Fabrication of hollow alumina microspheres via core/shell structure of polymethylmethacrylate/alumina prepared by mechanofusion

T. KATO, H. USHIJIMA, M. KATSUMATA
YAZAKI Parts Co. Ltd., 1500 Mishuku, Susono-shi, Shizuoka 411-1194, Japan

T. HYODO, Y. SHIMIZU, M. EGASHIRA*
*Faculty of Engineering, Nagasaki University, 1-14 Bunkyo-machi,
Nagasaki 852-8521, Japan
E-mail: egashira@net.nagasaki-u.ac.jp*

Core/shell microspheres of polymethylmethacrylate coated with Al_2O_3 or a mixture of Al_2O_3 and SiO_2 nanoparticles have been successfully prepared by a mechanofusion system. The microspheres were then subjected to removal of PMMA by firing in air, followed by sintering at 1600°C for 3 h. The shell structure was destroyed after the sintering when the shell layer consisted of only Al_2O_3. The addition of SiO_2 was found to be effective for maintaining the original shell structure, while the shell size expanded slightly and a hole was formed in each hollow microsphere during the removal process of PMMA.
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1. Introduction

Hollow ceramic microspheres have a variety of application fields. Several kinds of composites have been fabricated by mixing hollow ceramic microspheres with matrices such as metals [1], plastics [2] or ceramics [3]. The main advantage of the use of hollow ceramic microspheres is to reduce the weight of composites, leading to economical benefits and energy saving [1–4]. Besides the lightweight design, hollow ceramic microspheres have also been used to reduce a thermal shock [5] or to improve an adiabatic efficiency of composites. Since hollow ceramic microspheres are subjected to shear stress on mixing with the matrices of composites, certain strength of hollow structure is requested. In addition, development of a tailored preparation process is of importance for obtaining uniform and controlled size of hollow microspheres and then for improving the properties of composites.

Several methods have so far been demonstrated for preparing hollow ceramic microspheres. These include spray drying [6], sol-gel process [7], spray pyrolysis [8, 9], foaming [10, 11] and so on. Shirasu and silica balloons are typical hollow ceramic microspheres fabricated by foaming, but are characterized with their poor mechanical properties. Although mechanical properties of shirasu balloons have been successfully improved by coating with TiO_2 [12], difficulties for obtaining uniform and controlled size of the hollow microspheres still remained. Alumina balloons prepared by a spray method of molten alumina have high strength, but have the same difficulties.

The present study was directed to developing a new preparation method for strong hollow ceramic microspheres with controlled particle sizes. The principle of our method are the use of spherical polymethylmethacrylate (PMMA) with a given particle size as a core material, coating of PMMA with a fine particle of alumina or a mixture of alumina and silica powders, i.e. preparation of core (PMMA)/shell (alumina or alumina plus silica) structure by a mechanofusion system, followed by burning out the PMMA and then sintering of the shell layer.

2. Experimental

Spherical PMMA powder (MR-20G, Souken Kagaku Co., Ltd.) with a mean particle size of 20 μm was used as a core material. The same weight of PMMA and a fine powder of Al_2O_3 (Daimei Chemical Ind. Co. Ltd.) with a mean particle size of 0.2 μm was treated with a mechanofusion system (AM-15F, Hosokawa Micron Corp.) at a chamber rotation speed of 2500 rpm for 30 min and a distance of 1.0 mm between a chamber wall and an inner piece. This treatment enables us to mechanically embed a layer of the Al_2O_3 particles with certain thickness in the surface region of PMMA microspheres. Similar treatments were also conducted with the addition of 5.0 or 10 wt% SiO_2 fine powder (SIGMA Co., Ltd.) with a mean particle size of 0.011 μm to the Al_2O_3 powder.

