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A flexible route to high strength α-alumina and aluminate spheres

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The formation of hollow alumina spheres is accomplished by coating polystyrene beads of 3 μm and 50–80 μm diameter with carboxylic acid functionalized alumina nanoparticles (alumoxanes) from aqueous solution 2–8 wt%. The resulting coated beads were heated to 220°C to calcine the alumoxane to porous amorphous alumina before washing with toluene to remove the polystyrene from inside the ceramic coating. The resulting hollow spheres were sintered at 1000°C to form α-alumina. The α-alumina spheres have been characterized, by SEM (scanning electron microscopy), BET, and hardness measurements, that show the hardness of the hollow alumina sphere (1900 ± 100 Kg.mm^{-2}) approaches that of corundum (ca. 2000 Kg.mm^{-2}). Multilayered bi-phasic spheres may be prepared by subsequent coating the α-alumina spheres with a solution of a metal-doped alumoxane. After calcining, the mixed metal oxide phase ($CaAl_{12}O_{19}$, $Er_6Al_{10}O_{24}$, $MgAl_2O_4$, Al_2TiO_5, and $Y_3Al_5O_{12}$) forms outside of the alumina sphere resulting in a composite like ceramic bi-layer sphere. Pre-formed hollow alumina spheres were incorporated into a resin and ceramic thin film formed from a 1 wt% A-alumoxane aqueous solution. The hardness of the composites is compared to the matrix materials themselves. *© 2003 Kluwer Academic Publishers*

1. Introduction

Recognition that the macroscopic properties of materials depend not only on their chemical composition, but also on the size, shape and structure, has spawned investigations into the control of these parameters for various materials [1]. In this regard, the fabrication of uniform hollow spheres has recently gained much interest. Hollow capsules with nanometer and micrometer dimensions offer a diverse range of potential applications, including: utilization as encapsulants for the controlled release of a variety of substances, such as drugs, dyes, proteins, and cosmetics [2, 3]. When used as fillers for coatings, composites, insulating materials or pigments, hollow spheres provide advantages over the traditional solid particles because of their associated low densities [4]. A spherical morphology also allows for applications in optical devices [5–8].

The geometry of the spheres has been shown to increase the strength of composite materials. Incorporating hollow spheres into composite materials, improve the strength and the fracture strength of the material [9]. Typically, materials (organic or inorganic) are reinforced with fibers that retard the propagation of stress cracks. When hollow particles are incorporated into the fiber-reinforced composite, the crack growth is further stopped by the neighboring particles [10], for example, incorporation of glass beads into an epoxy resin [9].

Hollow particles have been fabricated from a variety of materials, such as polymers, metal, ceramics, and glass [3], however, a great deal of research has focused on various metal oxides, due to their chemical, thermal, and oxidative resistance, and because they have low dielectric constants and are optically transparent [11, 12]. Conventional methods to produce hollow ceramic spheres are vapor deposition, sputtering, molecular beam deposition and electrolytic deposition, however, these processes do not always provide a uniform coating of individual particles [13]. Ceramic spheres exhibiting a uniform coating and thickness have been achieved with the sol-gel route [3, 4, 14, 15]. Typically the spheres are formed by templating with either polystyrene spheres or silica spheres [2–4, 6, 16, 17]. The polystyrene or silica spheres are coated with the sol-gel, after which the core is etched away, and calicination results in a ceramic hollow sphere. Titanium dioxide, barium titanate, alumina, and aluminosilicate spheres have been fabricated using the sol-gel templating technique [6, 12, 13, 18, 19].

