Structural and Mechanical Properties Al_2O_3-ZrO_2 Dental Bioceramics

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Abstract- Alumina (Al_2O_3) and Zirconia (ZrO_2) was introduced as a ceramic material for implant abutments because of its superior mechanical properties. With this introduction, a composite ZrO_2 toughened Al_2O_3 (ZTA) is widely used as ceramic abutment. In the present study, samples of Al_2O_3 with varied ZrO_2 (10-40 wt %) were prepared. Samples were sintered at temperature 1550, 1600 and 1650 °C for 2 hours. The density, porosity, structural properties and mechanical properties of Al_2O_3- ZrO_2 composites with respect to ZrO_2 content as well as sintering temperature have been explored in the present work. About 22% higher density of ZTA composite has been achieved and the microstructures are highly homogeneous and finer with less porosity when compared to pure Al_2O_3. For pure Al_2O_3 the microhardness number is in the range 18-24 GPa while the decreasing of hardness value has been observed with the addition of ZrO_2 content. The lower hardness values imply that this system can achieve higher fracture toughness as it is known that fracture toughness and microhardness number has an inverse relation. The approach adopted in the present study may provide an alternative to design Al_2O_3 - ZrO_2 composites with improved mechanical properties.

Index terms- Alumina, Zirconia, composite, toughened, sintering, porosity, hardness, microstructures

1. Introduction

Biomaterials used to replace part of a living system or to function in intimate contact with living tissue have made a revolution in medical application as well as research area. Materials which are to be implanted into the human body are subjected to an environment which is both hostile and at the same time extremely sensitive. There is a crucial fact that the body's tissues are extremely sensitive to foreign material and are very easily stimulated into showing signs of poisoning and rejection. Thus, the success of an implant in the body depends on several factors, such as the materials properties, the design, the biocompatibility as well as other factors out of engineer control, including the technique used by the surgeon, the health of the patient, and his activities. Bioceramics have become an accepted group of materials for medical applications, mainly for implants in orthopaedics, maxillofacial surgery and for dental implants.

Dental bioceramics are very attractive because of their biocompatibility, long term color stability i.e. their aesthetics and their ability to be formed into precise shapes. The most widely used dental bioceramics materials are Alumina (Al_2O_3) and Zirconia (ZrO_2), because of their excellent biocompatibility as well as suitable mechanical properties. [**1**]

Al_2O_3 is one of the more widely used and studied advances ceramic materials. Using pure Al_2O_3 in dental application, one of drawbacks is that it exhibits low flexural strength and toughness. [**1**] There are many ways to overcome this weakness, including making it as composite materials. Composite means consisting of two or more distinct parts or phases. Addition of ZrO_2 to Al_2O_3 allows to receive ZrO_2 toughened Al_2O_3 (ZTA) ceramics, in which the strength and toughness have been improved due to stress induced tetragonal-monoclinic transformation. ZrO_2 is inert in physiological environment, presents greater flexural resistance and toughness and lower Young's modulus when compared with pure Al_2O_3.. It is generally known that Al_2O_3 – ZrO_2 composites have better mechanical properties than Al_2O_3 and ZrO_2 because of the dispersion of metastable tetragonal zirconia particles in the alumina matrix, which transform into the stable monoclinic phase under loading. The properties of these materials are determined by their microstructures; therefore, to control their microstructural development and to achieve fine microstructures, the sintering parameters must be optimized. Since both Al_2O_3 and ZrO_2 are biocompatible, this could prove to be a new approach to dental abutments.

The objective of the present work was to analyze the physical, structural and mechanical properties of Al_2O_3-ZrO_2 composites prepared by solid state technique where ZrO_2 content has been varied. To do so, density, porosity, elastic modulus, structural properties and mechanical properties of Al_2O_3-ZrO_2 composites with respect to ZrO_2 content as well as sintering temperature (T_S) have been explored.

