Effect of CTAB Addition on Improvement of Properties of $Al_2O_{3(w)}$–$Al_2O_{3(n)}$–$ZrO_{2(n)}$ (3mole% Yttria Stabilized Tetragonal Zirconia) Nanocomposite

Muhammad Abdullah, Jamil Ahmad, Mazhar Mehmood, and M.Mujahid

***Abstract*—Vickers hardness and density of composites, consisting of 20wt% Al_2O_3 (in form of nanoparticles and/or whiskers) as reinforcement and 3-mole% yttria stabilized tetragonal zirconia (abridged as TZ-3Y) as matrix, were significantly *enhanced* by addition of 1wt% CTAB. The Al_2O_3 whiskers were formed *in situ* from ammonium aluminum carbonate hydroxide (AACH) whiskers during sintering at 1450 ℃. An increase in hardness was also observed by increasing the fraction of alumina whiskers up to a critical value (5wt% $Al_2O_{3(w)}$ - 15wt%$Al_2O_{3(n)}$) followed by a decrease in hardness by further increase in whisker fraction. The maximum hardness (*i.e.*, at critical composition) was 14.29GPa and 13.65GPa, for samples with and without 1wt% CTAB, respectively. These hardness values are higher than already reported value of 12.4GPa for 2.5wt% $Al_2O_{3(w)}$ - 17.5wt% $Al_2O_{3(n)}$ by Nevarez-Rascon *et al.* The improvement in hardness was attributed to the use of whiskers with comparatively larger diameter as well as improved dispersion of whiskers due to CTAB. At higher whisker fractions, a decrease in hardness could be related with agglomeration of whiskers.**

***Index Terms*—deflocculant, tetragonal zirconia, whiskers, hydrothermal synthesis, cationic surfactant.**

I. Introduction

With advancement in manufacturing techniques the demand for new materials for dental and orthopedic applications with improved properties is increased [1]. Consequently, a lot of research has been focused on development of new materials for biomedical applications. The previous trend of using metals as dental materials has changed to the use of ceramic materials due to better biocompatibility, chemical inertness and aesthetics of the latter. Owing to its transformation toughening mechanism, Yttria-stabilized Tetragonal Zirconia occupies a unique position among these ceramics [2]. However its hardness (12GPa [3]) is lower than other competitive ceramics such as Al2O3, SiC, Si3N4 etc [4]. For load bearing applications, its hardness and toughness can be further improved through composite formation. Due to better compatibility with zirconia for medical applications, alumina may be a suitable candidate as reinforcement component. This has lead to a lot of research activity for zirconia-alumina composites [5].

Among various morphologies of reinforcement, fiber-like morphology is the best for the development of high toughness composites due to its toughening effects related with crack bridging etc. Similar effects may be obtained at significantly enhanced level through the use of strong ceramic whiskers as reinforcement. The whiskers are single crystals having high structural perfection along with excellent mechanical properties. For example the strength of SiC whiskers is 50GPa while for glass fibers it is 3GPa and for bulk glass only 0.1GPa [6-9]. Excellent mechanical properties of whisker reinforced composites are attributed to the presence of various toughening mechanisms such as crack deflection, crack bowing, whisker pullout and crack bridging [10-14] etc.

A number of reports on the use of SiC whiskers as reinforcement for zirconia matrix can be found in literature [15-20]. However, non oxide whiskers suffer limitations due to chances of high temperature oxidation or reaction with the matrix. Therefore, the use of oxide whiskers is more favorable, particularly, alumina whiskers which also show better biocompatibility. There are very limited reports on the use of alumina whiskers as reinforcement in zirconia matrix [21-24]. In general, the use of only alumina whiskers results in decrease in density due to agglomeration. Nevarez–Rascon [25] used a combination of alumina whiskers and alumina particulates as reinforcement to get good relative density but due to very small diameter of alumina whiskers (1-2nm), agglomeration was still severe and only 2.5wt% alumina whiskers were possible to be added to get good hardness. In the present work the emphasis has been on the development of TZ-3Y composite with high hardness and sintered density. With overall concentration of alumina at 20wt% [26], the change in hardness and density with varying fractions of whisker and powder alumina were studied. The whiskers' diameter was relatively higher. They were introduced in the form of AACH whiskers of 100-200nm diameter prepared by hydrothermal method [27], which were transformed in situ into alumina whiskers during calcinations / sintering at higher temperatures. Moreover, the effect of use of Cetyl Trimethyl Ammonium Bromide (CTAB) to disperse alumina nanoparticles and whiskers in zirconia matrix was also reported.