We have previously shown that for alumina films and bodies, a low cost, flexible, alternative to sol-gels are chemically functionalized alumina

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nanoparticles (carboxylate-alumoxanes) [20]. These alumina nanoparticles may be prepared, in the size range 10–100 nm with a narrow size distribution, by the reaction of the mineral boehmite with a wide range of carboxylic acids. Besides the use of aqueous reaction conditions, without mineral acids or other additives (resulting in high ceramic yields and low shrinkage [20]), the carboxylate-alumoxanes are infinitely stable in solution or the solid state (i.e., they do not precipitate or undergo changes in particle size ordinarily associated with aging of sol-gels [21]). We have previously shown that the carboxylate-alumoxanes may be used as ceramic precursors for the coating on carbon, SiC and Kevlar fibers [22]. A further advantage of the carboxylate-alumoxane nanoparticle approach is that the porosity of the ceramic formed upon thermolysis may be controlled by the substituent of the carboxylic acid, which has led to their application as precursors for ceramic membranes [23, 24]. A final advantage of the alumoxane approach over traditional sol-gel is the ease by which aluminate phases may be prepared, often at a lower temperature than previously observed [25, 26]. Thus, carboxylate-alumoxanes may be used to create hollow spheres of alumina or an aluminate. Furthermore, we have previously shown that layer-by-layer (LbL) growth of laminates is possible, which opens-up the possible fabrication of ceramic composites with increased applications, such as the formation of magnetic materials [27].

Herein we report the conditions for a simple fabrication of polycrystalline alumina and aluminate hollow spheres with a hardness approaching crystalline sapphire.

2. Experimental procedure

2.1. Materials

Acetate-alumoxane (A-alumoxane) was prepared by previously published methods [20]. Aqueous solutions of alumoxane were degassed before use. Ca-, Er-, Mg-, Ti-, and Y-doped methoxy(ethoxyethoxy)acetate-alumoxanes (MEEA-alumoxanes) were prepared by previously described methods [28, 29]. Polystyrene beads, in the dry form with a uniform 3 μm diameter and a mixture of beads with diameters ranging from 50 to 80 μm, were obtained from Polysciences, Inc. Flat alumina membranes were deposited by dip coating the surface of an alumina support by the previously published method [24].

2.2. Formation of hollow α-alumina spheres

A schematic representation of the process for forming hollow alumina spheres is shown in Fig. 1. Dry-form polystyrene beads (3 μm) were coated with an aqueous solution of A-alumoxane (1, 2, 5, 8, or 10 wt%). The solution was pipetted onto the beads that were placed in coated ceramic boat, and allowed to dry in air. The coating process was conducted in a ceramic firing boat so to minimize the amount of agitation subjected to the coated spheres. The spheres were coated three times to achieve a uniform coating of the spheres. The alumoxane coated polystyrene beads were fired to 220°C for 40 minutes to burn off organic substituents to allow for the dissolution of the polystyrene, not the alumoxane in toluene. The pre-ceramic coated beads were stirred in toluene for 1 h and then vacuum filtered. The washing process was performed 5 times before firing to 1000°C to set the alumina shell. It is important to conduct multiple washes to remove all the polystyrene, because the polystyrene solution tends to "gum up" the surface of the alumina shell precluding removal of additional polystyrene. To separate the free-standing spheres from any extra alumina resulting from the coating process, the fired (1000°C) material was placed in water, centrifuged and filtered. The same process was used for the 50–80 μm beads of polystyrene.

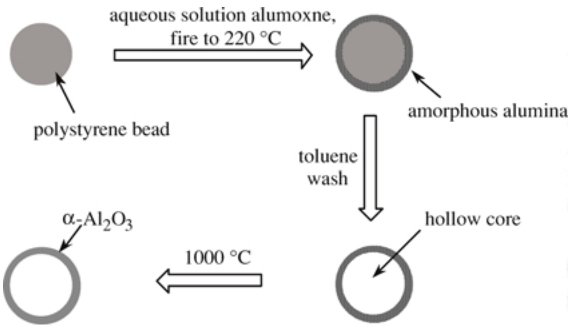

Figure 1 Schematic representation of the process used for forming hollow alumina spheres.

2.3. Formation of mixed metal hollow spheres

Previously formed hollow α-alumina spheres, described above, were coated with a 10 %wt aqueous solution of the appropriate metal-doped MEEA-alumoxane. The solution was allowed to dry in air and then the spheres were fired to 1000°C for 3 h. The metals used to form the mixed metal hollow sphere were Ca-, Er-, Mg-, Ti-, and Y-doped MEEA-alumoxane.