Thermal decomposition behavior of PMMA powder was analyzed by TG-DTA up to 800°C at a heating rate

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*Author to whom all correspondence should be addressed.

of 5 deg min^{-1} in air flowing at a rate of 100 ml min^{-1}. Based on the TG-DTA measurement, the PMMA microspheres coated with Al_2O_3 or a mixture of Al_2O_3 and SiO_2 were fired at a heating rate of 5 deg min^{-1} in the temperature ranges of RT-250°C and 400–1600°C in air flowing at a rate of 100 ml min^{-1}. A heating rate of 0.1 deg min^{-1} in the range 250–400°C was used to remove and burn out the PMMA. The resultant Al_2O_3 or Al_2O_3-SiO_2 shell layer was successively sintered in an alumina boat (SSA-S) at 1600°C for 3 h in flowing air.

Surface area of each raw powder, as-prepared core/shell particles and sintered particles was measured by a BET method (TriStar 3000, Micromeritics). Surface and cross-sectional views of particles before and after sintering were observed with scanning electron microscopy (SEM, S-2250N, Hitachi, Ltd.). Size distribution of these particles was measured with a laser diffraction scattering apparatus (HR850-B, Cilas). Crystal phases of the sintered particles were confirmed by X-ray diffraction analysis (XRD, Rigaku Corp., RINT 2000).

3. Result and discussion

Fig. 1 shows SEM photographs of a raw PMMA microsphere and a PMMA microsphere coated with Al_2O_3-5.0 wt% SiO_2. From these photographs, it was observed that Al_2O_3-5.0 wt% SiO_2 nanoparticles were embedded mechanically in the surface region of PMMA and that the resultant core/shell particles retained the original spherical shape of PMMA. SEM observation of PMMA coated with Al_2O_3 or Al_2O_3-10 wt% SiO_2 revealed appearances similar to that shown in Fig. 1b and no clear difference in surface state, irrespective of the additive amount of SiO_2 powder. However, the surface area of as-prepared core/shell particles increased with increasing the additive amounts of SiO_2, as summarized in Table I. By referring to the values of surface area of raw powders, this behavior confirmed the formation of a shell layer of a mixture of Al_2O_3 and SiO_2 nanoparticles in the surface region of PMMA, when SiO_2 was added during the mechanofusion.

Fig. 2 shows cumulative particle size distribution of raw PMMA and as-prepared core/shell particles. The curves for the core/shell particles well followed the curve for PMMA. In addition, mean particle size of these core/shell particles was comparable to each other and nearly agreed with that of PMMA, as summarized in Table I. Thus, it was confirmed that core/shell structure of PMMA coated with Al_2O_3 or Al_2O_3-SiO_2
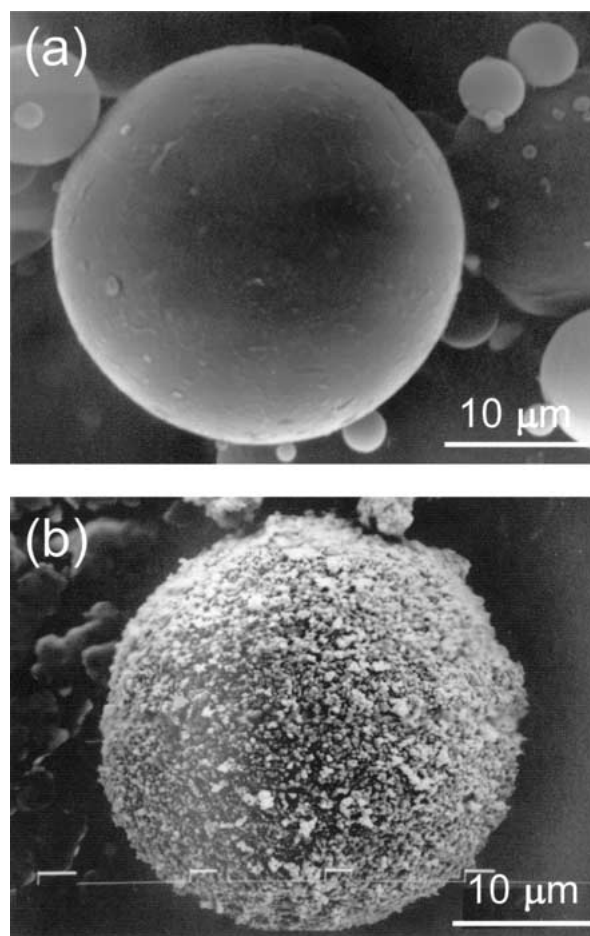