Manuscript received May 17, 2012; revised August 15, 2012.

This work was supported by the Higher Education Commision (HEC) of Pakistan.

Muhammad Abdullah, Jamil Ahmad and Mazhar Mehmood are with Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, Nilore, Islamabad, Pakistan (emails: mabhutta_99@yahoo.com, mjamil@pieas.edu.pk, mazhar@pieas.edu.pk respectively)

M. Mujahid is with of School of Chemical & Materials Engineering (SC&ME), National University of Sciences and Technology, H-12, Islamabad, Pakistan (email: mujahids@gmail.com).

DOI: 10.7763/IJIET.2012.V2.201

II. Procedure for Experiments

A. Preparation of AACH Whiskers

Alumina whiskers ($Al_2O_{3(w)}$) were produced *in situ* from transformation of AACH whiskers during sintering. The AACH whiskers were prepared through hydrothermal technique, the details of which have been reported elsewhere [24].

B. Preparation of Nanocomposites and Their Characterization

Five samples of each with and without 1wt% CTAB were prepared. The compositions of these samples are given in Table I

TABLE I: Compositions of Nanocomposite Samples.

Type	Composition	Variable
A	$[TZ\text{-}3Y]_{80}+[Al_2O_{3(W)}]_{20-x}+[Al_2O_{3(n)}]_x$	x = 0, 5, 10, 15, 20
B	$[[TZ\text{-}3Y]_{80}+[Al_2O_{3(W)}]_{20-x}+[Al_2O_{3(n)}]_x]_{99}+[CTAB]_1$	x = 0, 5, 10, 15, 20

The AACH whiskers along with Al_2O_3 nanoparticles ($Al_2O_{3(n)}$ average particle size of 150nm) and TZ-3Y (average particle size of 200nm) were dispersed separately in absolute ethanol. For B type samples 1wt%CTAB was also added in ethanol before addition of particles or whiskers. For breaking the agglomerates the suspension was sonicated for 30 minutes. AACH whiskers were added according to the stoichiometric amount of alumina whiskers required. Both suspensions were mixed together and the mixture was kept at 40 ℃~60 ℃ while stirring until all the ethanol was evaporated. The dried powder without CTAB was calcined at 400 ℃ while the CTAB containing mixture was calcined at 650 ℃ for 30minutes to remove volatile ingredients of AACH and CTAB.

The calcined mixture was uniaxially pressed under a load of $5x10^3$ Kg in a steel die to make pellets of 10mm diameter. The prepared green pellets were sintered at 1450 ℃ in air for 2 hours in a high temperature (Carbolite HTF-18/8) furnace. The density of the sintered pellets was measured using analytical grade ethanol following Archimedes principle.
The micro-hardness tester (Series 401MVD WOLPERT Group) was used to measure Vickers hardness of sintered pellets at room temperature. Four samples per composition and approximately 10-15 indents per measurement were made and the average hardness was calculated. The separation between the neighboring indents was kept more than 4 diagonal lengths of indentation impression as per ASTM standard of ASTM C 1327-99 [28]. For hardness testing, a load of 1Kg was applied for 15 seconds.

The microstructural study was carried out using JEOL JSM5910 scanning electron microscope (SEM) at 20 kV. The samples were then gold coated using SPI-Module sputter coater in order to avoid charging during exposure to electron beam. A Nicolet 6700 Fourier Transform Infrared Spectrometer (FTIR) was employed for the IR studies.

