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Preparation of Millimeter-scale Alumina Hollow Spheres by Oil_1-in-water-in-oil_2 Emulsions

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Abstract: To prepare millimeter-scale alumina hollow spheres by oil_1-in-water-in-oil_2 emulsions, the influence factors of formation of precursor and curing process were studied. Composite droplets with paraffin liquid as inner core and alumina sol as outer shell were used as precursor. Results showed that the com-droplets had homogeneous and complete core-shell structure when emulsion generator was designed that inner oil could be injected into water phase with the size of millimeters scale. Thickness and diameter of droplets were adjusted by both controlling the injection speed of oil and water phase in the range of 30–80 μm and 800–2200 μm. In the curing process, the semisolid spheres kept hollow structure and spherical when the speed of rotation between 20 r/min to 60 r/min and the flask being put in horizontal. Finally, the prepared hollow ceramic spheres with wall thickness in micrometer-scale and diameter in millimeter-scale formed complete hollow structure and high sphericity after calcining at 1200 ℃ for 4 h. The surface of sphere was relatively smooth with roughness of about 22 nm. The main crystal of the prepared ceramic hollow spheres was alpha alumina.

Key words: alumina hollow spheres; oil_1-in-water-in-oil_2 emulsion; composite droplets; flow focusing micro-channel

The suitability of target pellets requires high quality hollow micro-spheres with high sphericity and diameters that reach to millimeter-scale in the ICF energy technology[1]. The alumina hollow spheres have great potential application prospects using as targets because of the excellent physical and chemical performance[2]. In the current study, the ceramic hollow spheres have been prepared in various materials with wide sizes[3-8]. However, the size of prepared hollow spheres are mostly in nanometer and micrometer scale, the related literature reports are infrequent which the size of spheres reach to millimeter-scale. The preparation methods are mainly divided into chemical and physical methods[9-11]. The chemical reaction hardly reach to millimeter-scale[12], the advantage of physical template method is that the sizes of hollow spheres are easily controlled by changing sizes of template and reach to millimeter-scale[2]. Inspired by the micro-encapsulation technology, alumina hollow spheres with wall thickness of 30–100 μm and diameter of 600–2500 μm were prepared by Wang, *et al* using oil-in-water emulsion droplets as precursor by the method of soft template[13]. Liu, *et al* prepared the submicron Cu_2O hollow spheres composed of small Cu_2O nanoparticles of 22 nm in size *via* using a multiple emulsion (O/W/O) system as the template[14]. Yodthong, *et al* prepared hollow chitosan microspheres with 100 μm diameter by an oil_1-in-water-in-oil_2 emulsion solvent diffusion method though mixing and stirring[11]. Consequently, using double emulsion micro-encapsulation technology to synthesize ceramic hollow spheres is feasible.

The emulsion micro-encapsulation technology is based on the complex system multiple emulsion termed "emulsion of emulsion" which have received a great deal of attention due to their improved stability and facilitated control of their properties and play critical roles in various fields including foods, cosmetics, pharmaceuticals and chemicals[15-16]. Compared with the simple emulsions consisting of only one phase, each dispersed globule in the double emulsions forms composite droplets with core-shell structure made of two immiscible liquids, and multiple liquid phase compartments separated from the water phase by a layer of oil phase compartment[17]. Based on the combination way of two phase fluid, the major types of composite droplets formed by multiple emulsions are the water-oil-water (W/O/W) and oil-water-oil (O/W/O) double emulsions consisting of oil (water) droplets dispersed within larger water (oil) droplets, which are them-