2. Materials & Methods

2.1 This study was conducted in the department of Physics at Bangladesh University of Engineering & Technology during the period of 2008-2012.

2.2 Experimental Procedure:

The starting materials, powders of Al_2O_3 and ZrO_2 with purity 99.6% and 99.9% respectively were used in this work. Powders of Al_2O_3 and ZrO_2 were collected from Material Science Division of Bangladesh Atomic Energy Commission, Dhaka, Bangladesh. The average particle size was 150nm for Al_2O_3 and 30-60 nm for ZrO_2. Different compositions had been prepared by varying ZrO_2 from 0 to 40 wt. %. Thus four composites with 10, 20, 30 and 40 wt.% of ZrO_2 were prepared. A pure Al_2O_3 sample was also prepared to compare its properties with those of ZTA composites. In doing so, dry mixing for 05(Five) hours was carried out to obtain a homogeneous distribution and after that wet milling was carried out for 12 hours in pure acetone media in a motor driven ball mill. The green body (bulk sample) in the form of tablet of about 10 mm in diameter dimension was prepared by uniaxial compaction procedure. Polyvinyl alcohol (PVA) was used as a binder. The green body was sintered at low temperature to burn off the binder at 950 ^{0}C with heating rate 6 ^{0}C/min. Finally, the samples were sintered with a microprocessor controlled muffle furnace at temperatures 1550, 1600 and 1650 °C for two hours.

The bulk density (ρ) of the sintered sample was calculated from the ratio weight/volume and the theoretical density (ϱ_0) was calculated from the actual density of the starting powders and their weight percentages using the rule of mixtures. The percentage of total porosity φ was calculated from the ρ and ϱ_0 according to the standard formula **[2]**:

$$\varphi = \left(1 - \frac{\rho}{\rho_0}\right) \times 100 \quad \text{.....(1)}$$

To analyze the microstructure, Scanning Electron Microscopes (SEM) of model Philips XL-30, was used.

Identification of sintered sample phases was carried out by X-Ray Diffraction (XRD) technique using X-ray diffractometer of model: D8 ADVANCE, BRUKER, Germany. The data was collected on the 2θ range from 20° to 85° with a step of 0.02^0 and 0.6 sec of exposure time per position.

The microhardness was determined by using Vickers microhardness tester of model HMV 2, Shimadzu Corporation using an applied load of 2 kg for 6 sec. Vickers microhardness can be measured using the following formula **[1,3]**:

$$H_V = 0.0018544 \times \left(F \big/ d^2\right) \text{.....(2)}$$

Where,
H_v = Vickers microhardness (GPa)
F = Applied load (N)
d = Arithmetic mean of the two diagonal length of the indentations (mm).

3. Result and discussion

3.1 Density

In presence of ZrO_2 resulted in a continuous increase in density and denser structure (Fig.1). This can be described in the term of the density of each component. The density of ZrO_2 is around 6.58 g/cm^{-3} whereas that of Al_2O_3 is 3.97 g/cm^{-3}, therefore the effective density values of the alumina-zirconia rise with increasing ZrO_2 content and a compact structure is formed. It has also been observed that with the increase of sintering temperature (T_s), density was increased slightly. About 2-3% of density increases with 100°C increase in T_s. In this work about 97% of theoretical density calculated from rule of mixture was achieved for pure Al_2O_3 and 97-98% of theoretical density was achieved for ZTA sintered at 1650 °C for 2 hours. The density value conforms to some previous works those used pressure less sintering technique **[4-6].** The optimum density was also achieved for ZTA sintered at 1650 °C. Density of ZTA containing 40 wt% ZrO_2 was 22% higher than pure Al_2O_3. This is caused by the lowering of t-ZrO2 phase at higher content of ZrO2. The decrease in t-ZrO2 phase or simultaneous increase in m-ZrO2 phase may be explained by a rapid

increase in grain size of zirconia particles. However, the very fast grain growth rate has a detrimental effect on the density, since pore coalescence in alumina matrix and segregation of zirconia particles takes place [12].

