PLATELET ALUMINA: A POTENTIAL STRUCTURE REINFORCEMENT FOR HIGH PERFORMANCE REFRACTORIES

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ABSTRACT

Platelet alumina is a kind of 2D corundum synthesized at relatively lower temperatures by specific technologies different from that for tabular alumina. The well-known application of platelet alumina is in automobile industry as pearlescent pigments. However, more attention is paid to the use for materials strengthening. Like 1D structural reinforcement elements such as whiskers, rods and needles, such 2D elements should have a similar capability to resist crack propagation in material matrix. Examples of polymer, glass and bioceramics strengthened by platelet alumina have been evidenced in many literatures. The authors attempted to use such platelets to strengthen Al2O3-SiO2 based ceramics and significant increase in split tensile strength has been observed. Synthesis of platelet alumina with low cost aluminum hydrate was also attempted and the results have shown implications for refractory applications. Ideas and suggestions were put forward for further efforts.

Key word: platelet alumina, strengthening, toughening

INTRODUCTION

Strength and toughness are two important factors of engineering ceramics. Ceramics are of high strength but low toughness, because their crystalline structure does not have sufficient sliding system that lacks mechanisms to resist crack propagation. Various toughening techniques have been developed and some of them are successfully applied to engineering ceramics. Microcracking, grain boundary weakening, in-situ phase transformation and metallic phase inclusion are one kind of toughening approaches. They increase the material toughness by dissipating the strain energy at crack tips, but decrease the material strength in the meantime, due to introducing these “weak” zones. There is the other kind of toughening approaches able to perform strengthening and toughening simultaneously, known as fiber reinforced ceramics matrix, in which crack bridging, fiber pullout and fiber-matrix debonding are the major reinforcement mechanism. Although the latter two mechanisms require a relatively weak fiber-matrix interface, the interface bond can be tuned to be substantially strong because of the much stronger fibers.

Platelet alumina is a kind of 2-dementional reinforcement elements. Because of the appreciably high aspect ratio of the diameter to thickness, the platelets can have the similar strengthening and toughening effects to that of fibers. Refractories are kinds of special ceramics. Strong and tough refractories are of high capability to resist stress and thermal shock at server environment. In this paper, the feasibility of using platelet alumina to reinforce refractories is addressed.

PLATELET ALUMINA REINFORCED CERAMICS

Barium calcium aluminosilicate (BCAS) glass is used as seals for planar SOFCs to separate and contain the fuel and oxidant within the cell and to bond cell components together. The seal has to operate in thermal cycling from 600 to 1000 °C for thousands of hours, during which it is prone to cracking. Reinforcement of the glass was attempted by Bansal et al[1], who studied the effectiveness of 3YSZ and platelet alumina, respectively. Their experiment revealed that, while the both are able to increase the glass strength and toughness, platelet alumina resulted in larger toughness increment than 3YSZ.

Hydroxyapatite (HAp) is a calcium phosphate similar to the human hard tissues in morphology and composition. It is an important bioceramics for permanent implants to form a bioactive fixation with the surrounding bone tissues. The main restriction to use of this material is its low fracture toughness (KIc HAp $\approx$ 1MPa·m$^{1/2}$). Gautier[2] et al attempted to use of platelet alumina to improve the HAp’s toughness. Their study verified the toughening effect of the platelet. Furthermore, the toughening was dependent on the size of the platelet. While smaller platelets (ϕ3-7×0.6μm) could be used at an amount of 30 vol% and reach a toughness increment to 2.1 MPa·m$^{1/2}$, the use of larger platelets (ϕ10-15×1.0μm) could not be over 10 vol.%, at which the toughness increment was about 1.0 MPa·m$^{1/2}$ and beyond which the toughness increment began to decline. Such a phenomenon was attributed to a spontaneous microcracking of the HAp matrix which is detrimental to the mechanical reliability. This assumption is supported by the different toughness increments in two different directions, i.e. parallel and perpendicular to the basial plane of the platelets. Greater toughness increment was obtained in the parallel direction that was believe to take place via a pre-stress mechanism[3]. Smaller toughness increment was seen in the perpendicular direction that was attributed to the crack deflection mechanism.