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selves dispersed in the oil (water) continuous phase[18]. The composition of multiple emulsion is of significant importance since the different parameters, along with the nature and concentration of water and oil phase, that also affect the stability and size of the double emulsion crucially[19-20]. In addition, the geometry of microfluidic device is also the major generator which parameter affect the formation or manipulation of droplets. Microfluidic droplet-generation devices consisting of inter and outer connected channel configuration have been developed within the last decade[16-21]. Several types of microfluidic devices depending primarily on the capillary size and channel geometry have been proposed to generate mono-disperse emulsion droplets[22]. Microchannel (MC) emulsification as the first emulsion droplet generation technique using a microfluidic device, can formulate mono-disperse emulsions with droplet diameter from a few microns to hundreds microns[23]. According to the literatures, membrane emulsification can produce mono-disperse emulsions by forcing the dispersed phase into the continuous phase through a microporous membrane[24-25]. In addition to membrane emulsification, knowledge of drop formation at a capillary tip is also common device in many engineering processes. The most commonly used microfluidic channel configurations are T-junction and flow-focusing[26-28]. Droplet generation in a T-junction requires the cross flow of the continuous phase, and flow-focusing configurations are driven by the co-flow of the continuous phase.

In preparation of all kinds of droplet microfluidic devices, co-flow microchannel devices have received the widespread attention because of the simple structure and the controlled size. Therefore the aim of this study is to investigate the formulation of millimeter-scale alumina hollow spheres using the oil_1-in-water-in-oil_2 (O/W/O) emulsion droplets made by self-made co-flow device and study the effect of devices, flow ratio and the match of density and viscosity. Moreover, the speed and angle of rotation in the curing process is also discussed, the morphology of samples were displayed and analysed.

1 Materials and method

1.1 Materials

As the choice in this study, the oil_1-water-oil_2 micro-emulsion droplets were made of water phase and two different oil phase. The paraffin liquid and silicone oil (AR, Chengdu Kelong Chemical Co., Ltd.) were used as the dispersion phase (first oil phase) and external oil phase (second oil phase) respectively. The alumina sol was chosen as water phase (continuous phase). The reparation method of alumina sol was as follows: putting the aluminum isopropoxide (AR, Chengdu Kelong Chemical Co., Ltd.) in the mix solution of $n(C_9H_{21}AlO_3):n(H_2O):n(HNO_3)$= 1:100:0.25 with continual stirring for 10 h at 85 ℃, after stewing the mixed solution in a drying oven for some time at 90 ℃, uniform and stable alumina sol was obtained.

1.2 Experimental setup

The co-flow micro-emulsion generators were mainly made of two different diameter capillaries with wall thickness of 0.1 mm, diameters of 0.3 mm and 0.9 mm, respectively. The smaller capillary was inserted into the bigger one, both of them were stayed in a concentric shaft. Three kind of devices were designed according the different combinations of two capillaries. As shown in model A, the bottom of inner one was aligned with the outer one, the cross-section of bottom was in the same plane. The difference of model B compared with model A was the length of inner capillary which was bulged 0.5 mm than external one. The model C displayed that the inner capillary was embed in the middle of outer one. The other aspects of the capillaries were fixed by two special plastic connectors through the holes dogged beside the plastic stuff in different diameter. The connectors were bonded on glass sheet, as thus the interior keep airtight and connected with two syringes in the other side. The schematic diagram of co-flow micro-emulsion device was shown in Fig. 1.

1.3 Method

The paraffin liquid as first oil phase was used as disperse phase and soft template in the preparation of double droplets. The syringe connected to the upper plastic connector was initially filled with paraffin liquid that flow out from inner capillary. The under connector was concatenated with the other syringe filled with alumina sol that flow out from outer capillary. Two syringes were controlled by the two micro-injection pumps (BYZ-810, BEYOND Medical Devices Co., Ltd.) whose drainage rate was controlled with range 0.1 mL/h$\leqslant Q_{flow}\leqslant$300 mL/h. And two kinds of liquids flowed at different speeds in the respective channel, then converged in the end of capillary. Two liquids would form the droplets at the extreme of the capillary and then drop into the round flask filled with silicone oil. The combination of the droplets were various because of the different models. The produced droplets were moved into a rotary evaporator and curdled gradually, semisolid alumina gel spheres were obtained after rotating and evaporating for 12 h at 100 ℃. The gel hollow spheres were washed three times by diethyl ether and deionized water, then sintered at 1200 ℃ for 4 h in air. Finally, the millimeter-scale alumina hollow spheres were prepared.