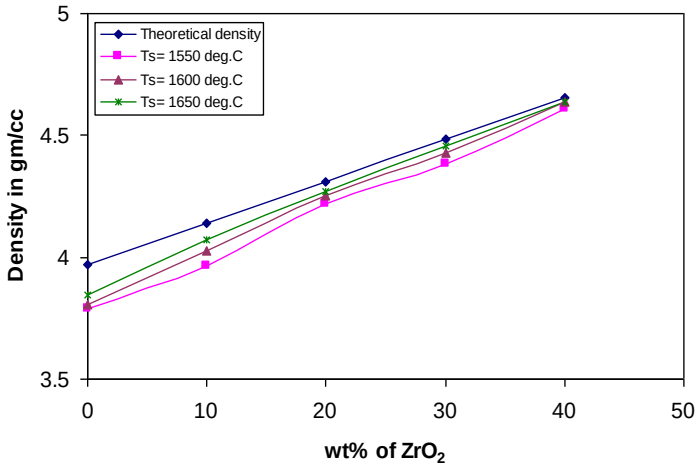


Fig 1: Effect of ZrO_2 content on density of ZTA ceramics

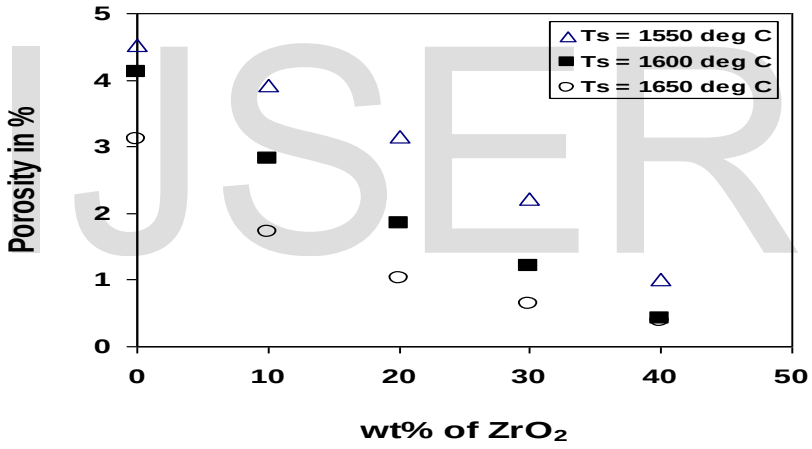


Fig 2: Effect of ZrO_2 content on porosity of ZTA ceramics

The densification process can also be described from the calculated result of porosity. It is observed that the porosity is decreased as ZrO_2 content as well as T_s increases (Fig.2). Due to the diffusion process during sintering, the pores of composite diminish or even close by the introduction of defects, resulting in reduction of porosity, improvement of densification of the composite as well as its mechanical properties. That is why the composite becomes more homogeneous with less porosity at higher T_s and also with the increased ZrO_2 content.

3.2 Microstructure

The influence of microstructure uniformity on mechanical properties has a great importance. From microstructures at different sintering temperatures (Fig.3) it can be observed that the microstructures are highly homogeneous without agglomerates, pores or abnormally grown alumina grains.

