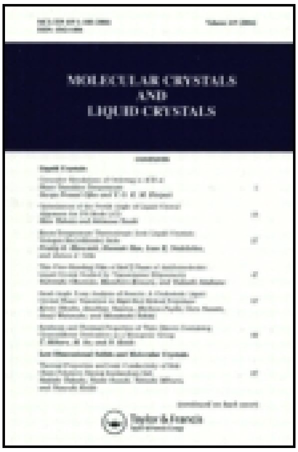

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Preparation of Core/Shell Microspheres of Polymethylmethacrylate/Alumina by Mechanofusion as a Precursor of Hollow Alumina Microspheres

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Preparation of Core/Shell Microspheres of Polymethylmethacrylate/Alumina by Mechanofusion as a Precursor of Hollow Alumina Microspheres

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Core/shell microspheres of polymethylmethacrylate (PMMA) coated with Al_2O_3 were successfully fabricated by a mechanofusion system. The microshperes were subjected to calcination to give hollow Al_2O_3 microspheres. The Al_2O_3 shell structure was destroyed during a pre-firing or sintering process without the addition of fine SiO_2 powder. In contrast, addition of 5.0 or 10.0 wt% SiO_2 was found to be effective for maintaining the original shell structure, while the size of hollow Al_2O_3 microspheres increased slightly and a small hole formed in each microsphere during the removal process of PMMA.

Keywords Core/shell microsphere; Hollow microsphere; Al_2O_3; SiO_2; Polymetylmethacrylate; Mechanofusion system

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INTRODUCTION

Core/shell and hollow microspheres have a variety of application fields. The main advantages of the use of core/shell and hollow microspheres are to improve the properties and to reduce the weight of composites [1-3]. Typical examples are hollow alumina microspheres prepared by a spray method of melted alumina [4] and silica microspheres by a sol-gel process [5]. However, mechanical properties and uniform particle size of the hollow microspheres need to be improved. Recently, titania microspheres with strong shell structure have been fabricated successfully by TiO_2 coating over shirasu balloons [6].

The aim of the present study is to establish a new fabrication process of core/shell microspheres of polymetylmethacrylate (PMMA)/ Al_2O_3, as a precursor of hollow Al_2O_3 microspheres, by employing a mechanofusion system. The core/shell particles may be utilized as a filler to increase the thermal conductivity of resin substrates for integrated circuits.

EXPERIMENTAL

Spherical PMMA powder (MR-20, Souken Kagaku Co., Ltd., mean particle size: 20 μm) was used as a core material. The same weight of PMMA and Al_2O_3 powder (Daimei Chemical Ind. Co., Ltd, mean particle size: 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. This treatment enables us to mechanically embed the Al_2O_3 nanoparticles in the surface region of PMMA spheres. Similar treatments were also conducted with the addition of 5.0 or 10 wt% SiO_2 powder (SIGMA. Co., Ltd., mean particle size: 0.011 μm) to the Al_2O_3 powder. Details for the mechanofusion system are available in the literature [7].

The PMMA microspheres coated with Al_2O_3 or a mixture of Al_2O_3 and SiO_2 was fired at a heating rate of 0.1°C/min in the temperature range of 250-400°C to remove PMMA and burn it out, and then were sintered at 1600°C for 3 h. The pre-firing conditions were determined based on the differential thermal analysis of PMMA.

The surface and cross-section of the resultant particles before and after calcination were observed with scanning electron microscopy (SEM, S-2250N, HITACHI, Ltd.). The size distribution of these particles was measured with a laser diffraction scattering apparatus (CILAS, HR 850-B).

RESULT AND DISCUSSION

SEM observation revealed that there was no clear difference in the surface state of the coated Al_2O_3 after mechanofusion, irrespective of coaddition of fine SiO_2 powder. The cumulative particle size distribution of raw PMMA and the resultant particles are shown in Fig. 1. The mean particle size is 21.6, 20.2 and 18.4 μm for the core/shell particles of Al_2O_3, Al_2O_3-5.0 wt% SiO_2 and -10 wt% SiO_2, respectively, and is almost comparable to that of PMMA. SEM photographs in Fig. 2 confirms that Al_2O_3-5.0 wt% SiO_2 nanoparticles are embedded mechanically in the surface region of PMMA and that the resultant core/shell particles retain the original spherical structure of PMMA. Thus, the resultant core/shell particles may be utilized as a filler to increase the thermal conductivity of resin substrates for integrated circuits.