1.4 Characterization

The density and viscosity were measured respectively by the oscillating U-tube method (Anton Paar, DMA-38) and digital rotational viscometer (NDJ-79A) at a tempera

25℃. The Scanning Electron Microscope (TM-1000, Hitachi High-Tech Science Systems Corp.) was used to characterize the morphology and size of spheres. The size of thickness and diameter of com-droplets and the overall appearance of spheres were displayed by the optical microscope (DM-2000, Lesia Microsystems). X-ray Diffraction (XRD) pattern of the prepared Al_2O_3 ceramic hollow sphere was recorded on an χ'Pert PRO diffractometer (PANalytical Company (formerly Philips Analytical), Holland) with Cu Ka radiation (λ=0.15406 nm) over a scan range of 10°~80° at rate of 8°/min. The surface roughness of spheres was detected by the atomic force microscope (SPA - 400, NSK Ltd.).

2 Results and discussion

2.1 Match of density and viscosity

In emulsion micro-encapsulation technology for preparation of microspheres, for considering the stability of double emulsion droplets, the match of density and viscosity of oil phase and water phase is prerequisite to obtain intact composite droplets, there is general requirement that the composite density of droplets should be close or slightly greater than the outer oil phase[28]. Therefore, we need to find a critical stage for composite droplets, by regulating the initial phase parameters to improve the composite average droplet density. Because the density of inner and external oil phase is invariable, the density of composite droplets is decided mainly by the density of water phase (alumina sol) which is inconstant according to the aging time. Moreover, when considering the injection of a liquid at a capillary tip into another immiscible liquid, additional effects arise from the viscous properties of the surrounding fluid (silicone oil). The ambient fluid exerts a viscous shear stress on the contiguous interface and keeps droplets complete. Thus the viscosity of different phase has a great influence on the integrity of the droplets. We count the change of density and viscosity of alumina sol aged for different time. As shown in Table 1, with the increasing of aging time, the density of sol has a slight change, but almost close to silicone oil. The viscosity changes significantly since the internal condensation gradually. In order to make the oil droplets package, the viscosity of sol shall be larger than paraffin. However, if the aging time is too long (more than 15 d), the sol gradually turn into solidification that viscosity is very big, but the liquidity is lost simultaneously. Therefore, the sols aged for 5 d to 15 d are appropriate to obtain composite droplets.

2.2 Phenomenon and analysis in different model and flow rate

In the process of two phase fluid combine, as the inner flow velocity increasing, the composite drops accommodate more fluid volume from the thread and become larger. The formation of droplets in the micro-channel can