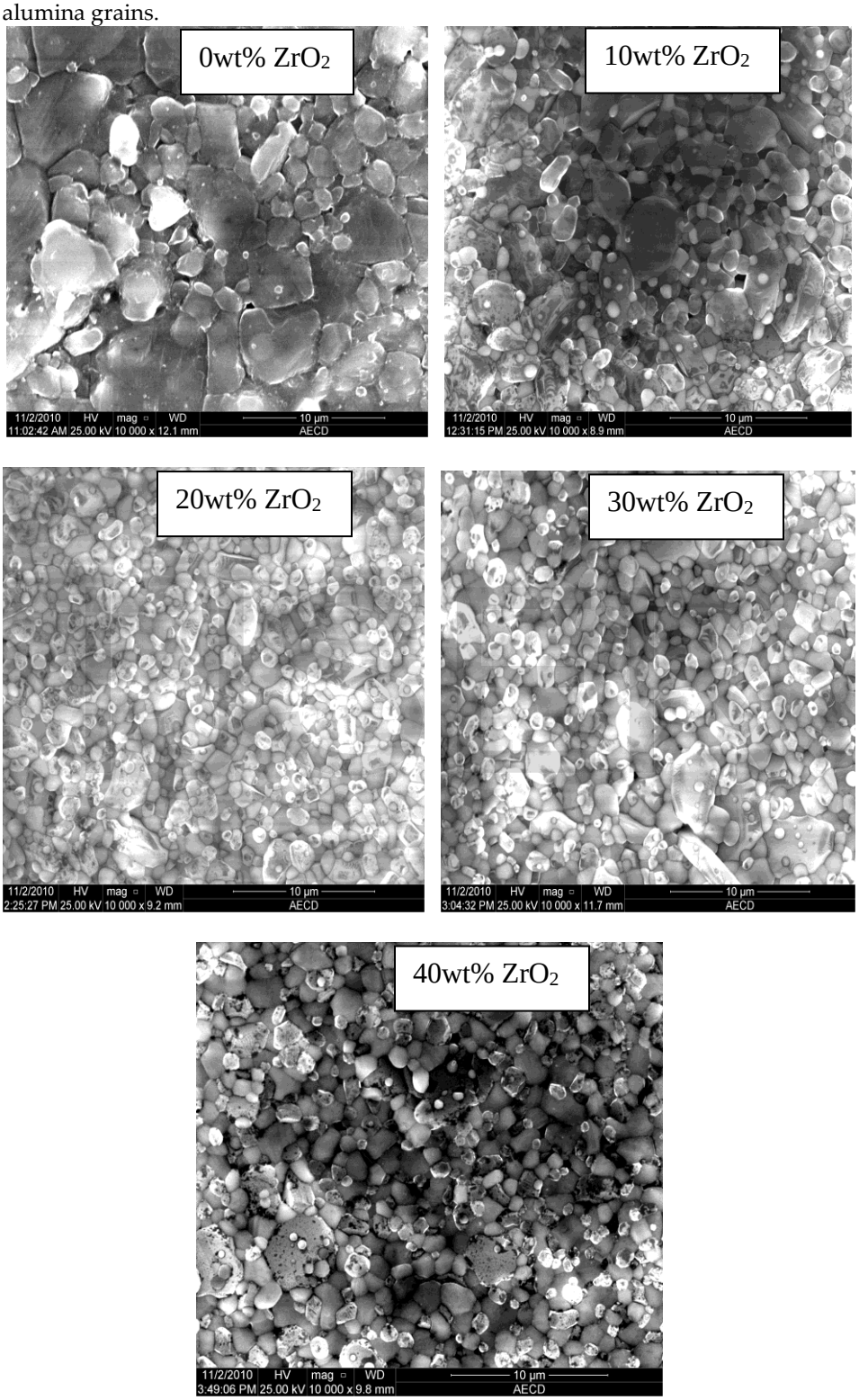


Fig.3: Microstructure of Al_2O_3 - ZrO_2 Composite sintered at T_s = 1600 ^{0}C

It is observed that the microstructures become highly homogeneous and finer at higher sintering temperature. It can also be observed that the grain sizes of ZrO_2 increase and hinders the grain growth of Al_2O_3 at 1650 ^{0}C compared to that at 1600 ^{0}C, which

contributes to the lowering of porosity (Fig.4). A fine grain size and refined microstructure are necessary for improved mechanical properties especially for wear resistance of dental implant.