Figure 1 SEM photographs of (a) raw PMMA and (b) PMMA coated with Al_2O_3-5.0 wt% SiO_2.
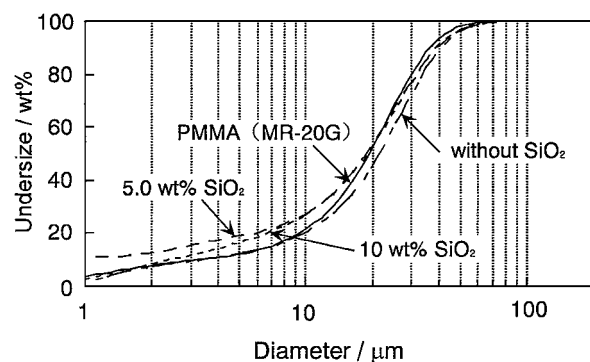

Figure 2 Cumulative particle size distribution of raw PMMA and mechanically fused PMMA/Al_2O_3-SiO_2 microspheres.

could be prepared by mechanofusion. These results also predict tailored design of both the mean size and the size distribution of core/shell particles by selecting raw PMMA powders of different size.

TABLE I Surface area and mean particle size of raw materials and resultant particles

Material	Surface area (m^2 g^{-1})		Mean particle size (μm)	
	Original[a]	After sintering[b]	Original[a]	After sintering[b]
PMMA	0.021	–	20	–
Al_2O_3	12.3	–	0.20	–
SiO_2	232	–	0.011	–
PMMA/Al_2O_3	8.52	Minute	21.6	33.2
PMMA/Al_2O_3-5.0 wt% SiO_2	9.62	0.011	20.2	30.5
PMMA/Al_2O_3-10.0 wt% SiO_2	13.0	0.094	18.4	27.2

[a]As-received for raw powders and as-prepared by mechanofusion for core/shell particles.
[b]For shell layers after sintering at 1600°C for 3 h.

TG-DTA was carried out with PMMA to confirm its thermal decomposition behavior and then to determine firing conditions of the core/shell particles prepared. A significant weight loss started around 300°C and
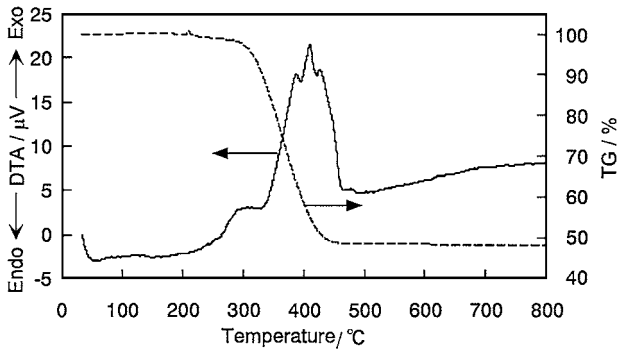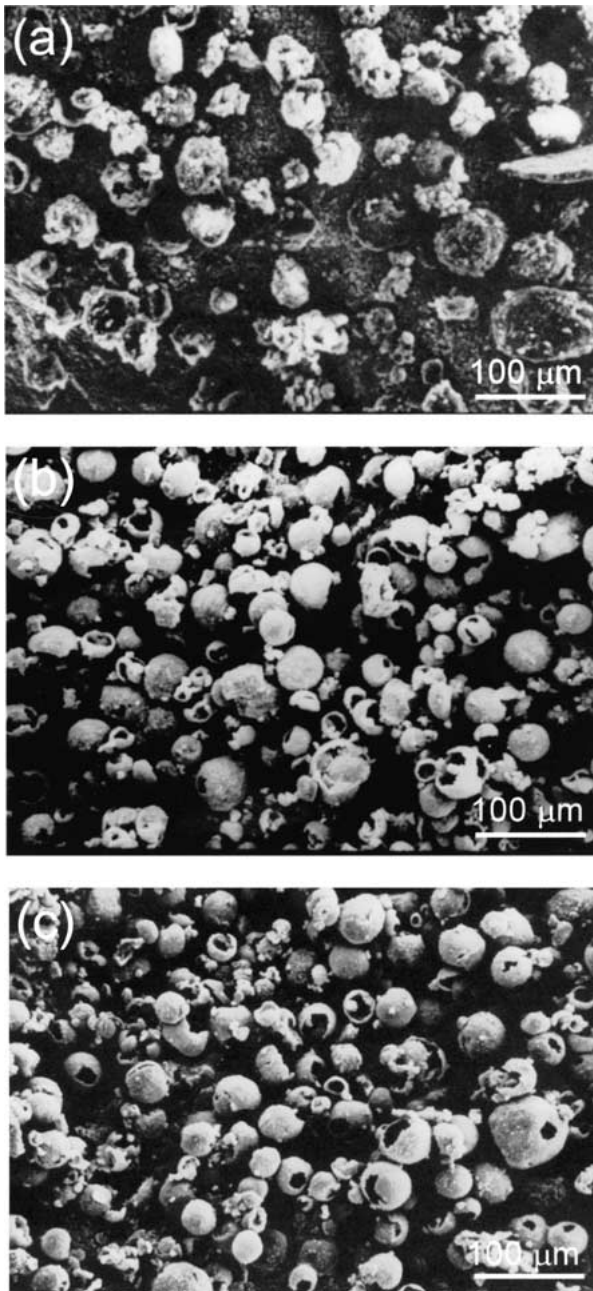