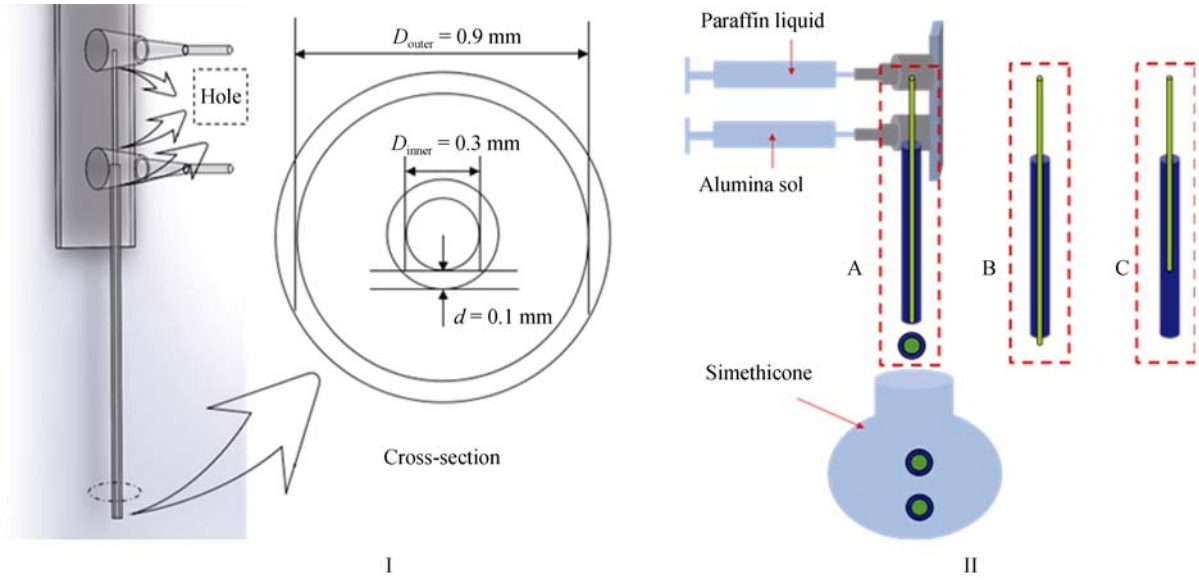

Fig. 1　Schematic diagram of co-flow micro-emulsion generator

Table 1　Parameters of materials (T=25℃)

Parameters	Alumina sol aged for differeut time/d					Paraffin	Silicone oil
	1	5	10	15	20		
Density, ρ / (g · mL^{-1})	1.012	1.024	1.027	1.052	1.073	0.835	0.963
Viscosity, η / (mPa · s)	26.56	37.90	48.23	58.44	98.36	35.98	400.00

be divided into three stages: droplet formation and growth, droplets combination and droplets falling off from the channel[29]. When a disperse phase is injected *via* a capillary tube into another immiscible liquid, two different drop formation mechanisms are observed: either drops are formed directly at the needle tip or break up from an extended lament. The transition point between the flow domains is of great importance both for theoreticians, experimentalists and operators since the dynamics of drop formation change significantly. In the beginning of combine process, surface tension plays a dominate role and holds the droplet hanging at the exit. With the growth of droplet, detaching force becomes more important. When these detaching forces achieve balance with the holding one, the forming droplet begins to break away from the thread and tends to develop as spherical shape by the surface tension.

Herein, three kinds of devices are designed according to different combination of the two capillaries. The kinds of combination droplets depended on the device geometry and the flow rates of disperse and continuous phase. As is shown the model A in Fig. 2, since the exits of inner and outer capillary are in the same plane and the density of oil phase is lower than the outer water phase, this leads to that the oil is upper in the composite droplets. However, in the model B, the inner oil is directly injected into the water phase because the inner capillary is bulged 0.5 mm than external one, this provides the original conditions for wall thickness uniformity of the hollow ball. The model C is designed that the oil flow out from in the water phase environment, there are several oil droplets in the composite droplets. In order to obtain the single homogeneous hollow structure, the only one oil droplet is allowed in the center of water droplets. So the model B is the most appropriate geometric construction.

Otherwise, the flow rate which affect the formation of composite droplets should be controlled in a suitable range.

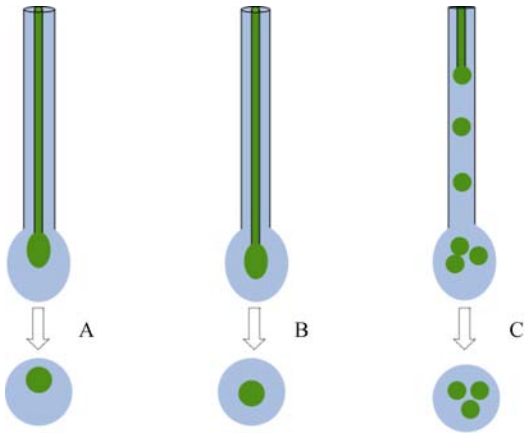

Fig. 2 Three kinds of composite droplets (model A, model B, model C)