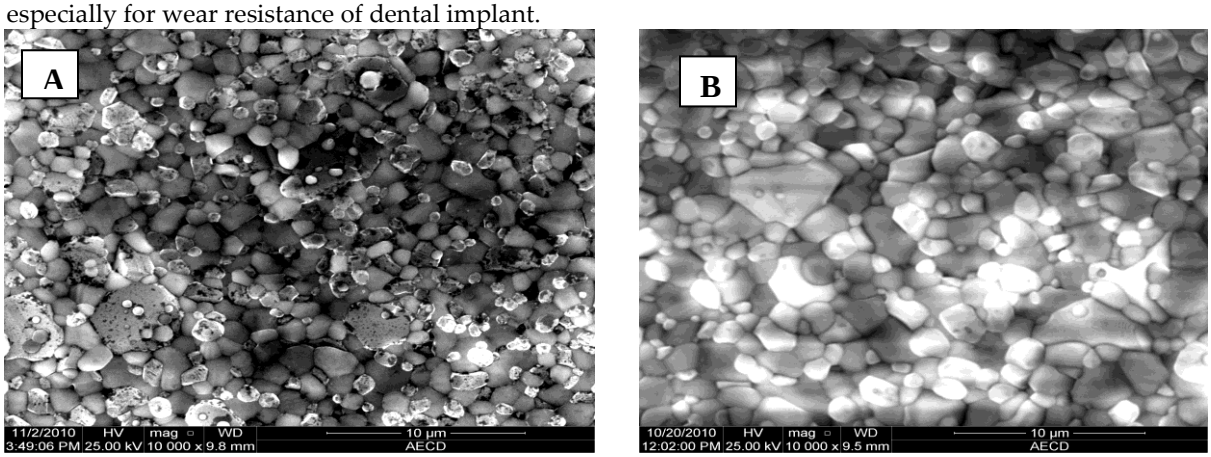


Fig. 4: ZTA composite with 40 wt% ZrO_2 at T_S = 1600 ^{0}C (A) and ZTA at T_S = 1650 ^{0}C (B)

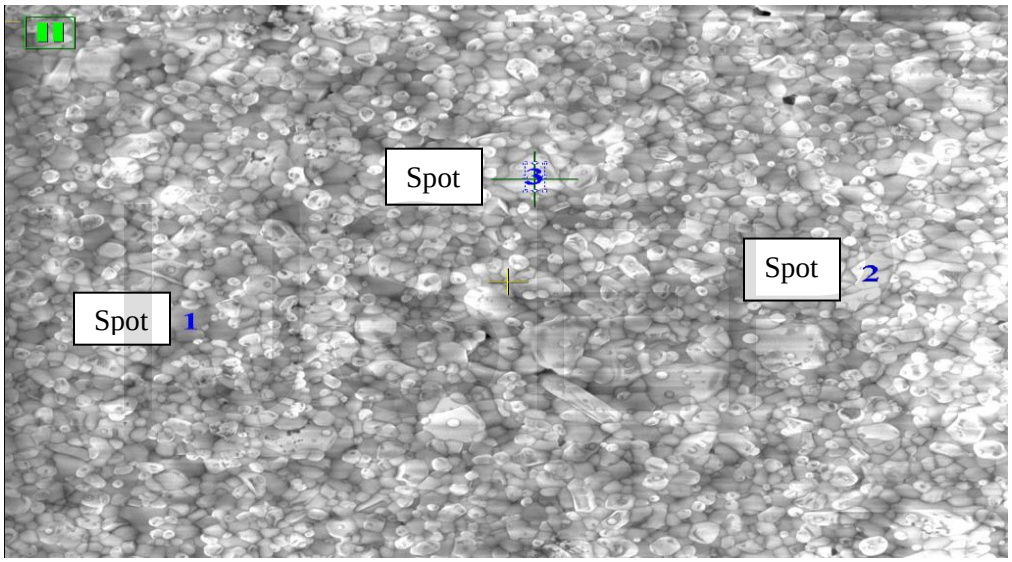
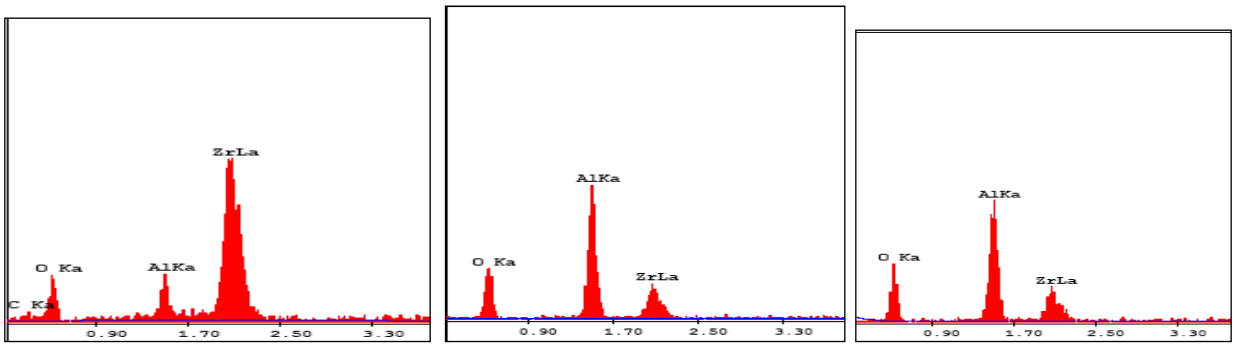


