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ScienceDirect
Ceramics International 37 (2011) 2621–2624
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Synthesis of Al_2O_3 whisker-reinforced yttria-stabilized-zirconia (YSZ) nanocomposites through in situ formation of alumina whiskers

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Received 12 March 2011; received in revised form 5 April 2011; accepted 6 April 2011
Available online 13 April 2011

Abstract

Enhanced mechanical properties of yttria-stabilized zirconia based composites were obtained by introducing alumina whiskers as reinforcement. The alumina whiskers were formed in situ by decomposition of ammonium aluminum carbonate hydroxide (AACH) whiskers during calcination. The whiskers thus formed were amorphous and were converted to α-alumina during sintering at 1450 °C. The AACH whiskers were produced by hydrothermal treatment of an aqueous solution of urea and aluminum nitrate at 120 °C for 24 h. The Vickers hardness of the sintered composite sample increased with an increase in the alumina content up to 10 wt% and then decreased. The maximum hardness achieved at 10 wt% of alumina whiskers was 13.8 GPa, which further increased to 14.4 GPa with the addition of 1.0 wt% of cetyl-trimethyl-ammonium bromide (CTAB). The improved mechanical strength of the composites was attributed to the enhanced dispersion of alumina whiskers due to four times volume decrease during transformation of AACH to alumina and relatively lower aspect ratio of AACH whiskers as well as the deflocculating effect of CTAB.

Keywords: B. Whisker; Zirconia; Alumina; AACH; Hydrothermal; CTAB

1. Introduction

The fracture toughness of monolithic ceramics is usually very poor which limits their applications. This has led to the focus of researchers on development of ceramic composites. For instance, highly improved toughness has been obtained with incorporation of fiber reinforcements [1].

The control of properties becomes even more critical when they are to be incorporated as human body parts such as in dental rehabilitation and bone replacement [2]. Ceramic composites offer a special advantage of chemical inertness in comparison with their metallic counterparts [3]. Among various ceramic composite systems investigated so far, ZrO_2–Al_2O_3 system has been proved to be a potential candidate for dental rehabilitation and 'femoral heads in hip replacement' type of applications [2,4]. The special feature of this system is the transformation toughening [5–7] of ZrO_2 (when doped with Y_2O_3, etc.)

Although it is generally known that whisker reinforcement may give many fold improvement in fracture resistance, so far a little work has been reported on alumina fiber/whisker reinforced zirconia composites, as far as our knowledge is concerned. A worth-mentioning report on alumina-whisker-reinforced zirconia composites is that by Nevarez-Rascon et al. [8]. In ZrO_2–Al_2O_3 composite with 30% alumina, a replacement of about 10% of particulate alumina by its whiskers resulted in some improvement in hardness; beyond this hardness decreased, with a very poor hardness when the whiskers completely replaced the particulate alumina. The main reason behind this appears to be the problem of agglomeration of fibers/whiskers during processing resulting in poor dispensability or agglomeration and thus failure to achieve desirable properties [8]. It may be worth-mentioning that whiskers/fibers used in this work have a high aspect ratio of

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.04.009

1400, which may possibly be responsible for agglomeration and poor dispersion.

In the present work, we prepared precursor ammonium aluminum carbonate hydroxide (AACH) whiskers [9,10], mixed them with zirconia powder by wet-dispersion method in ethanol with or without CTAB as a deflocculating agent. On calcinations AACH whiskers were successfully converted in situ into alumina. In this way, higher hardness has been achieved in comparison with previous reports with only 10% alumina in the form of whiskers.

2. Experimental procedures

Ammonium aluminum carbonate hydroxide (AACH) whiskers were prepared from precursor aqueous solution of aluminum nitrate and urea at 120 °C, following Li et al. [10], in a high pressure reactor (Limbo-350).

AACH whiskers and high purity (99.99%) tetragonal ZrO_2-3Y powder (average particle size of 300 nm) were separately suspended in ethanol using ultrasonic bath (Elma E 30 H, 37 kHz) with or without 1% CTAB. Both the suspensions were then mixed together, kept at 60 °C while stirring until nearly all the ethanol was evaporated. Samples with varying amounts of AACH corresponding to 5, 10, 15, 20, 30 and 50% Al_2O_3 were prepared.

Thermogravimetric anlaysis (TGA) (Mettler Toledo TGA/SDTA 851) was performed in the temperature range of 50–900 °C at a heating rate of 10 °C/min in air.