2.4. Formation of ceramic matrix composites with pre-formed hollow α-alumina spheres

Hollow α-alumina spheres (3 μm nominal diameter) prepared as described above were suspended in an aqueous solution of either A-alumoxane (1 wt%) or MEEA-alumoxane (10 wt%). The surface of an α-alumina support was dip coated in the resulting colloidal solution. The newly formed film was allowed to dry overnight before firing to 600°C for 6 h with a dwell time of 5 h. Similar composites with spheres of a nominal diameter between 50 and 80 μm may be prepared in the same manner.

2.5. Formation of polymer matrix composites with pre-formed hollow α-alumina spheres

Hollow α-alumina spheres (3 μm nominal diameter) prepared as described above were suspended in an 1:1 (wt) mixture of resin (Resin Services 302) and hardner (Resin Services 874) in an aluminum pan. A 2 wt% of the spheres to resin/hardner was used. The resin/hardner mixture containing the spheres were cured at 50°C for 24 h. Similar composites with spheres of a nominal diameter between 50 and 80 μm may be prepared in the same manner.

2.6. Characterization methods

Scanning electron microscopy (SEM) studies were performed on a Phillips XL-30 ESEM scanning microscope. The samples were attached to a metal mount using carbon tape. Due to the insulating nature of the materials, a thin layer of gold was applied as a coating to provide a conducting surface. Micro-indention testing was performed on a Micromet microhardness tester with a standard diamond tip. The size of the indentation (10 μm) is smaller than the size of the spheres (80 μm) and all indentions were made so as to minimize the effects of the curvature of the sphere. Hardness was determined by inserting the load weight and the area of indention into the Vicker's equation: $H_v = 1.85444\,(P/d^2)$ where P is the load in kg and d^2 is the area of indention in mm^2. Five indentation measurements were performed on each sample with a loading time of 10 sec per measurement. Powder X-ray diffraction patterns of A-alumoxane and metal-doped MEEA-alumoxane were determined by using a Siemens Diffractometer, with a scan area of 20–80 degrees, step size of 0.1 degrees, and count time of 10 sec. Porosity, surface area, and pore volume were obtained using nitrogen adsorption/desorption techniques using a Coulter^{TM} SA3100^{TM}. Helium was used to determine the free space in the sample tube and nitrogen as the absorbate gas. All samples were outgassed at 300°C for 2 h under a stream of dry nitrogen using a Coulter^{TM} SAPrep^{TM}. Calculations were based on the cross sectional area of nitrogen using the value of 0.162 nm^2. Surface area was calculated using the BET (Brunauer, Emmett and Teller) equation with 5 data points. Pore volume calculation was performed at a relative pressure of 0.9814. Thermogravimetric/differential thermal analyses were obtained on a Seiko 200 TG/DTA instrument using a carrier gas of either dry nitrogen or air.

3. Results and discussion

3.1. Formation of hollow alumina spheres

Multiple coatings of various concentrations of A-alumoxane were used to coat the outside of polystyrene beads of 3 μm diameter (Fig. 2a and b). The resulting coated beads were heated to 220°C for 40 min to calcine the alumoxane to porous amorphous alumina (Fig. 2c). Washing with toluene allowed for the removal of the polystyrene from inside the ceramic coating (Fig. 2d). The resulting hollow spheres were sintered at 1000°C to form α-alumina spheres (Fig. 2e).

Experimentation showed that the ceramic spheres formed using 3 μm diameter polystyrene beads as substrates were capable of shape retention more so than the other diameters investigated (1 μm to 80 μm). The use of larger polystyrene beads results in the ceramic spheres being unable to maintain their shape as free-standing structures. In contrast, the use of smaller polystyrene beads results in a thick ceramic coating, sufficient to preclude the dissolution of the polystyrene bead.