After calcination, however, the shape of the microparticles was quite different depending upon the case where only Al_2O_3 or a mixture of Al_2O_3 and SiO_2 was used as a coating material. In the case of Al_2O_3, spherical particles were rarely found: some of those are broken and others are deformed, as shown in Fig. 3. In contrast, Al_2O_3-5.0 wt%

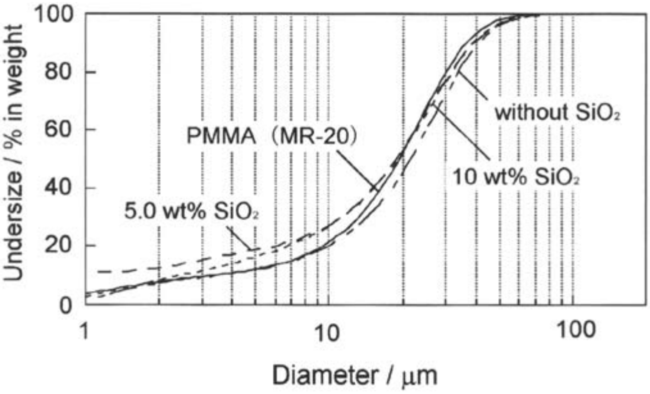

FIGURE1. Cumulative particle size distribution of raw PMMA and PMMA/Al_2O_3 microspheres.

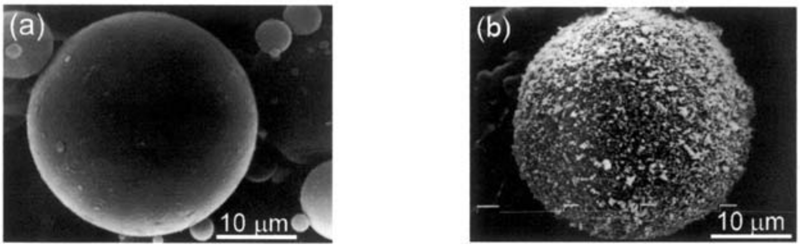

FIGURE2. SEM photographs of (a) PMMA and (b) PMMA coated with Al_2O_3-5.0 wt% SiO_2.

SiO_2 microparticles are nearly perfect spheres, whereas a small hole is found on the surface of each sphere, as shown in Fig. 4. Similar microstructure was observed also for Al_2O_3-10 wt% SiO_2 microparticles. Thus, the addition of SiO_2 is also effective for maintaining the original shell structure of Al_2O_3 over PMMA after high temperature calcination. It is considered that the observed holes formed during the removal process of PMMA, and this consideration forces us to modify the present removal process in future.

Figures 5 and 6 show surface and cross-sectional views of calcined Al_2O_3-5.0 wt% SiO_2 microspheres. The surface is still relatively rough,

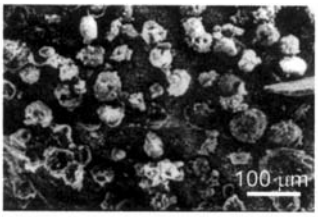

FIGURE 3. SEM photograph of Al_2O_3 microparticles.

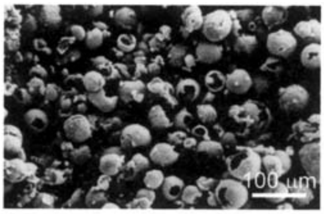

FIGURE 4. SEM photograph of Al_2O_3-5.0 wt% SiO_2 hollow microspheres.

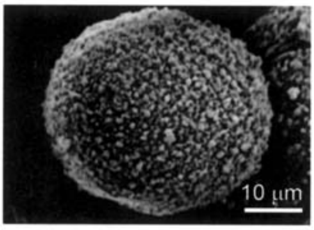

FIGURE 5. Surface of Al_2O_3- 5.0 wt% SiO_2 hollow microspheres.

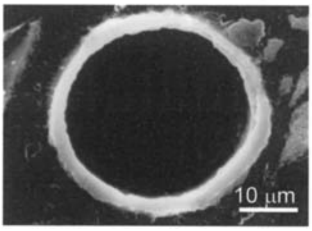

FIGURE 6. Cross-sectional view of Al_2O_3-5.0 wt% SiO_2 hollow microspheres.

but the Al_2O_3 and SiO_2 nanoparticles appears to be sintered densely. In addition, the Al_2O_3-5.0 wt% SiO_2 microspheres was confirmed to have hollow structure with a densely sintered wall thickness of 2.0 µm. The mean diameter of the calcined microspheres was slightly larger than that of PMMA. The distribution curves of Al_2O_3-5.0 wt% SiO_2 and -10 wt% SiO_2 microspheres well resembled the curve of PMMA, although the mean diameters were different, whereas the curve of Al_2O_3 (without SiO_2) widened slightly to the large particle size region. Thus, the coated shell expanded slightly during the pre-firing process, and the added SiO_2 is considered to act as an adhesive agent among the Al_2O_3 nanoparticles to prevent deformation and disintegration of the shell structure. Another important feature of this process is that we can control the size and its distribution of the hollow microspheres by those of the spherical PMMA used as a core material. The wall thickness of the microspheres may be controlled by the mechanofusion conditions.

CONCLUSIONS

Core/shell Al_2O_3 microspheres could be fabricated with a mechanofusion system by employing PMMA microspheres as a core material. These particles may be utilized as a filler for resin substrates for integrated circuits. Hollow Al_2O_3 microspheres could be also fabricated by firing and sintering the core/shell microspheres. Addition of a small amount of SiO_2 was essential for maintaining the shell structure during the removal process of PMMA. Further investigations are now in progress in order to reduce the frequency of hole formation. Such hole-free hollow microspheres may find an application as a filler to reduce the weight of metals- or ceramics-based composites.

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