III. Results and Discussion

Fig. 1(a) shows the SEM micrograph of as-prepared AACH whiskers. Smooth surfaced whiskers with approximate diameter of 100~200nm can be observed. Some whiskers are slightly bent with needle like shape at the end. This bending is useful in enhancing the mechanical interlocking in the composite [29]. Fig. 1(b) shows the surface micrograph of the pellets sintered at 1450 ℃. Uniform grains of 300nm diameter are clearly visible. However, no whisker-like morphology is observed on surface of the sample. To clarify this discrepancy, the scanning electron microscopy was performed on the fractured surface.

Fig. 2(a-b) shows the SEM micrographs of the fractured surface showing the whisker-shaped protrusions (encircled on Fig. 2(b). In our earlier studies [30] we have shown through EDS analysis that these whisker-like protrusions have aluminum rich composition as compared to matrix and are basically Al_2O_3 whiskers. It may be concluded that whiskers retain their morphology even after sintering and thus produce whisker toughening effects by crack deflection and crack bridging resulting in increase in strength of the composite. Moreover, no agglomerates of whiskers were observed at any part of the sample containing 5wt% alumina whiskers and 1wt% CTAB. So the addition of CTAB has improved the dispersion of alumina in the matrix of TZ-3Y.

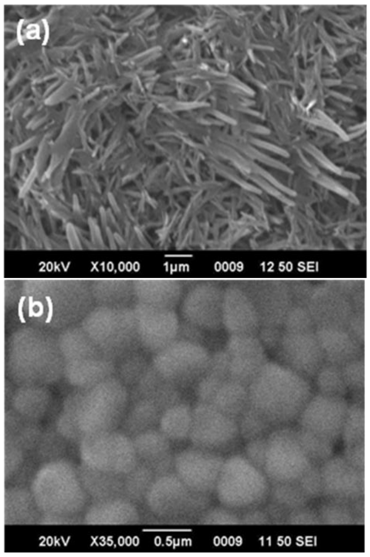

Fig. 1. SEM micrographs of (a) as prepared AACH whiskers; (b) sintered surface of sample with composition of 80wt% ZT-3Y + 5% Al2O3(w) + 15% Al2O3(n).

Fig. 3 shows the Fourier transform infrared spectroscopy of samples containing 20wt% alumina in the form of AACH ($NH_4Al(OH)_2CO_3$) before and after calcination. Most of the peaks correspond to AACH [31]. The peaks in the region $3173cm^{-1}$ and 1388 cm^{-1} are due to symmetric and asymmetric bond stretching of NH_4 of AACH. While the bands at 1382, 1444 and $1540cm^{-1}$ correspond to asymmetric stretching modes of CO_3^{-2} in AACH. However, after calcinations these peaks of NH_4 & CO_3^{-2} are eliminated. This means that volatile ingredients of AACH have been removed as a result of calcination.

Visually, the peaks of samples with and without CTAB have no clear difference. However, on magnifying the plot, a slight shift can be observed in some of the peaks of two types of samples. For example, the peak corresponding to O-H stretching appears at $3437cm^{-1}$ wavenumber. But with addition of 1wt% CTAB the peak shifts slightly to higher wavenumber of $3441cm^{-1}$ (Fig. 3(b)). This indicates that with the addition of surfactant or deflocculating agent (CTAB), the hydrophobicity of the particles and whiskers increases [32]. Otherwise one can say that CTAB has attached with particles or whiskers by replacing water molecules. As the CTAB is a cationic surfactant so it has produced the net positive charge on the particles and this results in increasing the inter-particle repulsion and hindrance in agglomerate formation and improvement in reinforcement dispersion. This conclusion is in good agreement with already reported work saying that zeta potential of Al_2O_3 particles increases with the addition of CTAB [33]. In general, electrostatic repulsive force between particles increases with the increase of zeta potential.