Various concentrations of A-alumoxane were also investigated to determine which concentration produced the optimum coverage. Of the five concentrations investigated solutions with 2–8 wt% alumoxane were found to be optimal. Spheres coated with 8 wt% A-alumoxane (prior to calcination) exhibited a smooth and uniform surface coating. If the concentration was low (1 wt% A-alumoxane) incomplete coverage resulted, however, where a higher concentration was used (10 wt%), failed to coat uniformly. The number of coatings is also important in obtaining a structurally sound alumina sphere. It was found that three coating/drying cycles were optimum to provide an alumoxane shell with superior shape retention and uniformity. If a single

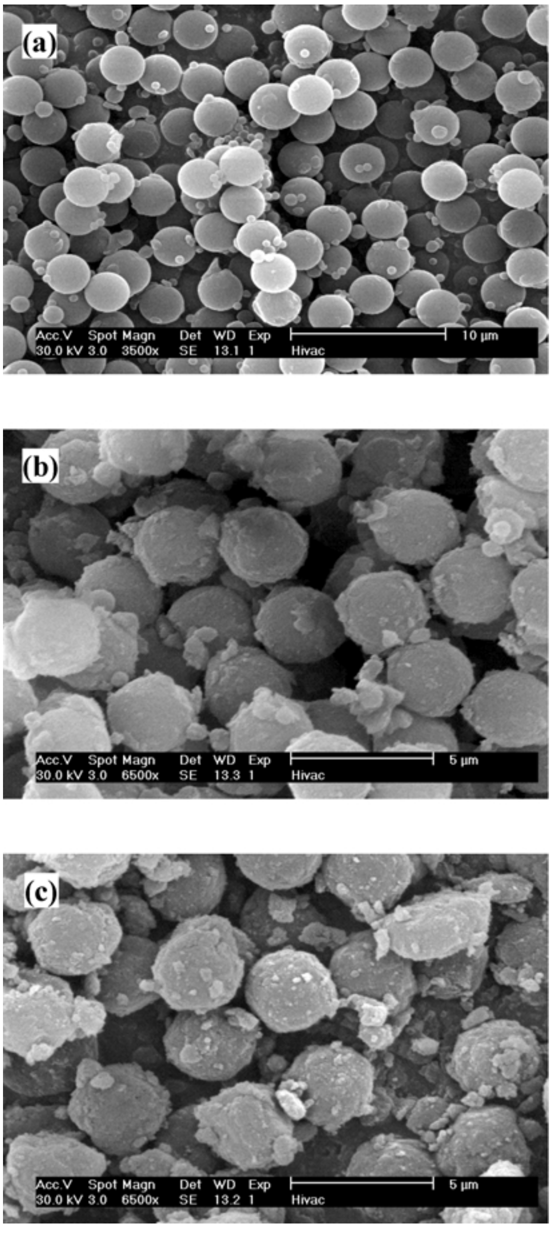

Figure 2 SEM images of (a) untreated 3 μm polystyrene beads, (b) coated with A-alumoxane, (c) calcined to 200°C, (d) after washing with toluene and (e) after sintering to 1000°C.

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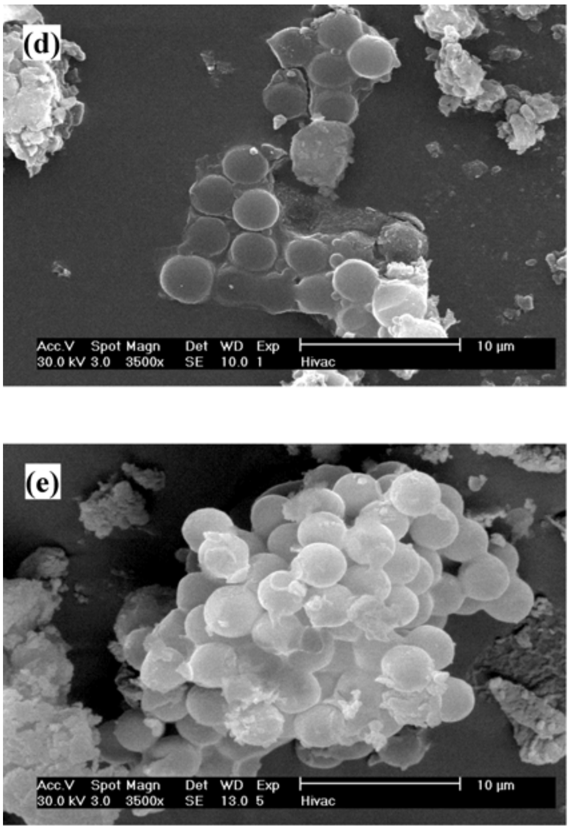

Figure 2 (*Continued*).

coating/drying cycle was used the spheres collapsed upon firing to 1000°C (Fig. 3).