Fig. 5.1: SEM Micrograph for EDX analysis of ZTA composite (70% Al_2O_3 + 30% ZrO_2) sintered at 1600 ^{0}C



Spot-1 **Spot-2** **Spot-3**

Fig. 5.2: EDX analysis of ZTA composite (70% Al_2O_3 + 30% ZrO_2) sintered at 1600 ^{0}C

From EDX analysis shown in fig. 5.1 & 5.2 it is confirmed that the dark areas represent ZrO_2 while white areas indicate Al_2O_3 matrix. Therefore from fig. 3, it can also be observed that ZrO_2 particles are uniformly dispersed throughout the alumina matrix. As the amount of ZrO_2 content increases, the Al_2O_3 grain size decreases significantly. The ZrO_2 phase creates a pinning effect around Al_2O_3 grain and obstructs its growth. ZrO_2 has quite small grain. When ZrO_2 is added with Al_2O_3, evenly distributed fine

ZrO_2 grains act as grain refiner and led to smaller Al_2O_3 grains. This is possibly increases density as well as enhances mechanical properties.

3.3 X-Ray Diffraction Analysis

XRD analysis of the samples indicated that only α-Al_2O_3, t and m- ZrO_2 are the crystalline phases present in both the pure Al_2O_3 and in the ZTA composites, Fig. 6(a). It is observed that with the increase of ZrO_2 content the m- ZrO_2 phase increases and the t-ZrO_2 phase decreases. However, t- ZrO_2 retention becomes much easier to trigger the transformation to monoclinic. As a result, its contribution to transformation toughening predominates. The extent of toughening achieved in this composite depend on the particle size of Al_2O_3 and ZrO_2, volume fraction of ZrO_2 retained in the metastable tetragonal phase as well as on the relative distribution of Al_2O_3 and ZrO_2 in the matrix **[7].** Finer particle size of both Al_2O_3 and ZrO_2 will not only enhance the chances of a uniform Al_2O_3 and ZrO_2 distribution, it also increases the possibility of ZrO_2 being retained as metastable tetragonal phase [**8**].