Figure 3 TG-DTA curves of PMMA.

Figure 4 SEM photographs of the particles obtained after sintering of (a) PMMA/Al_2O_3, (b) PMMA/Al_2O_3-5.0 wt% SiO_2 and (c) PMMA/ Al_2O_3-10 wt% SiO_2 at 1600°C for 3 h.

PMMA was consumed completely by firing in air up to 450°C with a clear exothermic peak around 400°C, as shown in Fig. 3. Thus, a slow heating rate of 0.1 deg min^{-1} was adopted in the temperature range of 250–400°C in the present firing process of the core/shell particles aimed at achieving complete removal of PMMA and then obtaining hollow microspheres.

Fig. 4a–c show SEM photographs of the resultant particles after sintering of PMMA/Al_2O_3, PMMA/ Al_2O_3-5.0 wt% SiO_2 and PMMA/Al_2O_3-10 wt% SiO_2, respectively. After sintering, the appearance of particles became quite different from each other depending on the existence of SiO_2 in the shell layer. When only Al_2O_3 was used as the shell constituent, spherical particles were rarely found: some of those were broken and others were deformed, as shown in Fig. 4a. In contrast, nearly perfect spheres were kept even after the sintering by the addition of 5.0 or 10 wt% SiO_2, whereas a small hole was found on the surface of each sphere, as shown in Fig. 4b and c. Thus, it was revealed that the addition of SiO_2 was effective for reducing the deformation of the shell structure. The SiO_2 added was considered to act as an adhesive agent among Al_2O_3 particles and then to promote the development of a strong shell structure during the sintering. Fig. 5a–c show XRD patterns of the resultant particles after
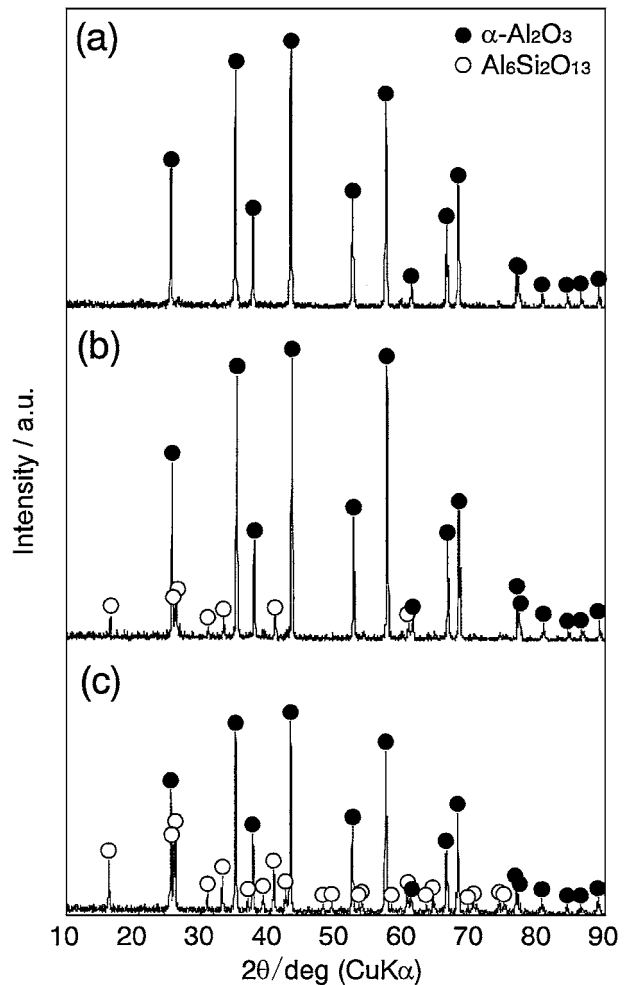