The calcination temperature of 220°C was chosen to fit within the boundaries of the decomposition of the alumoxanes to alumina ($>180°C$) and the decomposition temperature for polystyrene (230°C). Both values were obtained from thermogravimetric analysis (TGA) measurements. Firing to a sufficiently high temperature to form (amorphous) alumina is important because the coating must be sufficiently strong to be able to withstand the toluene washing cycle. In addition, the unfired alumoxanes are soluble in toluene so they must be rendered insoluble before the washing stage. Conversely, if the polystyrene is allowed to pyrolize, the gases evolved burst the amorphous alumina coating, causing destruction to the shell. The complete removal of the polystyrene after the washing cycle is confirmed by TGA measurements showing an absence of the decomposition curve due to polystyrene.

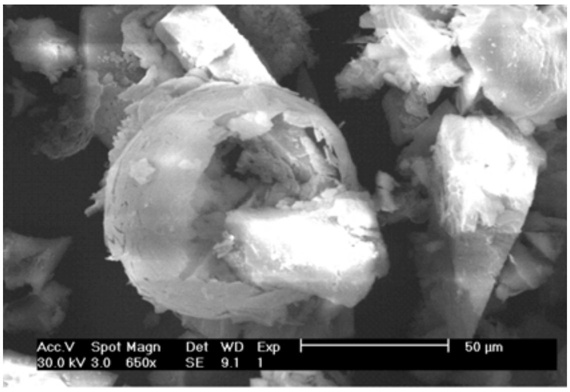

Figure 3 SEM image of a collapsed ceramic sphere resulting from a single coat/dry treatment of a 70 μm polystyrene bead with a 8 wt% solution of A-alumoxane.

TABLE I Surface area and pore volume for samples at each step in the fabrication of free-standing alumina spheres from polystyrene (PS) beads

Sequence	Surface area ($m^2 \cdot g^{-1}$)	Pore volume ($mL \cdot g^{-1}$)
Untreated PS beads	1.47	0.01
Alumoxane coated PS beads	182	0.22
A-alumoxane[a] after calcining to 220°C	216	0.26
A-alumoxane calcined to 220°C[a] after washing with toluene	146	0.25
After sintering to 1000°C	142	0.55
A-alumoxane fired 1000°C[a]	111	0.32

[a] Free-standing samples formed by evaporation of an aqueous solution of A-alumoxane onto a flat substrate. Used for comparative purposes.

A summary of the pore volume and surface area for the samples at each stage of the synthesis (as determined by BET measurements) is given in Table I. The surface area of the polystyrene beads is very low, signifying a relatively pore-free material. Once coated with A-alumoxane the surface area is dominated by the alumoxane coating as indicated by a comparison with a free-standing sample of the same alumoxane (see Table I). Firing the coated beads to 220°C doesn't significantly alter the pore volume and presumably allows for the removal of the polystyrene by the toluene wash. As expected, the surface area decreases on sintering, although the total pore volume does not decrease. This suggests that the final α-alumina spheres are highly porous materials. This is required in order to use this approach for the fabrication of ultrafiltration membranes [30].

A further indication of the surface porosity of the alumina spheres may be seen from SEM images. The surface of the untreated polystyrene spheres shows a smooth morphology, in contrast, the surface of the alumina spheres formed at 1000°C is granular corresponding to the formation of alumina. The size of the alumina grains present (ca. 25 nm) are consistent with the size of alumina grains formed from firing of A-alumoxane films [22, 31, 32]. The thickness of the hollow alumina spheres synthesized from a 2 wt% A-alumoxane is ca. 1 μm (Fig. 4); thicker walls are formed with increasing alumoxane concentrations.