The wall thickness and diameter of droplets are adjustable according to the cooperation ratio. At high injection rates of the disperse phase, the liquid jet out continuously and the droplets would not form at the export of capillary. According to the experimental observation, the average velocity of the flow phase would be controlled under 10 mL/h. The optical microscope (DM-2000, Lesia Microsystems) is used to measure the diameters of inner oil (d) and outer com-droplets (D). So the diameter of com-droplet is D and the thickness (t) of com-droplet is calculated by the formula: $t=(D-d)/2$. The changes of diameter and wall thickness of com-droplets made by model B are displayed in Fig. 3 and Fig. 4. When the flow rate of the oil phase is kept constant at V_{oil}=1 mL/h, the volume of inner oil phase is invariant, with an increase of the velocity of the water phase as the shell, the composite drops accommodate more fluid volume from the thread and become larger. When keeping V_{water}=6 mL/h, regulating the velocity of oil phase, as shown in Fig. 4, the diameter increases gradually and wall thickness decreases reciprocally. Thus, the thickness droplets range from 30 μm to 80 μm and the diameter range from 800 μm to 2200 μm by adjusting the speed of oil and water phase respectively.

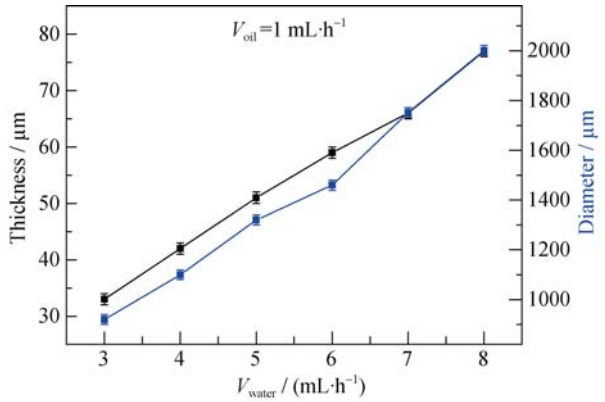

Fig. 3 Diameter and wall thickness of com-droplets at different velocities of water phase (V_{oil}=1 mL·h^{-1})

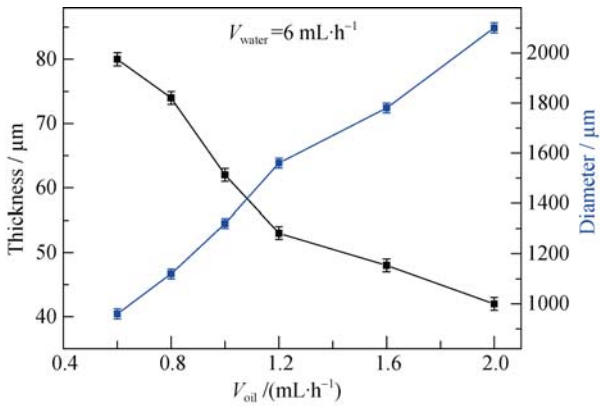

Fig. 4 Diameter and wall thickness of com-droplets at different velocities of oil phase (V_{water}=6 mL·h^{-1})

2.3 Effect of rotation angle and speed

The density of liquid droplets are inconstant since heated and shrink in curing process, so the solidification process must be carried out in a rotating fluid field. Under the influence of centrifugal forces, the composite droplets remain suspended in the round bottom flask filled with silicone oil. As rotary fluid field applied, the spin of droplets will improve decentration and unsphericity, at the same time, the stability of droplets may be further improved. The collision of microsphere has a great influence on the surface defects, with the decrease of the microsphere collision frequency, the surface defects will be alleviated, so the number of composite droplets in the round bottom flask rotating and solidifying should remain under ten in order to prevent the collision and fusion of each other. The droplets are worked by gravity, buoyancy and centrifugal force in rotating and curing process. Three different rotational modes shown in Fig. 5 are researched which are horizontal type, vertical type, diagonal type. When the flask are rotated in vertical type, the droplets which density is larger than silicone oil will gradually settle in the bottom of the flask. All the droplets will be mixed together, the spherical structure of droplets are destroyed. When the flask are rotated at a certain inclination angle, the centrifugal force suffered droplets also is inclined and not on the same axial with the gravity and buoyancy in vertical direction, droplets will become oval and even rupture. Putting the flask in horizontal, the gravity, buoyancy and centrifugal force suffered in droplets are in the same plane, droplets are almost in a state of balance and keep spherical as much as possible. So the flask is in horizontal which is the most suitable angle.