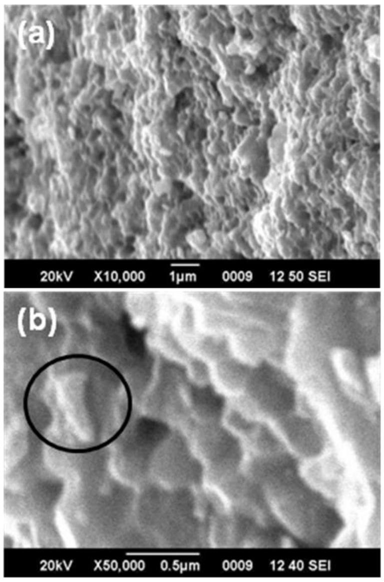

Fig. 2. SEM micrographs of fractured surface os sample with composition of 80wt% ZT-3Y + 5% Al2O3(w) + 15% Al2O3(n)

Fig. 4(a) shows the change in relative density with increase in the amount of alumina whiskers. For the composition of 5wt% $Al_2O_{3(w)}$+15wt% $Al_2O_{3(n)}$+80wt%TZ-3Y$_{(n)}$, relative densities of 94.3% and 93.3% were obtained for samples with and without 1wt% CTAB, respectively. This means that with the addition of CTAB the densification of composite is enhanced, which may be attributed to better dispersion of whiskers with the addition of CTAB. If the green compacts have good dispersion of reinforcement, it would result in uniform shrinkage during sintering and increase in the sintered density. Moreover, the increase in relative density with addition of CTAB is more pronounced at higher concentration of alumina whiskers. As at higher whisker concentrations the agglomeration is more severe, the effect of CTAB is also more prominent.

The effect of increase in proportion of alumina whisker on the hardness of composite is shown in Fig. 4(b). The maximum hardness is obtained for 5wt% $Al_2O_{3(w)}$+15wt% $Al_2O_{3(n)}$ composition, which is 14.29GPa and 13.65GPa for samples with and without 1wt% CTAB, respectively. These values are higher than already reported maximum hardness of 12.4GPa at concentration of 2.5wt% $Al_2O_{3(w)}$+17.5wt% $Al_2O_{3(n)}$ by Nevarez-Rascon *et al.* They used alumina whiskers of 1~2nm diameter. Due to smaller diameter, the surface energy of the whiskers was high resulting in the formation of hard agglomerates. These agglomerates created low density regions in the composite. The presence of these low density regions was responsible for decreasing the hardness of composites with increase in the whisker content beyond 2.5 wt%. But in the present case, whiskers used were of comparatively larger diameter, *i.e.*, of the order of 100nm which resulted in decreasing the agglomeration tendency and improvement in hardness. Moreover, the whiskers were added in the form of AACH which has comparatively better sorption properties and thus gives better dispersion than direct alumina [34].