Hardness testing was performed on the α-alumina spheres using Vicker's indention testing (Fig. 5). The hardness of the hollow alumina sphere ($1900 \pm 100\,Kg.mm^{-2}$) approached the hardness of corundum (ca. 2000 $Kg.mm^{-2}$) [33] and drastically harder than a planar piece of A-alumoxane sintered under the same conditions (Fig. 5) [34]. This latter observation confirms the benefit of the spherical structure with regard to using shape and structure to obtain a higher structural strength than inherent in a specific material. The hollow α-alumina spheres are also almost twice as hard as an infiltrated α-alumina substrate, and harder than the $LaAl_{11}O_{18}/Al_2O_3$ infiltrated alumina composites were have recently demonstrated to have the highest improvement in hardness for porous α-alumina substrates [34].

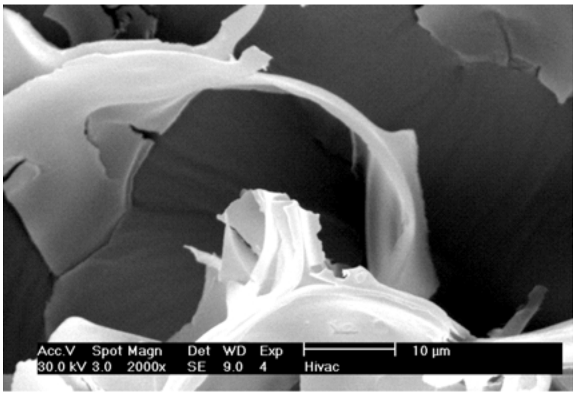

Figure 4 SEM images of the wall for an alumina sphere prepared from a 2 wt% A-alumoxane solution.

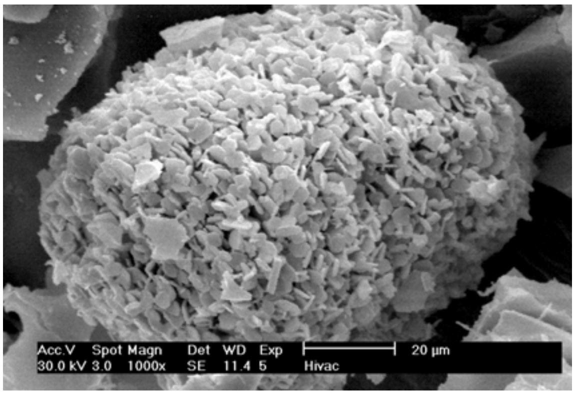

Figure 6 SEM images of the surface of a α-Al_2O_3/$CaAl_{11}O_{18}$ sphere showing the morphology of the $CaAl_{11}O_{18}$ outer layer.

Fiber reinforced ceramic matrix composites (FR-CMCs) are commonly employed where the performance of the ceramic matrix alone is insufficient. In fiber-reinforced ceramics, the reinforcement is primarily utilized to enhance the fracture toughness. The fiber reinforcement prevents catastrophic brittle failure by providing mechanisms that dissipate energy during the fracture process. The operation of various toughening mechanisms, such as crack deflection, fiber pull out, and fiber bridging, to a large extent depend on the degree of chemical and/or mechanical bonding at the fiber-matrix interface. Although the spheres would not simulate pull out, they would provide crack deflection. The added issue with the spheres described herein, is that their density is significantly lower than the bulk ceramic, since approximately 90% of their volume is air. Thus, the overall density of a composite is decreased with respect to increased loading. Furthermore, the bulk dielectric constant of any body containing these spheres will be reduced with increased loading.

The inclusion of a ceramic reinforcement relies on the degree of chemical and/or mechanical bonding at the reinforcement-matrix interface. It is necessary to control the interfacial bond in order to optimize the overall mechanical behavior of the composite. In this regard, we have previously shown that aluminate coatings on fibers provide superior performance characteristics as compared to the native fiber [22, 32]. We have shown that not only alumina spheres may be formed but also that multiplayer spheres can be prepared that mimic the interfacial layer often applied as a coating on fibers to prevent deleterious chemical reactivity and provide a mechanism that promotes graceful failure at the fiber-matrix interface.

