section images are taken from the upper part of the thin shell, where $\theta < 90°$. The sphericity of the double-curvature shells is obtained through projection and calculation [28]. As shown in Fig. 3(a) and (b), the
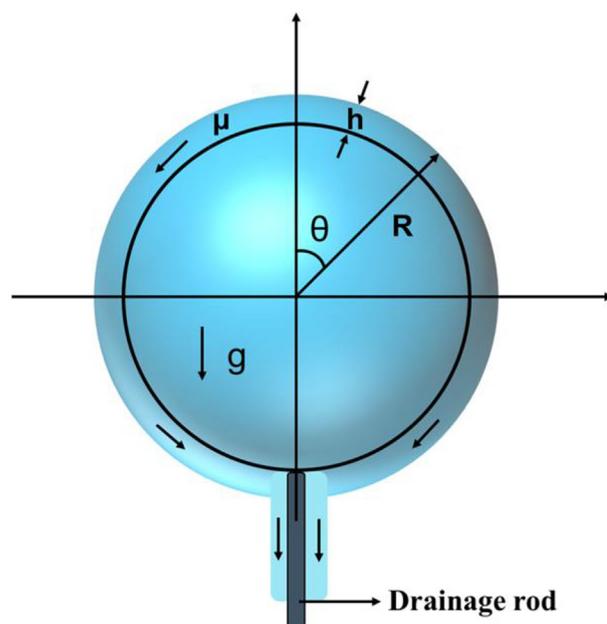

Fig. 1. Schematic diagrams of the experimental setup.

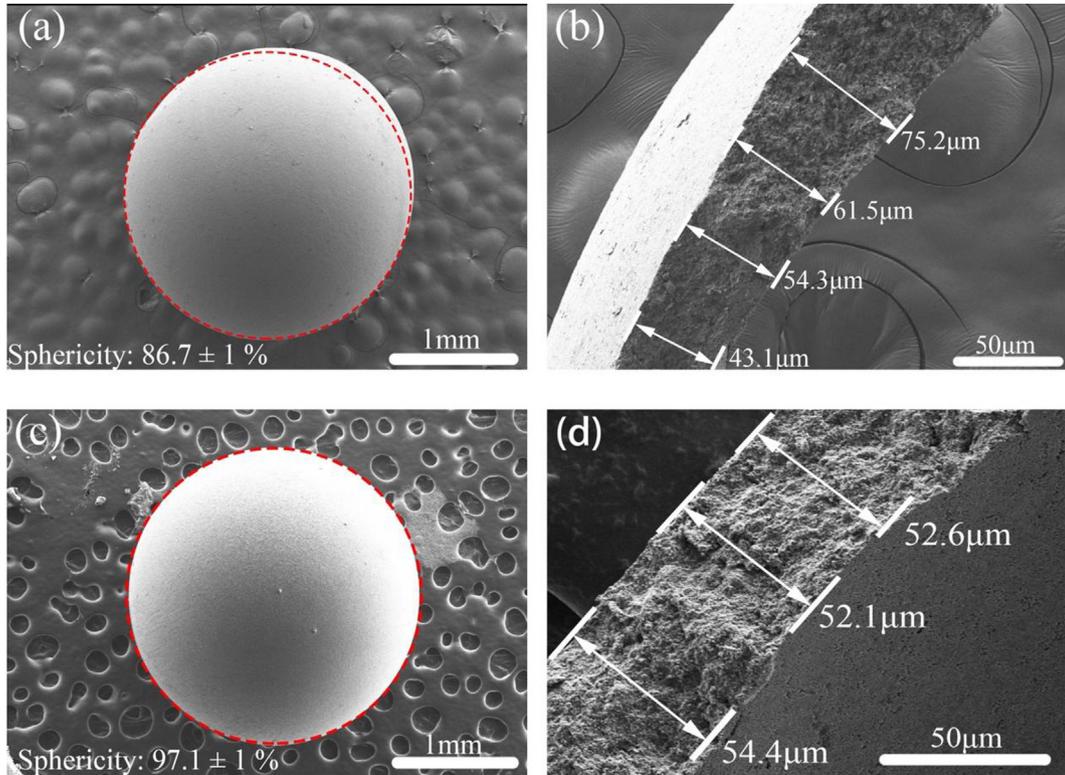**Fig. 2.** Sketch of the B_4C slurry driven by gravity.