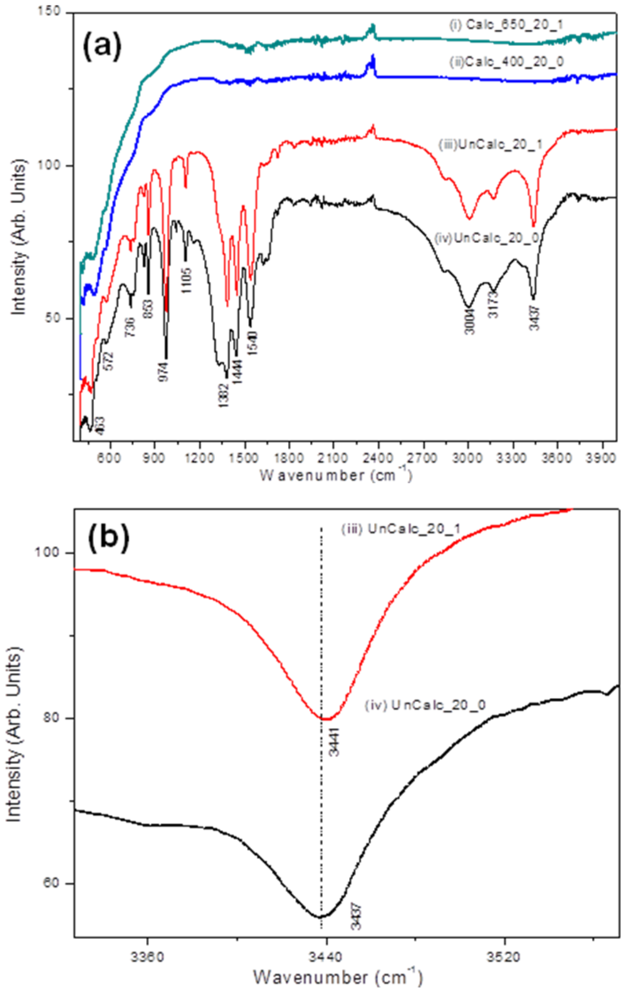

Fig. 3(a) FTIR spectrum for samples containing 20wt% alumina inform of AACH, with and without 1wt% CTAB, before and after calcinations. (i) AACH with CTAB calcined at 650 ℃ (ii) AACH without CTAB calcined at 400 ℃ (iii) AACH with CTAB uncalcined (iv) AACH without CTAB uncalcined. (b) magnification of the FTIR peak at wave number of 3437cm-1.

IV. Conclusions

1) With the addition of alumina whiskers, the hardness of alumina reinforced TZ-3Y nanocomposites increases. The whiskers retain their morphology even after sintering and improve the hardness of the composites by various whisker toughening effects.
2) The addition of CTAB also increased the sintered density and hardness of the composites. The maximum hardness obtained, *i.e.*, 14.29 GPa is higher than the already reported value of 12.4GPa for similar composites.

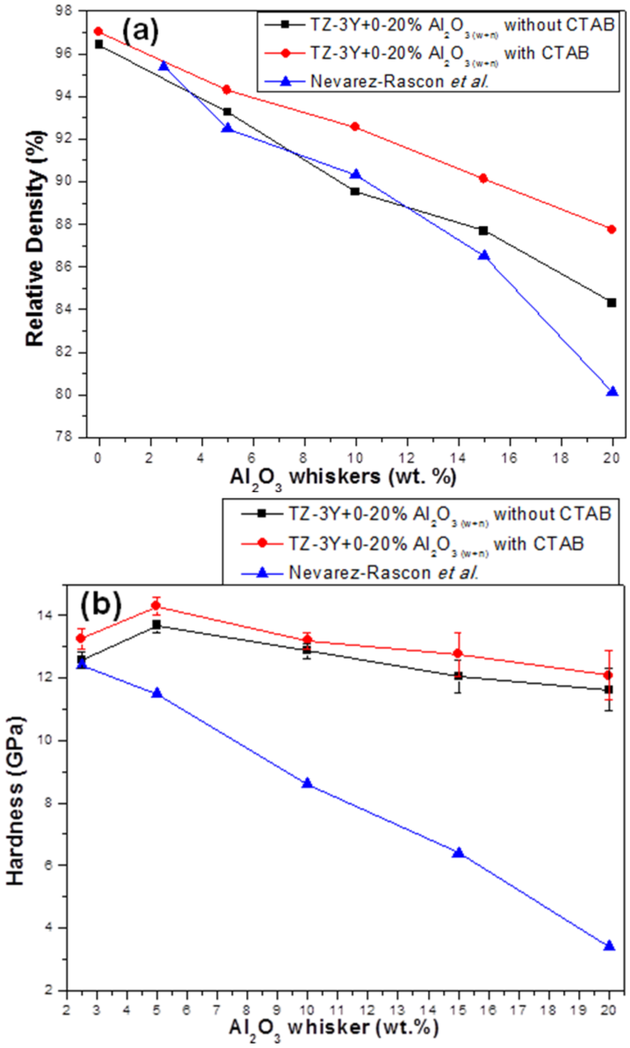

Fig. 4(a) Relative density and (b) Vickers hardness of 80%TZ-3Y+20%Al2O3(whisker + particles) with and without 1wt% CTAB.