The samples without CTAB were calcined at 400 °C. The samples with CTAB were calcined at 650 °C for complete decomposition of CTAB. Pellets of about 1.5 g with a diameter of 10 mm were then prepared at a load of 5×10^3 kg. The pellets were then sintered for 2 h at 1450 °C in a muffle furnace (Carbolite HTF-18/8). Heating and cooling rates were maintained as 1 °C/min.

The density of the sintered pellets was measured by geometric method, while the hardness was determined by using Vicker Microhardness Tester (KARL FRANK, Germany) at a load of 10 kg.

3. Results and discussion

Fig. 1(a) shows the scanning electron micrograph of as prepared AACH rods. The apparent diameter of these rods is about 500 nm while the length is several micrometers. A higher magnification image (Fig. 1(b)) reveals thinner and smooth surfaced nanowires with a diameters of about 100–200 nm, which possibly form initially and join sidewise giving rise to comparatively thicker rods (of flakes). The results are almost comparable with Li et al. [10].

Fig. 2 shows typical XRD patterns of sintered pellets with varying amounts of alumina prepared from the above whiskers dispersed in zirconia powder, as detailed in experimental methods. Formation of α-alumina in the matrix of tetragonal zirconia is confirmed. Weak reflections of α-alumina in patters XRD patterns for 10% alumina (pattern ii) and 20% alumina in XRD patters for (iii) may be due to low concentration, and low X-ray cross section of aluminum as compared to zirconium. Nevertheless, existence of X-ray reflections was confirmed at slow scans as typically shown in Fig. 2(b) for the sample with 10% alumina. The XRD patterns of the sintered pellets were not affected by the addition of CTAB in the precursor suspensions.

Fig. 3(a) shows a fracture surface of the sample with 10% alumina, with corresponding EDS spectrum that confirms 10% alumina in the sample. A corresponding high magnification image is shown in Fig. 3(b), along with EDS spectrum obtained from a typical whisker confirming it to be alumina. (The counts of zirconium seem to come from the matrix). It is clear that the whiskers retain their shape during their transformation from AACH to alumina and subsequent sintering. The whiskers are also seen to be well surrounded by zirconia matrix. SEM images were also obtained after mechanical polishing with subsequent thermal etching, as typically shown in Fig. 3(c) and (d). Relatively compact structure is obtained at 10% alumina, while high porosity regions are numerously seen in sample with 50 wt% Al_2O_3, the poor ability to sinter at higher concentrations may possibly be related with agglomeration.

As shown in Fig. 4(a), relative density of sintered pellets decreases with alumina content. Nevertheless, addition of CTAB results in a slightly higher density. This strengthens our view that improved dispersion of alumina whiskers in zirconia may enhance the ability to form relatively compact composites.

Fig. 4(b) shows hardness of the sintered ZrO_2–Al_2O_3 pellets as a function of alumina content, with or without the addition of CTAB in the precursor suspensions. A maximum hardness of about 14 GPa is observed for 10 wt% of Al_2O_3 whiskers. For all the cases, addition of CTAB results in a relatively higher

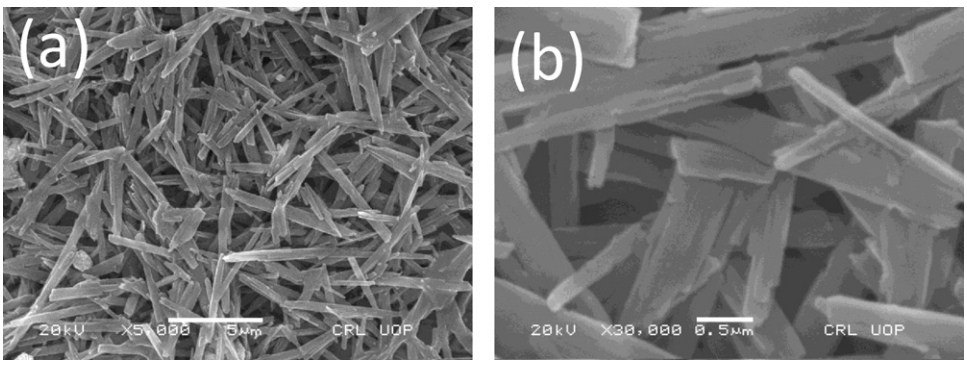

Fig. 1. SEM micrographs of as-prepared AACH whiskers.