In order to determine the appropriate speed of rotation, ten com-droplets are chosen and rotated at different speed in horizontal type. As is shown in Fig. 6, if the speed of rotation is too quick, the droplets will break up immediately ($v \geqslant 60$ r/min). However, the speed is too slow, most of droplets will combine gradually ($v \leqslant 20$ r/min). Therefore, the speed of rotation shall be controlled in the range from 20 r/min to 60 r/min, the best chose is 30 r/min which droplets can keep good concentricity and sphericity and would not break as the flow movement.

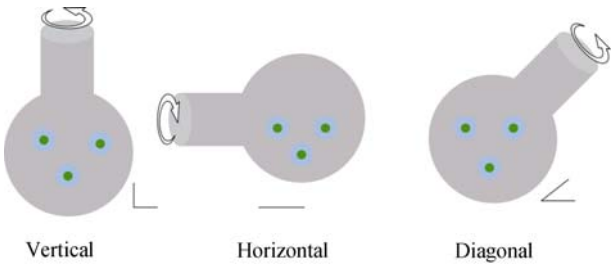

Fig. 5　Schematic of three different rotate types

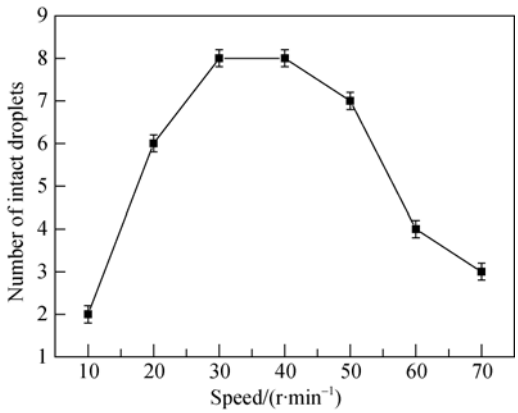

Fig. 6　Number of intact droplets at different speed after curing (n=10)

2.4 Display of result

Figure 7 displays the photographs of com-droplets, semisolid spheres and SEM of ceramic spheres made by model A, B and C respectively. Because the oil phase is

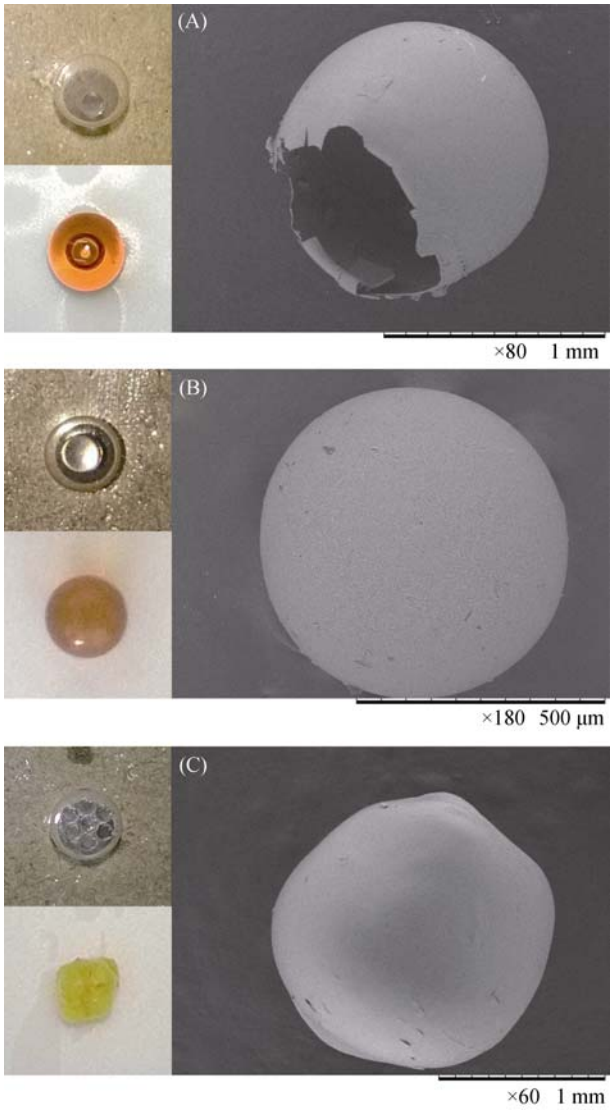

Fig. 7　Photographs of com-droplets, semisolid spheres and SEM images of ceramic spheres by model A, B and C