Fig. 3. SEM morphology of the surface and cross-section of the B$_4$C double-curvature shell prepared by (a) and (b) AM-MBAM, (c) and (d) ISOBAM-104 system with the slurry viscosity of 0.3 Pa s, respectively.

thin shell prepared by AM-MBAM system is inhomogeneous, the sphericity is only $86.7 \pm 1\%$, and the cross-section shows an uneven distribution of the wall thickness. On the contrary, the double-curvature shell prepared by ISOBAM-104 system has a smooth surface and the sphericity is $97.1 \pm 1\%$ seen in Fig. 3(c). Also the cross-section shows a quite uniform curved thin shell structure (Fig. 3(d)) with an average wall thickness ~53 μm.

In addition, we study the dependence of the sphericity on the viscosity in a range of 0.12–0.56 Pa s. It can be observed in Fig. 4

Fig. 4. The sphericity of B$_4$C double-curvature shell as a function of viscosity of the slurry prepared by AM-MBAM and ISOBAM-104 system.

that the sphericity of the B$_4$C slurry prepared by ISOBAM-104 (30.00, 33.20, 36.25, 40.20 and 42.66 vol% solid content) and AM-MBAM (31.12, 35.34, 39.10, 43.25 and 48.05 vol% solid content) system decrease with increasing the viscosity; while under the same viscosity, the double-curvature shell prepared by the ISOBAM-104 system always has a better sphericity than that by the AM-MBAM system.

To explain the difference in morphology caused by different slurry systems, we develop a detailed physical description of the whole coating process. In a word, whether the thickness of any positions are equal throughout the drainage process will directly affect the final sphericity and uniformity of the double-curvature shells. It is well known that the wall thickness of a thin film draining on a spherical substrate is given by

$$h \approx \sqrt{\frac{3\mu R}{4\rho g K}} \left(1 + \frac{\theta^2}{10}\right)$$

where ρ is the density of slurry and K is the fitting parameter [24]. The R, g and K can be treated as constant values in the drainage process. The ρ is approximately constant because the B$_4$C particles are in situ fixed in the three-dimensional network formed by AM and MBAM [29]. As a direct deduction from the equation, the thickness of the thin shell increases with the increase of θ, causing the shell in the bottom to be thicker than those in other positions. However, the effect of the θ is independent of the choice of systems and also causes an insignificant difference in uniformity [30,31]. Therefore, we assume that the inhomogeneity of the shell thickness mainly is a result of the instability of the slurry viscosity during the drainage process. Fig. 5(a) shows the viscosity of the slurry as a function of time, with the initial viscosity as 0.12, 0.21, 0.30, 0.42 and 0.53 Pa s. It can be observed that the viscosity of the slurry prepared
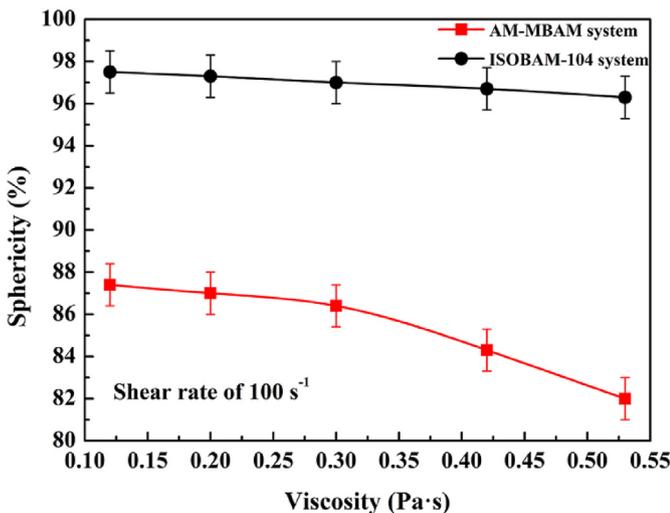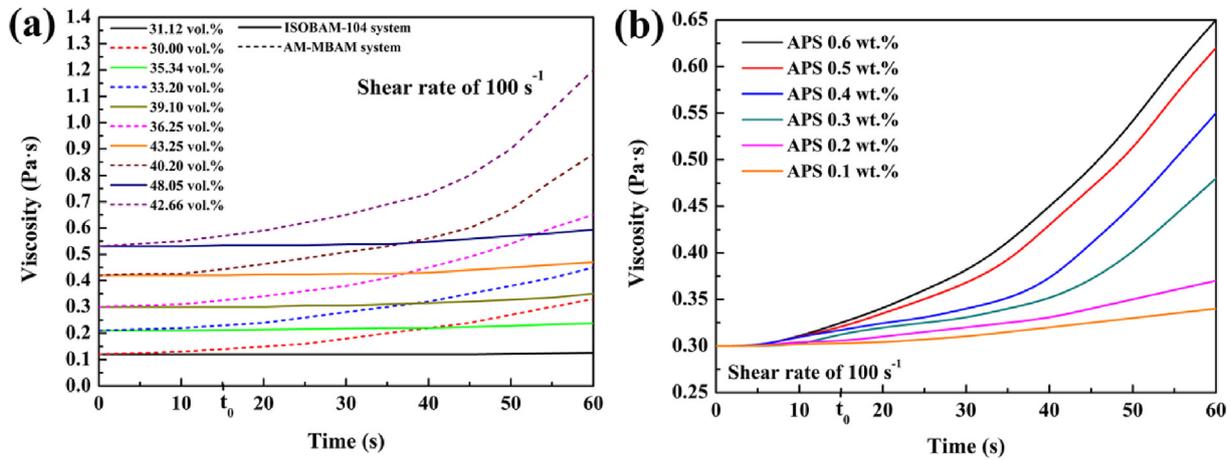
Fig. 5. (a) Viscosity of B$_4$C slurry prepared by ISOBAM-104 and AM-MBAM system influenced by different solid content; (b) Viscosity of 36.25 vol% B$_4$C slurry prepared by AM-MBAM system influenced by the addition of APS.