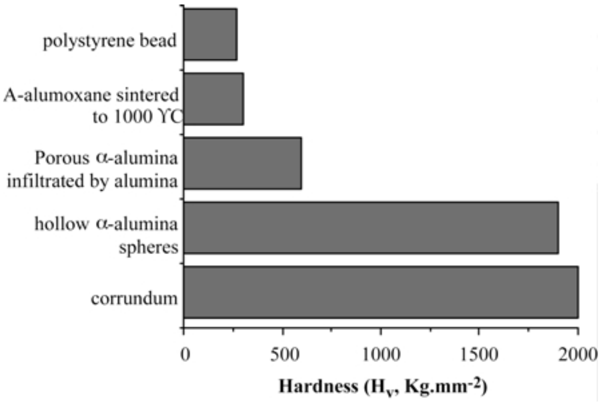

Figure 5 Selected Vickers hardness (Kg·mm^{-2}) in comparison with hollow α-alumina spheres. Values for corundum and an infiltrated α-alumina substrate from references 33 and 34, respectively.

Hollow mixed metal oxide spheres have also been synthesized using the hollow α-alumina spheres as a template. The hollow alumina spheres are coated with a solution of a metal-doped alumoxane. After calcining to 1000°C, the mixed metal oxide phase forms outside of the alumina sphere resulting in a composite like ceramic bi-layer sphere. Suitable mixed metal oxides were prepared using Ca-, Er-, Mg-, Ti, and Y-doped MEEA-alumoxane to forming $CaAl_{12}O_{19}$, $Er_6Al_{10}O_{24}$, $MgAl_2O_4$, Al_2TiO_5, and $Y_3Al_5O_{12}$, respectively [28]. The formation of each phase was confirmed by XRD measurements. The morphology of the surface of the sphere is the same as the appropriate metal oxide. For example, the α-Al_2O_3/$CaAl_{11}O_{18}$ sphere exhibits plate-like crystals confirming the formation of hibonite (Fig. 6). We have previously shown that $CaAl_{12}O_{19}$, $Er_6Al_{10}O_{24}$, and $MgAl_2O_4$ are effective interphase coatings for fiber reinforced ceramic matrix composites (FRCMCs) [31].

3.2. Incorporation of hollow alumina spheres into an alumina and polymer matrix composites

Pre-formed hollow alumina spheres were incorporated into a ceramic thin film formed from a 1 wt% A-alumoxane aqueous solution (see Experimental). Since the 2, 5, and 8 wt% A-alumoxane solutions produced hollow alumina spheres with good shape retention, spheres using these concentrations were incorportated into the thin films.

A flat ceramic thin film (of approximately 1 μm thickness prepared using A-alumoxane [24]) on a porous alumina support were used as a base for the composite structure. The surface of a flat ceramic substrate was brought into contact with a suspension of α-alumina spheres in an aqueous solution of A-alumoxane solution for 2–5 sec. The newly made thin film was dried in air overnight before firing to 600°C. SEM images of the surface and cross section show the incorporation of the hollow spheres into an alumina matrix. The hardness of the SRCMC as compared to the matrix material (in the absence of the ceramic spheres) shows an improvement from 220 to 370 and 650 Kg·mm^2 after heating the composite to 600 and 1000°C, respectively.

Incorporation of the hollow α-alumina spheres (2 wt%) into an epoxy resin (DER 302/874) results in an increase of the hardness from 170 to 570 Kg·mm^2. SEM images of a cross section show the spheres are reasonably dispersed, however, further improvement in compatability may be obatianed by surface functionalization of the α-alumina spheres [35].

4. Conclusions

We have demonstrated that highly uniform α-alumina spheres may be fabricated. The use of the alumoxane-nanoparticle precursors simplifies processing and allows for simple scale-up. A further advantage of the present technique is the ability to fabricate spheres consisting of α-alumina/aluminate layer by layer grown laminates. While the best results were obtained using 3 μm polystyrene preforms, some success has been obtained with sizes from 1 μm to 80 μm. However, further optimization of these sizes is required. The hardness of the spheres is far supiror to a planar structure of the same material and this property is extended to composite structures with ceramic and polymer matrices.

Acknowledgments

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