upper in the water droplets by model A, the sphere is broken after curing and sintering. However if there are too much oil droplets in the water droplet, the oil droplets will combine together gradually, thereby collapse happens in the sphere, so spherical structure is destroyed (Fig. 7(C)). It is obvious that the com-droplet obtained by the device of model B has an apparent core-shell structure which oil phase as core and water phase as shell. The com-droplets after curing under the condition of proper control are transformed into semisolid spheres which have complete sphericity. After sintering at 1200℃ for 4 h, the obtained ceramic spheres still keep spherical totally (Fig. 7(B)).

Seen from image of Fig. 8(B)and (C), the ceramic sphere has a high sphericity with the diameter of about 1.7 mm which reach to millimeter scale and the thickness of about 27 μm.The optical images D, E, F of spheres display that the sphere is a complete spherical ball with a single hollow structure, and the shell is uniform. The surface of sphere is relatively smooth with the roughness of about 22 nm (Fig. 8(G) and (H)). Otherwise, Fig. 8 I shows XRD pattern of alumina ceramic hollow sphere. The diffraction peaks are sharp and correspond to the standard card of alpha alumina (JCPDS- PDF#No.75-1865, space group: R-3C). This suggests that the aluminum isopropoxide is translated into alumina ceramic after hydrolysis, curing and sintering at last.

3 Conclusions

The alumina hollow spheres in millimeter scale were prepared by oil_1-in-water-in-oil_2 emulsions within flow focusing micro-channel. The composite droplets which the oil phase as inner core and water phase as outer shell were used as the precursor for the preparation of alumna hollow spheres. Meanwhile, the match of density and viscosity of oil phase and water phase was the prerequisite to obtain intact composite droplets. The co-flow micro- emulsion generator that mainly made of two capillaries with diameters of 0.3 mm and 0.9 mm respectively and kept the length of inner capillary bulged 0.5 mm than external one was the most appropriate geometric construction to obtain the millimeter-scale com-droplets which the oil phase was in the center of water phase. The size of droplets could be adjusted by controlling the injection speed of oil and water phase with the thickness of 30-80 μm and diameter of 800–2200 μm. The semisolid spheres kept hollow structure

