Structural evolution of hollow Al2O3 particles formed on excimer laser-induced bubbles

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Pulsed laser ablation of Al in aqueous solutions could generate hollow Al2O3 particles due to laser-induced bubbles, but the generation depends on the laser wavelength. Herein, the structural evolution of amorphous and hollow Al2O3 spheres produced by 248 nm laser ablation in water–ethanol mixture has been studied. The amorphous phase could crystallize into γ-Al2O3 by thermal annealing while maintaining the shell structure. The 248 nm laser-induced photodissociation of water and ethanol could aid the formation and increase the lifetimes of bubbles, which are critical for the formation of hollow particles.

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1. Introduction

Alumina (Al2O3) is one of the most important ceramic materials for a multitude of applications [1,2]. γ-Al2O3 particles, in particular, can be used as catalysts or as catalyst carriers, adsorbents and additives in nanofluids due to its surface acidity and good thermal stability [1–3]. All of these applications would benefit from particles with a high surface-to-volume ratio. Hollow particles are attractive due to their lightweight and large specific surface area. Several approaches have been explored to fabricate hollow Al2O3 particles, including template-based methods using polymethyl methacrylate (PMMA) beads [4,5] or carbon powders [6], emulsion combustion methods [7,8], and thermal decomposition of AlOOH hollow structures [9,10]. Precursors containing Al3+ ions were generally used in these methods [5–10]. Recently, we found that KrF excimer laser (λ = 248 nm) ablation of bulk Al in water or water solutions could directly produce hollow Al2O3 particles [11]. The hollow particles were formed on laser-induced bubbles during the excimer laser ablation [11,12]. Several groups also studied the pulsed laser ablation of Al in water recently using Nd:YAG lasers with visible and infrared (IR) wavelengths of 532 nm or 1064 nm [13,14], but in their results they only observed solid Al2O3 particles. The difference in our results suggests that the shorter wavelength (higher photon energy) of excimer laser could promote the formation of hollow Al2O3 particles, though the mechanism needs investigation.

For hollow Al2O3 particles formed on laser-induced bubbles, no templates need to be removed, nor have precursors to be used in the fabrication. This, in turn, could result in cleaner particle surface which are important for catalytic applications. The laser produced Al2O3 were found to be predominately amorphous due to the thermal quenching in liquid [11]. The amorphous structure provides a known starting point to generate crystalline structures, such as γ- or α-phase, by thermal treatment. Ideally, it is desired that the amorphous Al2O3 could transform into γ-Al2O3, which is suitable for catalytic applications, by annealing while maintaining the shell structures. Herein, we report on the structural evolution of amorphous and hollow Al2O3 particles upon thermal annealing and discuss the impact of laser photon energy on the formation of hollow particles.

2. Experimental

In a typical pulsed laser ablation in liquid experiment, an Al target (99.999%, 1 in. in diameter) was attached to the bottom of a rotating glass beaker filled with a water–ethanol mixture (Vwater:Vethanol = 3:1). The solution was ~6 mm in depth. A pulsed KrF excimer laser (wavelength 248 nm, frequency 10 Hz, pulse width 30 ns) was focused onto the target surface with laser fluence of 5.9 J cm−2, and the ablation lasted for 30 min. The resultant particles were collected by centrifugation of the mixture and dried at room temperature. Some products were then annealed at 800–1000 °C in air for 2 h, separately. The gas-included bubble dynamics were studied by using an ArF excimer laser equipped with a co-linear CCD camera to ablate the Al target in water and the ethanol–water mixture. The micro/nanoparticle products were characterized by scanning electron microscopy (SEM, JEOL JSM-6330F) with...
energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM, Philips CM12) with selected area electron diffraction (SAED).