ACKNOWLEDGMENT

Authors are thankful to the Higher Education Commission, Pakistan (HEC) for their financial support to conduct this research.

REFERENCES

[1] J. K. M. F. Daguano, et al., “Properties of ZrO_2-Al_2O_3 composite as a function of isothermal holding time,” *Int J Refract Met H*, vol. 25, pp. 374-379, 2007.

[2] R. C. Garvie, et al., “Ceramic steel?,” *Nature*, vol. 258, pp. 703-704, 1975.

[3] Y. Zhang, et al., “Pressureless-sintering behavior of nanocrystalline ZrO2–Y2O3–Al2O3 system,” *Mater Lett*, vol. 60, pp. 2302-2305, 2006.

[4] C. Santos, et al., “Effect of Al2O3 addition on the mechanical properties of biocompatible ZrO2-Al2O3 composites,” *Advanced Powder Technology V*. vol. 530-531, pp. 575-580, 2006.

[5] D. Nikolay, et al., “Manufacturing and properties of ZTA-ceramics with nanoscaled ZrO2,” *CFI-Ceram Forum Int*, vol. 83, pp. E35-37, Apr 2006.

[6] B. Lawn, *Fracture of brittle solids*, 2nd Edition ed. London: Cambridge University Press, 1993.

[7] H. H. K. Xu, et al., “Material removal and damage formation mechanisms in grinding silicon nitride,” *J Mater Res*, vol. 11, pp. 1717-1724, Jul 1996.

[8] H. Iwanaga and C. Kawai, “Tensile strength of silicon nitride whiskers synthesized by reacting amorphous silicon nitride and titanium dioxide,” *J Am Ceram Soc*, vol. 81, pp. 773-776, Mar 1998.

[9] H. H. K. Xu, et al., “Dental resin composites containing ceramic whiskers and precured glass ionomer particles,” *Dent Mater J*, vol. 16, pp. 356-363, 2000.

[10] D. H. Carter and G. F. Hurley, “Crack deflection as a toughening mechanism in SiC-whisker-reinforced MoSi2,” *J Am Ceram Soc*, vol. 70, pp. 79-81, 1987.

[11] H. Liu, et al., “Crack Deflection Process for Hot-Pressed Whisker-Reinforced Ceramic Composites,” *J Am Ceram Soc*, vol. 72, pp. 559-563, 1989.

[12] K. T. Faber and A. G. Evans, “Crack deflection processes--I. Theory,” *Acta Metallurgica*, vol. 31, pp. 565-576, 1983.

[13] M. Rühle, et al., “On the toughening of ceramics by whiskers,” *Scripta Metallurgica*, vol. 21, pp. 681-686, 1987.

[14] P. F. Becher, et al., “Toughening Behavior in Whisker-Reinforced Ceramic Matrix Composites,” *J Am Ceram Soc*, vol. 71, pp. 1050-1061, 1988.

[15] C. C. Lin, et al., “Microscopic mechanisms of oxidation in SiC-whisker-reinforced mullite/ZrO_2 matrix composites,” *J Am Ceram Soc*, vol. 82, pp. 2833-2840, Oct 1999.

[16] G. Y. Lin and T. C. Lei, "Microstructure, mechanical properties and thermal shock behaviour of Al_2O_3+ZrO_2+SiC_w composites," *Ceram Int*, vol. 24, pp. 313-326, 1998.

[17] G. Y. Lin, et al., “Microstructure and mechanical properties of SiC whisker reinforced ZrO2 (2 mol% Y2O3) based composites,” *Ceram. Int.*, vol. 22, pp. 199-205, 1996.

[18] G. Y. Lin, et al., “Microstructure and Mechanical-Properties 0f SiC Whisker-Reinforced ZrO_2-6mol-Percent-Y_2O_3 Composites,” *J Mater Sci Technol*, vol. 9, pp. 659-664, Aug 1993.