10YSZ is the solid electrolyte of SOFC. It is the most commonly used electrolyte in SOFC owing to its high oxygen ion conductivity, stability in both oxidizing and reducing environments, availability, and low cost. However, the material is brittle and susceptible to fracture due to the existence of flaws. Choi et al[4] tried to use nano particulate alumina (50nm) and platelet alumina (ϕ10-15×1μm) to reinforce the material. The results showed that, for a given alumina content, flexure strength of the particulate composites was greater than that of the platelet composites at higher alumina contents ($\geq$ 20 mol%); whereas, fracture toughness of the platelet composites was greater than that of the particulate counterparts, regardless of the alumina content. This phenomenon is understandable, because the nano particulates are of higher reactivity that may result in higher grain boundary bonding and favor the crack bridging mechanism. On the other hand, the reinforcement induced by platelet alumina might favor the crack deflection, interface debonding and platelet pullout mechanisms. The former contributes primarily to strength whereas the latter contributes primarily to toughness.

Zirconia toughened alumina (ZTA) is the composite of YTZP and alumina. YTZP is a purely tetragonal phase, fine grain material. The material offers the highest flexural strength of all Zirconia based materials. It exhibits a trait called transformation toughening which allows it to resist crack propagation. Applied stress, magnified by the stress concentration at a crack tip, can cause the tetragonal phase to convert to monoclinic, with the associated volume expansion. However, YTZP is unsatisfactory for its lower compressive strength, lower hardness and higher density. ZTA is able to overcome these drawbacks of YTZP, but the cost is decreased of the toughness. Zhou et al[5] improved the toughness of ZTA by introducing 10 vol% platelet seeds into the composite. The toughness was increased from below 6 MPa·m$^{1/2}$ to about 12 MPa·m$^{1/2}$.

The combined zirconia and platelet alumina toughening was still unsatisfactory in terms of hardness and compressive strength. These drawbacks limited the use of the composite for ball heads and cups in total hip prostheses (THR) system, which demands high wear resistance. In order to meet the requirement and produce a strong, tough and hard material, chromium oxide is incorporated into the composite's formula. The new composite is named as ZPTA[6]. It contains three material phases, i.e., submicron-sized Y-TZP grains finely dispersed within the matrix, alumina platelets and a matrix of Al_2O_3-Cr_2O_3 solid solution, which is an essential phase for the hardness. ZPTA exhibits a combined merit in terms of density, bending strength, compressive strength, fracture toughness and hardness, compared to alumina, YTZP and ZTA.

POTENTIAL APPLICATION TO REFRACTORIES

Currently there are two approaches for producing platelet alumina: molten salt synthesis and solid solution synthesis. The former uses alumina salt, such as $Al_2(SO4)_3$ or $Al(NO)_3$ as the feedstock, which is heated in molten K2SO$_4$ or Na_2SO_4 at 900°C~1200°C for a few hours. During the process, α-Al_2O_3 nucleate and grow into platelets, as shown in Fig.1a. The later uses organic aluminum compound as the feedstock, into which fluorine species was dispersed as platelet growth promoter. Growing of the platelet takes place at about 1200°C, during which the organic aluminum decomposes into alumina crystallites and F^- dissolve into the alumina lattice to catalyze epitaxial growing of the alumina crystallites. Fig.1b illustrates a sample of alumina platelet synthesized by solid solution approach.

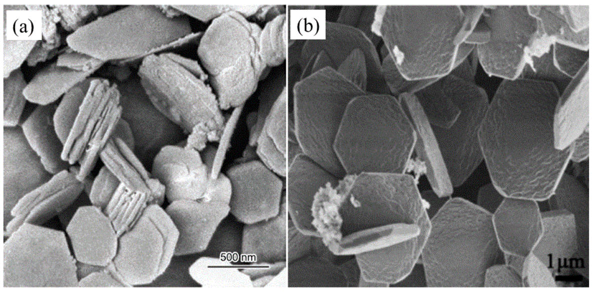


Fig.1: Platelet alumina synthesized by (a) molten salt and (b) solid solution approaches

The both are of low yield processes. The molten salt approach has to use sufficient amount of the alkaline salts, in order to facilitate the platelets growing. Usually the molar ratio of alkaline to aluminum has to be in a range of 6 to 12[7,8]. The solid solution approach has to use aluminum compounds with large organic ligands, in order to provide the crystallites with a non-obstructive growing environment. In a typical example, the aluminum compound was $NH_4AlO(OH)HCO_3$, which can only convert to 36.7 wt.% alumina[9]. The low yield processes may not be economically viable for refractory applications.