3. Results and discussion

Fig. 1(a) shows a typical SEM image of the as-prepared sample. Hollow spheres with diameters ranging from hundreds of nanometers to 1–2 μm can be observed. The particles contain both aluminum and oxygen elements as revealed by EDS analysis, since the laser ablation produced Al species at high temperature could be easily oxidized into Al2O3 by water [11]. Al3+ ions in aqueous solutions may also generate AlOOH precipitate under some conditions [9,10,15]. AlOOH can be characterized by absorption bands at 3285 and 3099 cm−1 in Fourier transform infrared spectrum due to (Al)O–H stretching vibrations [15]. However, the laser-produced particles in water or water–ethanol mixture do not show these bands, instead, a broad band at 804 cm−1 corresponding to the Al–O vibration of (AlO4) could be observed, verifying the existence of Al2O3 [11]. Fig. 1(b) shows several typical particles, displaying spherical and smooth surface. The broken shell of the microparticle exhibits its hollow structure. It is interesting that some hollow particles contain smaller particles as those shown in Fig. 1(c) and (d). The smaller particles may fall into the cavities through the broken shells of larger particles, but they were also likely trapped by the laser-produced bubbles before the formation of the larger hollow particles. An example is the hollow particle in Fig. 1(d) which seems to have a closed shell, but still contains three smaller particles. Fig. 2(a)–(d) shows the SEM images of particles annealed at 800 °C and 1100 °C, respectively. Analysis reveals that the particles are still dispersed after 800 °C annealing, but limited neck formation is present after 1100 °C calcination as indicated by the arrow in Fig. 2(c), while hollow particles could be still observed in Fig. 2(d).

The structural evolution of the samples was investigated by TEM and SAED. Fig. 3 shows the TEM images and SEAD patterns of typical particles in different samples. Fig. 3(a1) and (a2) show that most of the as-prepared particles are hollow with smooth and continuous shells. The particle in Fig. 3(a2) has amorphous structure as indicated by the halo rings of the SAED pattern shown in Fig. 3(a3). In our previous study, some particles prepared in ethanol/water mixture may contain unoxidized Al [11], but the experiments herein used higher laser fluence and longer ablation time that effectively generated Al2O3. Annealing at 800 °C could induce crystallization of the amorphous Al2O3. Nanogranules nucleate in the shells, but the hollow structures are maintained as shown in Fig. 3(b1) and (b2). The SAED pattern in Fig. 3(b3) indicates that the nanogranules are γ-Al2O3 and the shell is polycrystalline. Annealing at 1100 °C could induce necking of adjacent particles, but the hollow structures still exist as shown in Fig. 3(c1) and (c2). The structure of some nanogranules further evolves into θ-Al2O3 and α-Al2O3 as indicated by the SAED pattern in Fig. 3(c3). The results for the structural evolution show that post-annealing at 800 °C for 2 h can generate dispersed hollow γ-Al2O3 particles with well-defined shell structures; and the particles are good candidates for catalysis and other applications.

During the pulsed laser ablation of Al target in liquid, bubbles could be generated on the laser-heated target surface, or by the
laser-produced plasma, or even on the laser-heated particle surface as indicated by the hollow particles shown in Fig. 1(c) and (d). The laser-induced bubbles provide templates for the formation of hollow particles [11,12], and a schematic illustration of the formation process is shown in Fig. 4. The laser-induced bubbles are dynamic, similar to acoustic cavitation bubbles [16]. There have been reports showing that the acoustic cavitation bubbles could serve as templates to induce hollow particles either in a synthetic environment [17] or in a colloidal solution [18]. The laser-produced Al₂O₃ clusters may be contained in the laser-induced bubbles due to condensation and nucleation of laser-produced plasma in the bubbles, or in the liquid after collapse of bubbles. The latter case is more possible considering that the hollow Al₂O₃ particle with double cavities could be also observed as shown in our previous report [11], and also considering the hollow particles containing smaller particles as those shown in Fig. 1(c) and (d). Driven by the decrease of total surface free energies of bubbles and Al₂O₃ clusters [19], Al₂O₃ clusters in the liquid will diffuse and attach to the surface of bubbles, and the expanding surface could also trap the surrounding clusters as shown by the steps of (a) and (b) in Fig. 4. During the bubbles’ shrinkage, the areal density of the trapped Al₂O₃ clusters on the surface of bubbles will increase and the clusters finally inhibit further motion of the surface as shown by Fig. 4(c) [12,16]. The clusters bond to each other due to the transient high temperature during bubbles’ shrinkage [18], and finally form hollow particles (Fig. 4(d)). Therefore, enough Al₂O₃ clusters must diffuse to the surface of a bubble before it finally collapses. And then longer bubble lifetimes, which will permit the diffusion of Al₂O₃ clusters, are required to effectively produce hollow Al₂O₃ particles.