[19] G. Y. Lin, *et al.*, "Mechanical-Properties of Al_2O_3 and Al_2O_3+ZrO_2 Ceramics Reinforced by SiC Whiskers," *J Mater Sci*, vol. 28, pp. 2745-2749, May 1993.

[20] A. Zangvil, *et al.*, "Microstructural Studies in Alkoxide-Derived Mullite Zirconia Silicon-Carbide Whisker Composites," *J Am Ceram Soc*, vol. 75, pp. 1254-1263, May 1992.

[21] M. Abdullah, et al., “Effect of Sintering Temperature on Properties of Al_2O_3 Whisker Reinforced Yttria-Stabilized-Zirconia (TZ-3Y) Nanocomposites,” *Compos Part B-Eng*, vol. 43, pp. 1785-1790, 2012.

[22] M. Abdullah, et al., “Synthesis of Al_2O_3 whisker-reinforced yttria-stabilized-zirconia (YSZ) nanocomposites through in situ formation of alumina whiskers,” *Ceram Int*, vol. 37, pp. 2621-2624, 2011.

[23] M. Abdullah, et al., “Effect of deflocculants on hardness and densification of YSZ–Al_2O_3 (whiskers & particulates) composites,” *Compos Part B-Eng*, vol. 43, pp. 1564–1569, 2011.

[24] M. Abdullah, et al., “Single Step Hydrothermal Synthesis of 3D Urchin like Structures of AACH and Aluminum Oxide with Thin Nano-Spikes,” *Ceram Int*, vol. 38, pp. 3741-3745, 2012.

[25] A. Nevarez-Rascon, et al., “$Al_2O_{3(w)}$-$Al_2O_{3(n)}$-ZrO_2 (TZ-3Y)$_n$ multi-scale nanocomposite: An alternative for different dental applications?,” *Acta Biomater*, vol. 6, pp. 563-570, 2010.

[26] K. Tsukuma, et al., “Strength and Fracture-Toughness of Isostatically Hot-Pressed Composites of Al2O3 and Y2O3-Partially-Stabilized ZrO2,” *J. Am. Ceram. Soc.*, vol. 68, pp. C4-C5, 1985.

[27] J. Li, et al., “Synthesis and formation of alumina whiskers from hydrothermal solution,” *J Mater Sci*, vol. 45, pp. 177-181, 2010.

[28] ASTM.org, *Standard test method for vickers indentation hardness of advanced ceramics*, Philadelphia, PA,: West Conshohocken, PA, 1991.

[29] H. H. K. Xu and J. B. Quinn, “Effect of silicon carbide whisker-silica heat treatment on the reinforcement of dental resin composites,” *J Biomed Mater Res*, vol. 58, pp. 81-87, 2001.

[30] M. Abdullah, et al., “Influence of Al_2O_3 Whisker Concentration on Flexural Strength of $Al_2O_{3(w)}$-ZrO_2 (TZ-3Y) Composite,” *Ceram Int*, vol. Article in Press, 2012.

[31] Z. Zhu, *et al.*, "PEG-directed hydrothermal synthesis of alumina nanorods with mesoporous structure via AACH nanorod precursors," *J Mater Sci*, vol. 45, pp. 46-50, 2010.

[32] W. Xue, et al., “FTIR investigation of CTAB-Al-montmorillonite complexes,” *Spectrochim Acta A*, vol. 67, pp. 1030-1036, 2007.

[33] L. Chen, et al., “Effect of surfactant on the electrodeposition and wear resistance of Ni-Al_2O_3 composite coatings,” *Mater Sci Eng: A*, vol. 434, pp. 319-325, 2006.

[34] J. Corrochano, et al., “Whiskers of Al_2O_3 as reinforcement of a powder metallurgical 6061 aluminium matrix composite,” *Mater Lett*, vol. 62, pp. 103-105, 2008.