We attempted gibbsite as the precursor for platelet synthesis. The molecular formula of gibbsite is $Al(OH)_3$, which contains 65.4 wt.% Al_2O_3. As gibbsite was used as a replacement of $NH_4AlO(OH)HCO_3$, the yield was increased by 78.2%, and the AlF_3 was reduced from 5 wt.% to 2.5 wt.%. The SEM micrography of the synthesized powder is illustrated in Fig.2a. It was full of platelets, although the size and aspect ratio appeared smaller than those shown in Fig.1a.

Growth of the gibbsite derived alumina platelet can be accelerated by microwave heating. Fig.2b shows a sample that was synthesized in microwave furnace. The other synthesis conditions were the same as those for the sample shown in Fig.2a. It is obvious that platelet size and the aspect ratio were significantly enlarged.

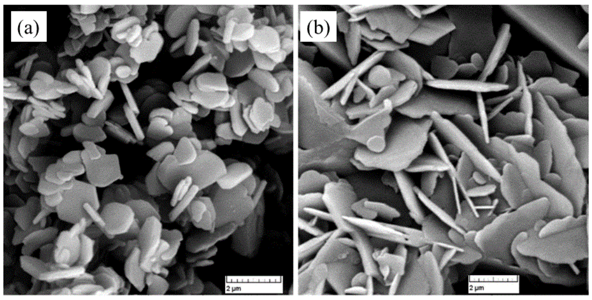
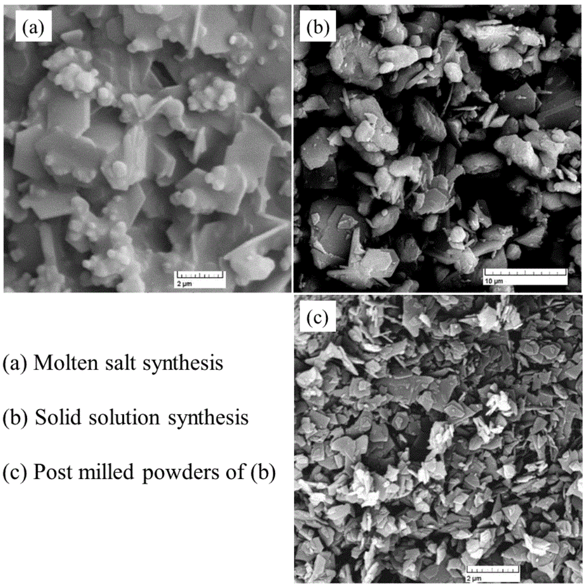


Fig.2: Solid solution synthesized platelet alumina with gibbsite as the precursor in (a) conventional furnace and (b) microwave furnace at 1200°C for 1 hour.

Use of bauxite for synthesis of platelet alumina was also attempted by our team. The bauxite contained 82.25 wt.% Al_2O_3 and 9.06 wt.% SiO_2. The total amount of Fe2O3, TiO2, Na2O, K2O, MgO and CaO in the bauxite was 6.82 wt.%. It implies a potentially higher yield of platelet (max. 82.75 wt.%). Samples synthesized by means of molten salt showed well grown platelets, as illustrated in Fig.3a. Samples synthesized by mans of solid solution showed some platelet clusters along with some seemingly non-platelet particles, as shown in Fig.3b. However, this appearance changed dramatically after milling the as-synthesized samples. As shown in Fig.3c, the sample was full of platelet fragments. It implicates that the particles shown in Fig.3b were aggregates of loosely bonded platelets.