Figure 5 XRD patterns of the particles obtained after sintering of (a) PMMA/Al_2O_3, (b) PMMA/Al_2O_3-5.0 wt% SiO_2 and (c) PMMA/ Al_2O_3-10 wt% SiO_2 at 1600°C for 3 h.
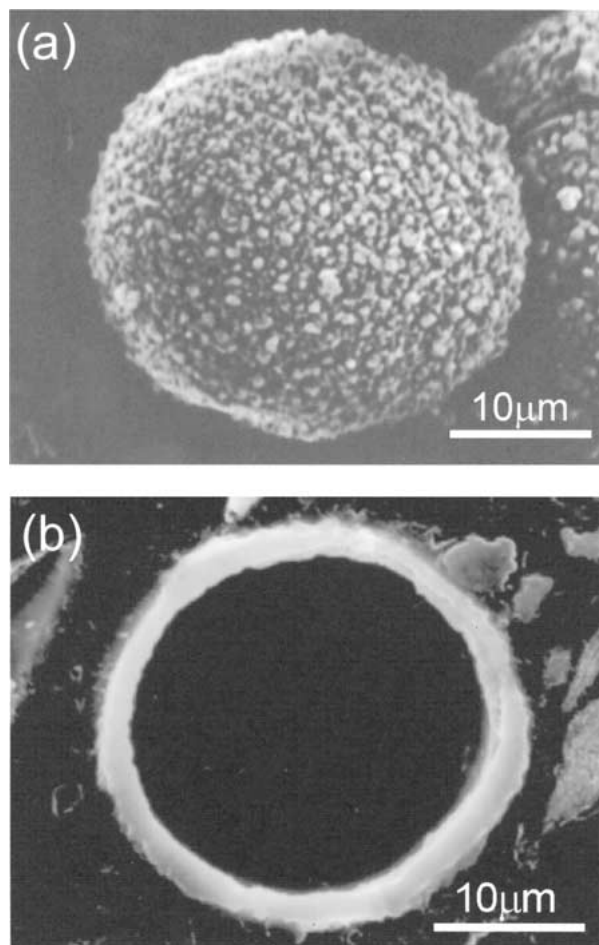
Figure 6 (a) Surface and (b) cross-sectional views of an Al$_2$O$_3$-5.0 wt% SiO$_2$ hollow particle after sintering at 1600°C for 3 h.