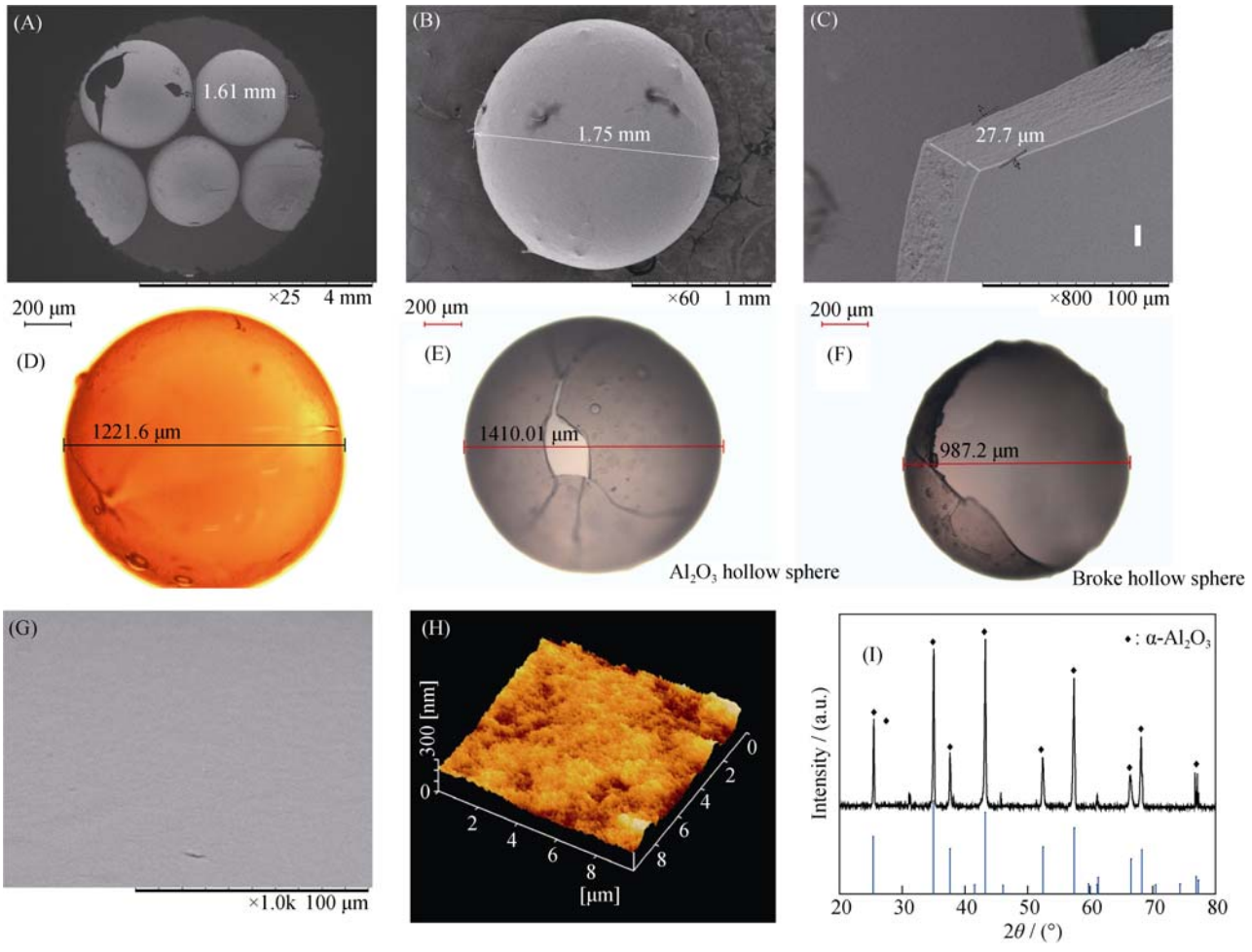

Fig. 8 Characterization of the ceramic sphere

(A, B, C): SEM of spheres; (D, E, F): optical images of spheres; (G, H): surface roughness analysis; (I): XRD patterns

and spherical after curing when the speed of rotation was controlled from 20 r/min to 60 r/min and the flask was in horizontal. Finally, the prepared hollow ceramic spheres with the wall thickness in micrometer-scale and diameter in millimeter-scale had the complete hollow structure and high sphericity after calcining at 1200 ℃ for 4 h. The surface of sphere was relatively smooth with the roughness of about 22 nm. The main crystal of the ceramic hollow spheres was alpha alumina. This emulsification device and method of curing were expected to be applicable to the production of millimeter-scale mono-disperse emulsion droplets which was used as for preparation of core-shell structure and millimeter-scale hollow spheres.

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O/W/O 多重乳液法制备毫米级氧化铝空心球

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摘 要: 采用 O/W/O 多重乳液法, 以液体石蜡为内核, 氧化铝溶胶为外壳层组成的复合液滴作为前驱体, 制备毫米级氧化铝空心球, 研究了装置几何结构对前驱体的形成和固化过程对空心球结构的影响。结果表明, 内部油相通过直流通道直接注射到水相液滴内部时, 形成的复合液滴具有均一核壳结构, 壁厚和直径在 30~80 μm 和 800~2200 μm 可控。液滴置于水平方向旋转固化, 保持转速在 20~60 r/min, 所得凝胶球可以保持完整的球形度和核壳结构。1200℃高温煅烧制备出的氧化铝空心微球维持高的球形度和空心结构, 表面粗糙度大约 22 nm, 壁厚达到几十微米, 直径达到毫米级, 主要晶型为稳定的α-Al_2O_3。

关 键 词: 氧化铝空心球; O/W/O 多重乳液; 复合液滴; 直流通道

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