(a) Molten salt synthesis

(b) Solid solution synthesis

(c) Post milled powders of (b)

Fig.3: Alumina platelets synthesized from bauxite

A few experiments were carried out to evaluate the effectiveness of using the platelets synthesized from the low-cost approaches for ceramics reinforcement. The platelets addition varied from 6, 12, to 18 wt.%, respectively. The final composition of the ceramics had 71.97 wt.% Al_2O_3 and 21.82 wt.% SiO_2. The total amount of Fe2O3, TiO2, Na2O, K2O, MgO and CaO in the bauxite was 6.14 wt.%. Fig.4a illustrates the split strength of the specimen sintered at 1300°C for 1 hour. It can be seen that the strength increased over 70% as the platelets addition reached to 12 wt.%. Further addition did not result in further strength increase. It is in good agreement with the work on hydroxyapatite.

Our study was further advanced to reinforcement by in-situ grown platelets. For these studies, 2.5 wt.% AlF_3 or 0.5 wt.% Nb_2O_5 was added into the corresponding ceramic formulas, respectively. The chemical composition of the

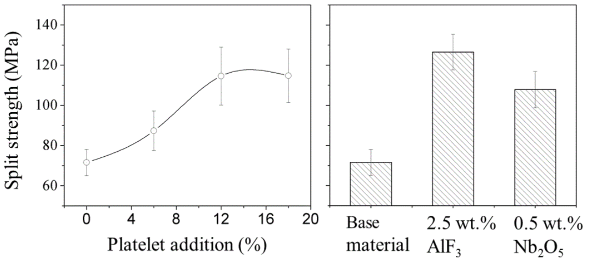


Fig.4: Strengthening ceramics by means of (a) low cost ex-situ platelets and (b) in-situ grown platelets.

AlF_3-containg sample was similar to that of the sample with ex-situ platelets and their sintering profiles were also identical. The chemical composition of the Nb_2O_5-containig sample had 98 wt.% Al_2O_3. It was sintered at 1600°C for 2 hours. Fig 4b illustrates the split strength of strengthened samples. For comparison, the strength of the specimen without the promoters (base materials) is also included. The figure proves the in-situ strengthening effect. Fig.5 shows the SEM images of the fracture surfaces of the in-situ strengthening surfaces. It can be seen from the figure that the strengthening in AlF_3-sample was accomplished via crack deflection mechanism (Fig.5a), whereas the strengthening in Nb_2O_5-sample was realized by means of platelet pullout (Fig.5b).

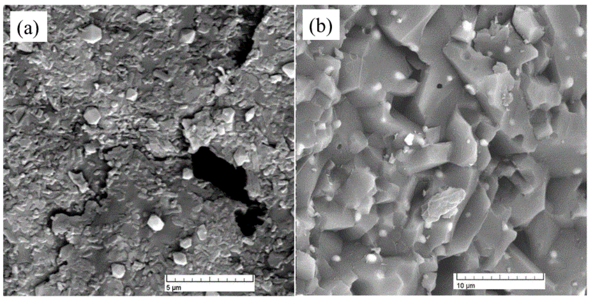


Fig.5: Fracture surface of samples containing (a) low cost ex-situ platelets and (b) in-situ grown platelets.

CONCLUSION REMARKS

Reinforcement of ceramics by means of platelet alumina takes place via similar mechanisms as that by means of fibers. The advantage of using platelets is that they are oxide that do not have oxidation problems at elevated temperatures. Compared to mullite needles and rods, alumina platelet has higher strength and application temperature. The capability of alumina platelets to reinforce ceramics is a proven technique that is documented in technical literatures.

A major factor for using alumina platelets to strengthen and toughen of refractories is the cost. The conventional approaches for producing the platelets, either the solid solution approach or the molten salt approach, are expensive. Our efforts demonstrated the feasibility to use aluminum hydrates and bauxites as raw materials for producing alumina platelets. Use of these raw materials could reduce the platelet cost to a certain extent.

The reinforcement by the platelets synthesized from low cost approach was demonstrated. The technical concept of platelet reinforcement was further advanced to strengthening of ceramics by in-situ grown platelets. The effort opened a new avenue for an economically viable technology for reinforcement of high performance refractories.

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