by the ISOBAM-104 system (30.00–42.66 vol% solid content) has not changed significantly over time, especially in the drainage time. On the contrary, the viscosity of the B$_4$C slurry prepared by the AM-MBAM system (31.12–48.05 vol% solid content) increases over the drainage time, as well as the growth rate. This finding shows that under the same viscosity, the slurry prepared by the AM-MBAM system cured faster than that of ISOBAM-104 system. Furthermore, it seems that a longer curing time has a positive effect on ensuring the slurry with a relatively constant viscosity during the drainage process. Thus, we increased the curing time of the B$_4$C slurry by reducing the content of initiator in AM-MBAM system. Fig. 5(b) shows the effect of APS content on the viscosity of 36.25 vol% B$_4$C slurry prepared by the AM-MBAM system, which is negligible on the initial viscosity of the B$_4$C slurry. In addition, we observed that the growth rate of slurry viscosity decreased with the decrease of APS content, suggesting that reducing the content of APS is equivalent to increasing the curing time of the B$_4$C slurry. For the slurry with 0.1 wt% APS, the viscosity is almost constant in the whole drainage process, which perfectly fulfills our needs.

Fig. 6 shows the effect of APS content on the sphericity of the B$_4$C double-curvature shell prepared by the AM-MBAM system
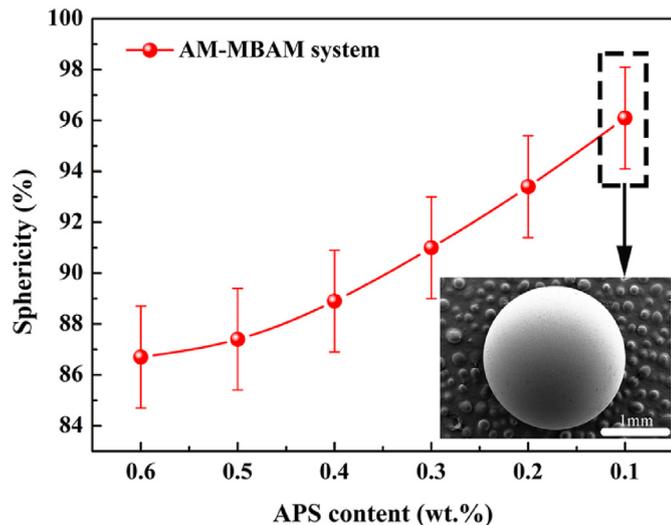
(36.25 vol%). It can be seen that with the decrease of APS content, the sphericity of the as-prepared B$_4$C thin shell improved from 86.7 to 96.1%. Particularly, the morphology of the B$_4$C thin shell prepared by AM-MBAM system with 0.1 wt% APS is shown inside of Fig. 6. It can be observed from the diagram that the sphericity of the B$_4$C double-curvature shell is obviously improved, and the surface of the thin shell is smooth without any cracks. In order to improve the mechanical properties of the double-curvature shells, it must be calcined at high temperatures. However, the mismatch of thermal expansion coefficients between the core and the shell at high temperatures can easily produce cracks in the shells. According to our previous literature [32], the B$_4$C core-shell structured microspheres