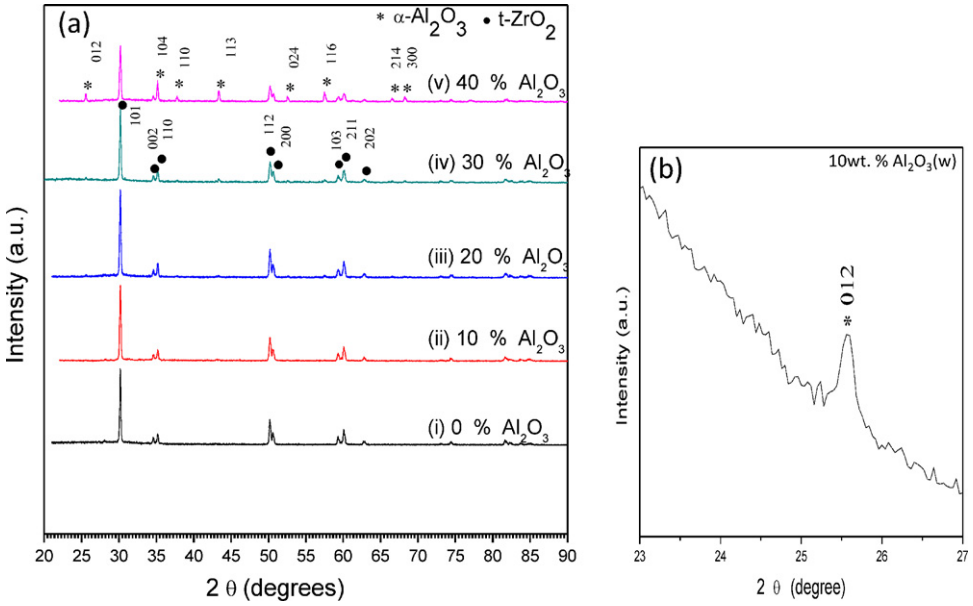

Fig. 2. (a) XRD patterns of sintered ZrO_2 + $Al_2O_{3(w)}$ nanocomposites with various amounts of Al_2O_3 whiskers; (b) Slow scan rate XRD pattern around (0 1 2) reflection of α-Al_2O_3 for the sample with 10 wt% Al_2O_3 whiskers.

hardness as related with improved compactness of the composites (Fig. 4(a)). Possibly due to similar reasons (i.e., increased porosity) hardness decreases significantly with the addition of 20% alumina whiskers and above. For comparison, hardness of composites formed by Nevarez-Rascon et al. [8], employing high aspect ratio alumina whiskers has also been shown in the figures. High achievable hardness in case of our results seems to be related with improved dispersion, and compactness. Improved dispersion may also partly be related with ease in dispersion of precursor AACH instead of alumina whiskers.

An important factor in improvement of dispersion of alumina whiskers may be a drastic volume change (up to ∼4 times) associated with transformation of AACH whiskers into alumina whiskers. This results into production of mesoporous alumina nanostructure [11]. This mesoporous structure at higher energy state seems also to assist in improving the sinterability of the composite. Since the ultrasonic bath with a frequency of 37 kHz was used to disperse AACH whiskers and zirconia powder in alcohol and it is known that the minimum agglomerate size in ultrasonic bath is dependent on the frequency [12], an average agglomerate size between 100 and