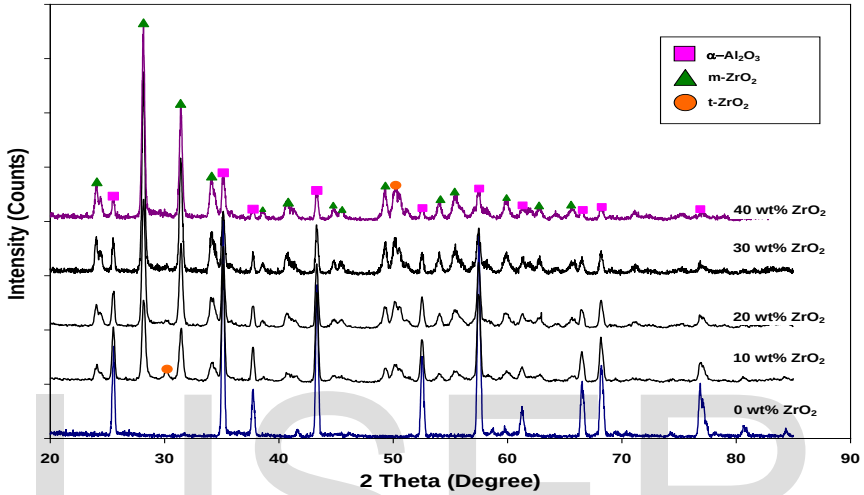


Fig.6(a) XRD pattern of ZTA ceramics containing different vol.% ZrO_2 and sintered at 1600 °C for 02 hours investigated in present work

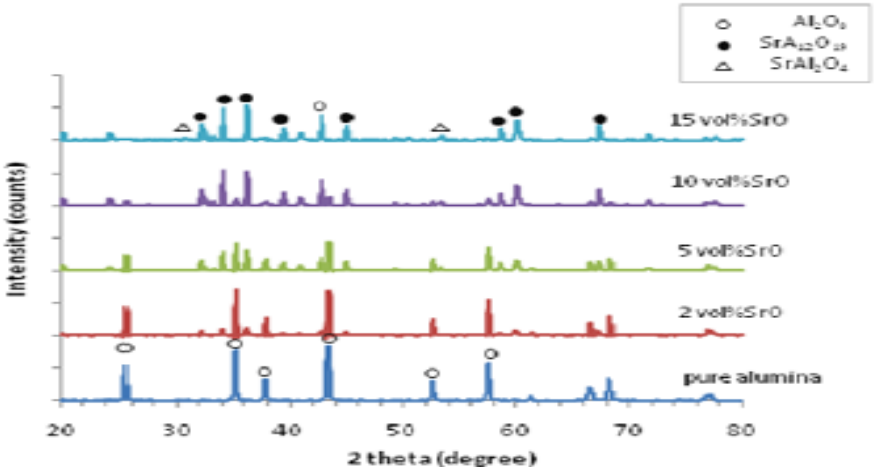


Fig.6(b) Some standard XRD patterns found in the works of some researchers **[6]**

The XRD patterns of present study were also compared with some standard patterns found in the works of some researchers, Fig. 6(b) **[6].** From this earlier work, it was observed that a characteristic sharp peak of tetragonal zirconia was found in the XRD patterns at $2\theta = 30°$. This peak is also found in the present work, Figs 6(a) but with the increase of ZrO_2 content, this peak is diminished. So it can be said that tetragonal phase is indeed retained at the room temperature as a metastable phase due to the presence of the hard alumina matrix around, and this phase is responsible for fracture toughness improvement by transformation toughening mechanism.

In earlier works it was also described that in Al_2O_3–ZrO_2 composites, the tetragonal phase was stable at room temperature only if the ZrO_2 grain size lies between two critical values (from about 0.1 μm up to 0.5 μm), which depend on strains in the Al_2O_3 matrix and on the amount of ZrO_2 **[9]**. The fraction of tetragonal phase increases when the quantity of ZrO_2 decreases (30% of tetragonal phase for 5 vol.% of ZrO_2, but only 5% of tetragonal phase for 20 vol.% of ZrO_2) **[10, 11].**

3.4 Microhardness

As it is observed from micrographs that the grain size is increased with T_S, it can be concluded that higher sintering temperature gives lower hardness values (Fig. 7a). It has been noticed that the investigated ZTA composites obey Hall–Petch relationship which states that microhardness decreases with increasing particle size.