The formation of hollow particles strongly depends on the wavelength of the laser. Our previous study showed that pulsed excimer laser ablation of Al in water could easily produce hollow Al₂O₃ particles [11]. Other researchers have used visible and IR lasers to ablation Al in water, but did not observe hollow particles in the products [13,14]. We consider that this is due to the fact that the KrF excimer laser used in our experiments has a larger photon energy (5.0 eV) than the 532 nm (2.3 eV) and 1064 nm (1.2 eV) lasers. It is well known that the 248 nm excimer laser can induce photodissociation of water molecules to free radicals, which requires an energy of \( E = 6.41 - 6.71 \text{ eV} \) [20–22]. At the laser photon energy and fluence used in the current experiment, the water dissociates via two-photon process:

\[
\text{H}_2\text{O}_2\xrightarrow{2hv}\text{OH} + \text{H},
\]

and the dissociation results in the formation of atomic hydrogen gas nanobubbles [22]. The hydrogen radicals may further interact with each other and form hydrogen molecules [20]:

\[
\text{H} + \text{H} \rightarrow \text{H}_2.
\]

The atomic/molecular hydrogen gas could serve as cavitation nuclei for laser-induced bubbles, and the gas content in a cavitation bubble will increase its lifetime relative to the theoretically empty cavitation bubble [16]. Without the gas content and thermal effects,
Fig. 3. TEM images and SEAD patterns of (a1–3) as-prepared particles, (b1–3) particles annealed at 800 °C, and (c1–3) particles annealed at 1100 °C, in which the parts (1) are the general view of the samples, parts (2) are magnified images of typical hollow particles and parts (3) are the corresponding SAED patterns.

Fig. 4. Schematic illustration of the formation process of a hollow particle (not drawn to scale). The symbol * represents an Al2O3 cluster. Steps (a) and (b) show the expansion of a bubble, and (c) shows the shrinkage of the bubble and the formation of a dense shell of Al2O3 clusters which have been trapped by the surface of the bubble. The clusters bond to each other, resulting in a hollow particle as shown by step (d).
the time $t_c$ required for total collapse of a spherical bubble from $R = R_m$ to $R = 0$ is described by the Rayleigh’s formula [16]:

$$ t_c = 0.915 \sqrt{\frac{\rho_l}{P_\infty - P_v}} R_m, \quad (3) $$

where $\rho_l$ is the density of the liquid, $P_\infty$ is the ambient pressure and $P_v$ is the vapor pressure. However, if the bubble contains gas, the mass diffusion of the gas from the bubble/liquid interface to the liquid will largely increase the collapse time (the time before the final collapse) of the bubble, which can be calculated by [16]:

$$ t_{cs} = \frac{\rho_c R^2}{2D(c_s - c_\infty)}, \quad (4) $$

where $\rho_c$ is the density of the gas in the bubble, $D$ is the diffusion coefficient of the gas in the liquid, $c_s$ and $c_\infty$ are the saturated concentration of the gas at the bubble/liquid interface and the ambient concentration of the gas, respectively. To reveal the dynamics of excimer laser-induced bubble in water, we used an ArF excimer laser (10 Hz, ~5 J cm$^{-2}$) equipped with a co-linear camera to ablate Al in water and recorded the ablation process. Most bubbles disappeared in 1 s, partly because they drifted away from the focal plane of the camera (namely, the target surface). However, their lifetimes can be still longer than that determined by the Rayleigh’s formula. Fig. 5 shows the image of several bubbles, and the evolution of a bubble is shown in a sequence of images at the bottom. The maximum radius of the bubble is $\sim$8.3 $\mu$m with a lifetime of $>0.1$ s. This time is longer than $2t_c \approx 1.5$ $\mu$s as calculated by Eq. (3), indicating that the bubble is not ideally empty. In particular, the size evolution of a bubble staying at the focal plane of the camera is shown in Fig. 6(a). The maximum size of the bubble is $\sim$9.5 $\mu$m with collapse time of $\sim$2.4 s, much longer than that calculated by Eq. (3). Instead, considering the typical value of $(c_s - c_\infty)/\rho_c (-0.01)$ [16], and diffusion coefficients of hydrogen (4.25 $\times$ 10$^{-5}$ m$^2$ s$^{-1}$) in water at 20 °C [23], $t_{cs}$ of a hydrogen-included bubble with $R_m \approx 9.5$ $\mu$m is 2.1 s as calculated by Eq. (4). Moreover, the square of the bubble radius is almost linearly proportional to the collapse time as shown in Fig. 6(b). Therefore, the size evolution of the bubble is in consistent with Eq. (4), indicating that the photodissociation of water molecules by excimer laser irradiation can increase the lifetimes of laser-induced bubbles and the formation of hollow particles, while for lasers with smaller photon energies, the gas effect is not prominent and only solid Al$_2$O$_3$ particles were obtained [13,14].

Water–ethanol mixtures have been used in the laser ablation procedure because ablation in the mixture could generate larger bubbles and when using a mixture the bubbles have even longer lifetimes compared to water alone [12]. Fig. 7 shows the square of the bubble radius versus collapse time of a bubble generated by the ArF excimer ablation in water–ethanol mixture ($V_{water} : V_{ethanol} = 3:1$). The bubble with $R_m \approx 20.8$ $\mu$m has collapse time of 41 s. Moreover, at $R = 9.5$ $\mu$m the collapse time is $\sim$6 s as read from the curve, which is larger than that in water. This may be because that the bubbles in water–ethanol mixture are ethanol-rich due to the lower boiling temperature of ethanol and the microscopic phase separation of the ethanol–water mixture [12,24], which causes significant thermal effects and mass diffusion during the shrinkage. Moreover, the absorption of laser photons by the ethanol molecules should be considered. At ambient conditions the lowest absorption band of ethanol has a threshold of $\sim$6.9 eV [25], thus the 5.0 eV photons could induce electronic excitation of ethanol through a two-photon absorption process. Recent research on photoinduced reactivity of ethanol under 350 nm light irradiation has shown that at pressures of a few megapascals, two-photon absorption of ethanol mainly produces $H_2$ [26]. Therefore, $H_2$ gas may be generated by the photodissociation of ethanol, especially in cavitation bubbles which could have pressures of up to $\sim$100 MPa [18]. In the gigapascal range, ethane, 2-butanol, 2,3-butanediol, and other compounds are the main products [26], which may form in the laser-produced plasma. Products like CH$_4$, H$_2$O, and CO$_2$ become the main products only when ethanol is exhausted [26].
Moreover, the hydrogen radicals from photodissociation of water could react with ethanol and form hydrogen gas by [27]:

\[ \text{H} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}_2 + \text{CH}_3\text{CHOH}, \]  

(5)

which can also serve as cavitation nuclei and increase the lifetimes of the bubbles.

4. Conclusions

We have studied the structural evolution of amorphous hollow Al$_2$O$_3$ particles. The particles were fabricated by pulsed excimer laser ablation of bulk Al in water–ethanol mixture and formed on cavitation bubbles. The amorphous structure crystallized into γ-Al$_2$O$_3$ nanograins in the shells by thermal annealing at 800 °C for 2 h, and the shell structures were maintained. Annealing at 1100 °C for 2 h caused necking of adjacent particles, and the microstructure further evolved into θ-Al$_2$O$_3$ and α-Al$_2$O$_3$. The photodissociation of water and ethanol molecules during the excimer laser ablation could provide H$_2$ gas content in the cavitation bubbles, which could increase the lifetime of the bubbles and the chance to form hollow particles. We have shown a novel method to fabricate hollow γ-Al$_2$O$_3$ particles that have potential applications as catalysts or catalyst carriers, adsorbents and additives in nanofluids, and an understanding of the underlying mechanism will enable further development of this technique.

References