Figure 7 Cumulative particle size distribution of raw PMMA and the particles obtained after sintering of PMMA/Al$_2$O$_3$-0 ∼ 10 wt% SiO$_2$ at 1600°C for 3 h.

sintering of PMMA/Al$_2$O$_3$, PMMA/Al$_2$O$_3$-5.0 wt% SiO$_2$ and PMMA/Al$_2$O$_3$-10 wt% SiO$_2$, respectively. A single phase of α-Al$_2$O$_3$ was observed without the addition of SiO$_2$, while additional formation of Al$_6$Si$_2$O$_{13}$ was confirmed in the resultant particles after the addition of 5.0 or 10 wt% SiO$_2$. Fig. 6 shows surface and cross-sectional views of sintered Al$_2$O$_3$-5.0 wt% SiO$_2$ spheres. The surface was still relatively rough, but the Al$_2$O$_3$ and SiO$_2$ nanoparticles appeared to be sintered densely. In addition, the Al$_2$O$_3$-5.0 wt% SiO$_2$ particle was confirmed to have hollow structure with a dense sintered wall of 2.0 μm thickness. Although the sintered particle shown in Fig. 6b exhibited apparently a perfect hollow structure, a hole may be formed on the back-side of the particle, by referring to the photo shown in Fig. 4b. It is anticipated that the hole on the sphere surface was formed during the removal process of PMMA. A possible mechanism is an increase in internal pressure inside the shell due to gas evolution by the oxidation of PMMA, followed by gas release from a weak part of the shell layer to the outside, then an enlargement of hole size during sintering. Therefore, to reduce the hole formation, further modification of firing conditions of the core/shell particles is now under investigations.

Fig. 7 shows cumulative particle size distribution curves for the resultant particles after sintering at 1600°C for 3 h, together with the data of raw PMMA for reference. Surface area and mean size of these par-
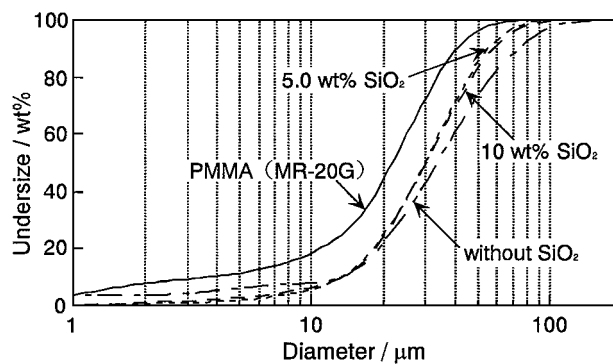
ticles are also summarized in Table I. The distribution curves for Al$_2$O$_3$-5.0 wt% SiO$_2$ and −10 wt% SiO$_2$ were quite similar in shape to that of PMMA with a parallel shift to larger particle size. Indeed, the mean size of Al$_2$O$_3$-5.0 wt% SiO$_2$ and −10 wt% SiO$_2$ shell particles increased by a factor of about 1.5 from that of raw PMMA. It was suggested that the removal process of PMMA, i.e. gas evolution on heating, was responsible for the enlargement of mean size. The curve for Al$_2$O$_3$ alone was different in shape from the others, especially in the range >20 μm diameter. The results shown in Figs 4–7 imply that the shell layer consisting of only Al$_2$O$_3$ particles is weak in mechanical strength and that the mechanical strength of the shell structure is improved by the addition of SiO$_2$, which prevents deformation and disintegration of the particles during the PMMA removal process and the following sintering process.

4. Conclusion
A mechanofusion system enables us to prepare core/shell microspheres of PMMA coated with Al$_2$O$_3$ or a mixture of Al$_2$O$_3$ and SiO$_2$ nanoparticles. The core/shell microspheres nearly maintained the original size distribution of PMMA. The shell structure was destroyed after sintering at 1600°C for 3 h when the shell layer consisted of only Al$_2$O$_3$. The addition of SiO$_2$ was found to be effective for maintaining the original shell structure, while the shell size expanded slightly and a hole was formed in each hollow microsphere during the removal process of PMMA. It was confirmed that hollow Al$_2$O$_3$-SiO$_2$ microspheres with tailored size and its distribution could be prepared by employing mechanically fused core/shell particles of PMMA/Al$_2$O$_3$-SiO$_2$, though further studies are needed to reduce the formation of a hole in the shell well during the removal process of PMMA.

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