calcined at 1400 °C have good mechanical properties and morphology. However, further rising the calcination temperature can result in a substrate expansion force that is greater than the stress of the shells and consequently leads to the cracking of the shells. Therefore, the thin shells are calcined at 1400 °C under the protection of N$_2$. During the calcination, the size of B$_4$C particles grows with the increase of temperature, and the pores between the particles gradually shrink and finally realize the densification, which can greatly improve the mechanical properties of the thin shells. As shown in Fig. 7(a), the B$_4$C ceramic double-curvature shell still maintains a good sphericity during the ceramization [33], and has a less roughness in the surface of the thin shell as a result of the grain growth. The cross-section of the double-curvature shell is compact and uniform, with an average wall thickness of ~61 μm (Fig. 7(b)). Fig. 8 shows the XRD pattern of the B$_4$C ceramic double-curvature shell calcined at 1400 °C, the most of positions and relative intensities of the diffraction peaks in the graph can be identified by standard crystallographic data (JCPDS card No. 35-0798).

As aforementioned, the final thickness of ceramic double-curvature shell is directly connected to the viscosity of the coating slurry, and the initial viscosity can be continuously tuned by the solid content. In Fig. 9(a), the final wall thickness is plotted versus the slurry viscosity. We found that the final wall thickness can be controlled in the range of 45–98 μm by adjusting the initial viscosity of the B$_4$C slurry. Moreover, in the same viscosity, the thickness of the thin shell prepared by the AM-MBAM system is greater than that by the ISOBA-104 system, which may be due to the faster curing rate of the coating slurry prepared by AM-MBAM system. Remarkably, as can be seen from Fig. 9(b), the final wall thickness of the as-prepared B$_4$C ceramic double-curvature shell was found to be independent of the volume of the dropped slurry.
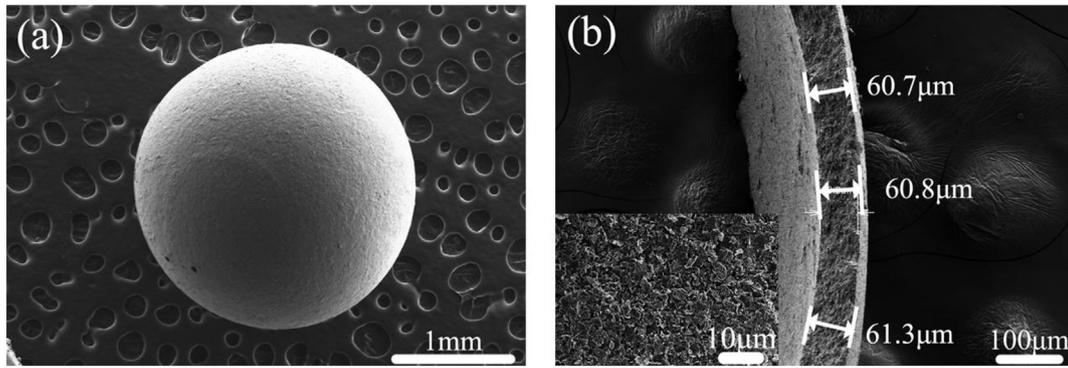

Fig. 6. Sphericity of as-prepared thin shell influenced by the APS content of 36.25 vol% B$_4$C slurry prepared by AM-MBAM system.