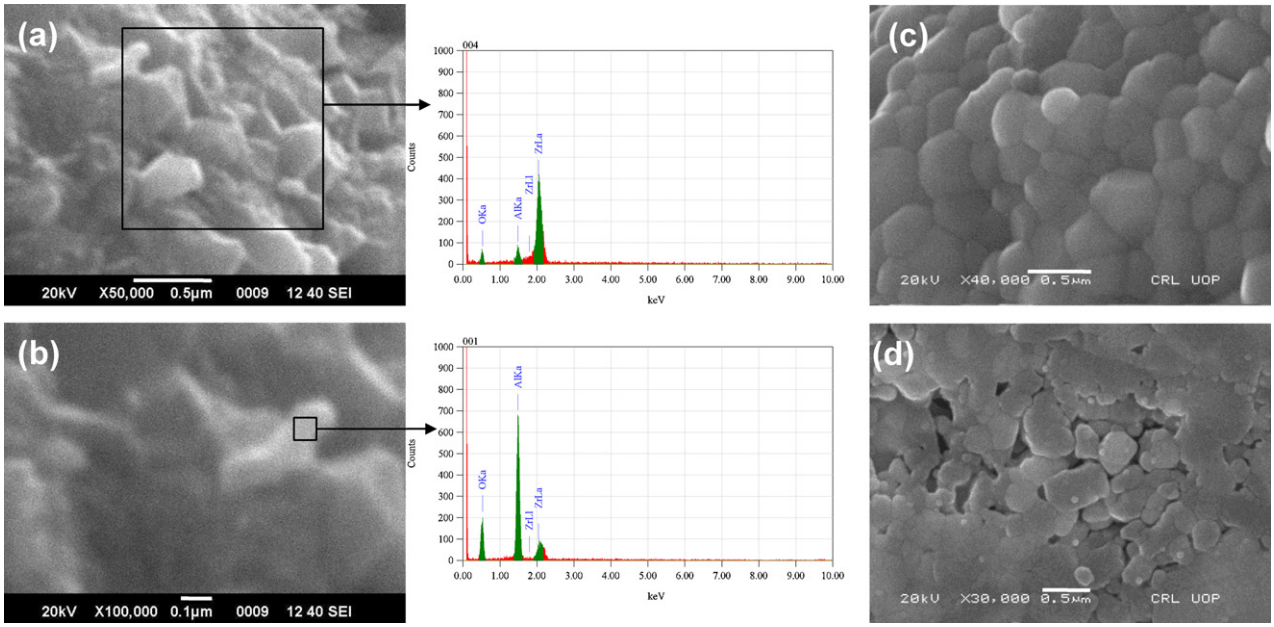

Fig. 3. SEM micrographs of: (a) and (b) as-fractured 90% ZrO_2(3Y)-10% $Al_2O_{3(w)}$ pellet along with EDS spectra on a 1.5 μm × 1.5 μm area in (a) and a whisker in (b); (c) and (d) polished and thermal etched surfaces of samples with 10 wt% and 50 wt% alumina whiskers, respectively.

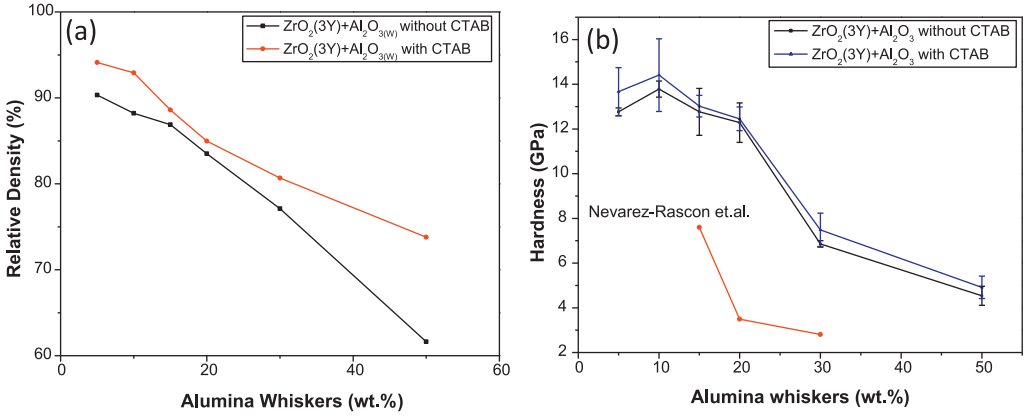

Fig. 4. (a) Relative densities and (b) Vicker hardness of sintered pellets having various amounts of alumina whiskers, with and without CTAB. For comparison hardness values from Nevarez-Rascon et al. are also given.

200 nm would be expected [13]. A subsequent drastic decrease in size during calcination results in very small alumina agglomerate size at any localized region provided that sufficient zirconia particles are present around to surround it. However, as the volume percentage of AACH whiskers is increased, sufficient zirconia particles may not be available to surround the dispersed whiskers and re-agglomeration of whiskers may take place. A further improvement in dispersion has been obtained due to deflocculating effect of cationic surfactant CTAB [14].

4. Conclusions

A new facile technique has been developed for improvement of dispersion of alumina whiskers in ZrO_2 matrix. In this technique, AACH whiskers were first dispersed into ZrO_2 powder and the mixture was calcined at 400 °C resulting in the formation of alumina whiskers. This transformation from AACH to alumina is accompanied by about four times decrease in the volume of whiskers, thus decreasing the size of whisker agglomerate at any localized position and resulting in better dispersion. Further improvement in dispersion was obtained by addition of CTAB, a deflocculating agent. The hardness value of as high as 14.4 GPa was obtained in this way by the addition of just 10 wt% of alumina whiskers.

Acknowledgement

One of the authors (Muhammad Abdullah) is thankful to the Higher Education Commission, Pakistan (HEC) for financial support provided for this research work.

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