Fig. 7. (a) and (b) SEM morphology of the surface and cross-section of the B$_4$C double-curvature shell prepared by AM-MBAM system with 0.1 wt% APS and calcined at 1400 °C.
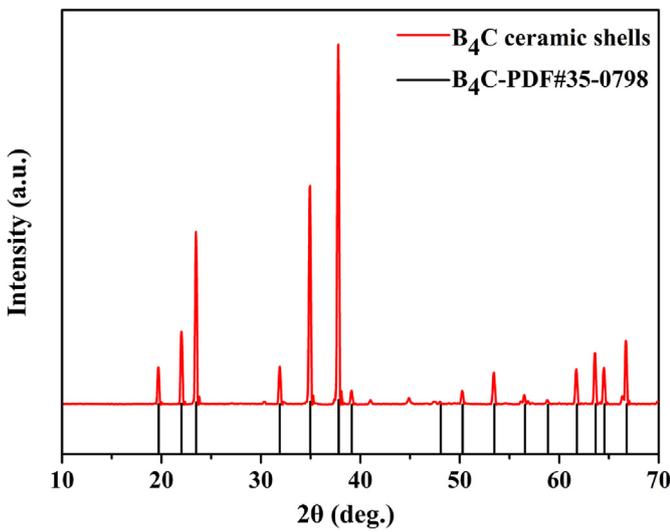

Fig. 8. XRD pattern of the B$_4$C ceramic double-curvature shell calcined at 1400 °C.

In other word, dropping an excess volume of slurry does not increase the thickness of the double-curvature shell, which makes the preparation process more flexible and operable.

4. Conclusion

In summary, the B$_4$C ceramic double-curvature shell with a high sphericity and uniformity can be obtained by both AM-MBAM and ISOBAM-104 slurry systems. Sufficient curing time can ensure a relative constant viscosity of the slurry during drainage process that results in a more uniform double-curvature structure. The sphericity of the double-curvature shell prepared by AM-MBAM system can be increased from 86.7 to 96.1% by increasing the curing time of the slurry. Moreover, the final thickness of the as-prepared thin shell was controlled in the range of 45–98 μm by continuously adjusting the initial viscosity of the slurry in the range of 0.12–0.56 Pa s. The further analysis illustrated that the final thickness of the as-prepared thin shell is found to be independent of the volume of the dropped slurry. This work demonstrated a feasible method to fabricate B$_4$C ceramic double-curvature shells for the potential application as an ICF capsule, and that would also be valuable to other ceramic double-curvature thin shells in terms of applications in uniformity control.
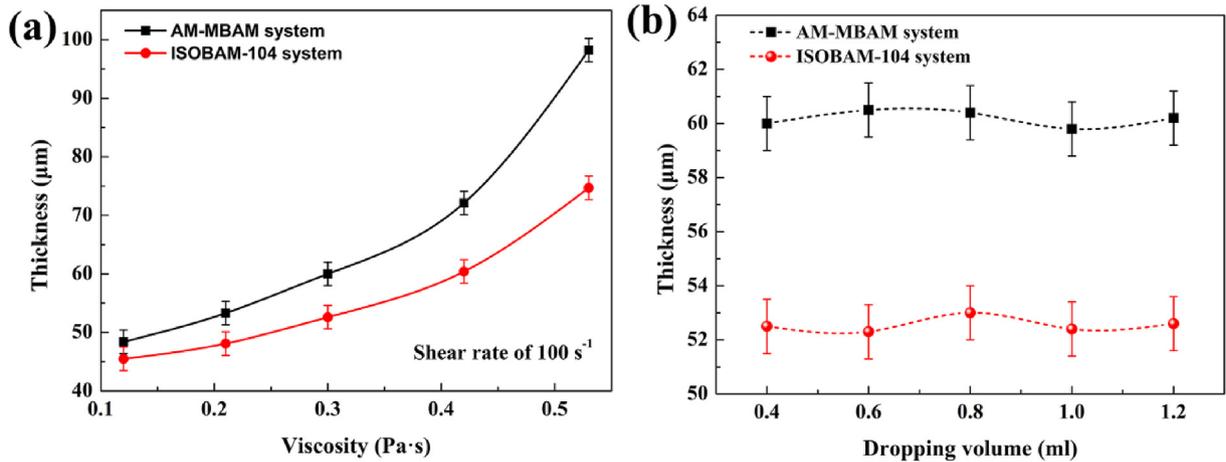

Fig. 9. (a) Effect of slurry with different viscosity on thickness of B$_4$C ceramic double-curvature shell (AM-MBAM and ISOBAM-104 system); (b) Effect of the volume of the dropped slurry on thickness of B$_4$C ceramic double-curvature shell (AM-MBAM and ISOBAM-104 system with viscosity of 0.3 Pa s).

Acknowledgements

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