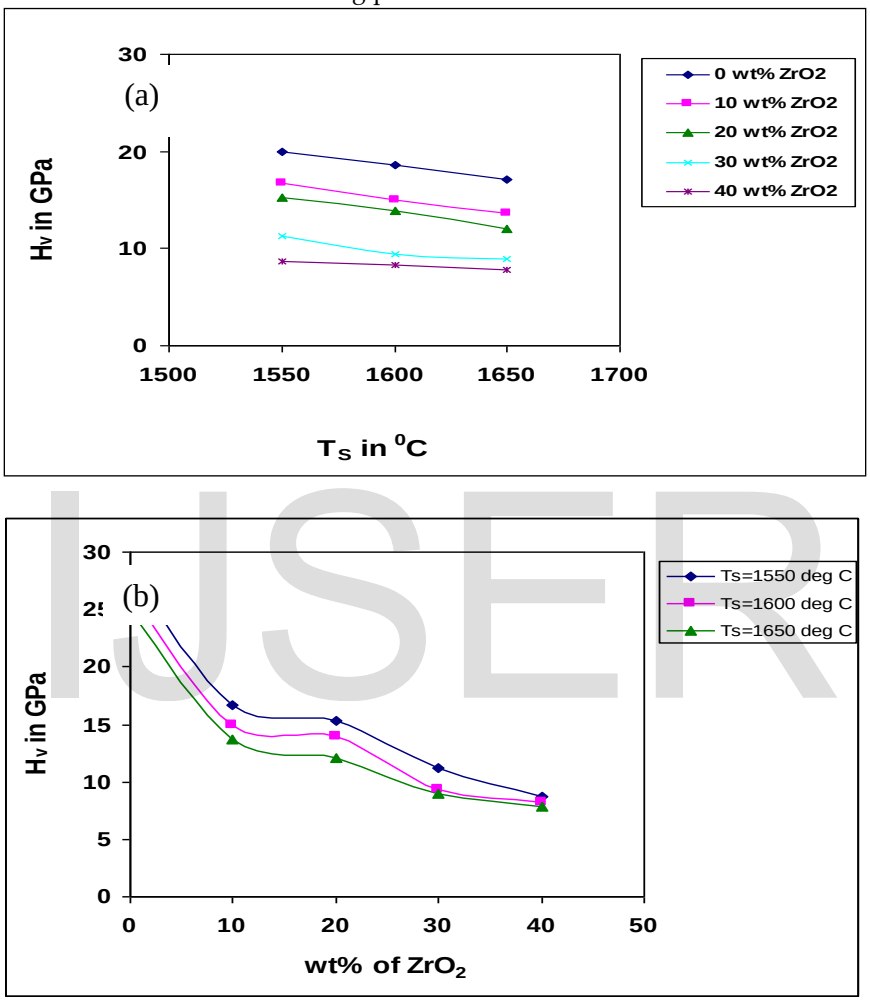


Fig. 7: Effect of sintering temperature (T_S) on hardness of ZTA composite (a) Effect of ZrO_2 content on hardness of ZTA ceramics (b)

Moreover, the microhardness of the ZTA composite decreases with the addition of ZrO_2 shown in Fig. 7 (b) as Al_2O_3 is harder than ZrO_2. Higher amount of ZrO_2 has an adverse effect on the microhardness of the composites due to coarsening of the ZrO_2 grains and formation of subsequent porosity. However, below a critical grain-size, hardness decreases with decreasing grain size. This is known as the inverse Hall-Petch effect.

4. Conclusions

A variation in physical and mechanical properties of Al_2O_3 with the addition of ZrO_2 has been focused in the present work. The analysis has shown that the addition of ZrO_2 promotes composites with higher densities. So a greater strength of Al_2O_3 can be achieved by using proper amount of ZrO_2 with Al_2O_3. ZrO_2 grains acted as grain refiner which is necessary for improved mechanical properties especially for wear resistance of dental implant. Partially stabilized ZrO_2 shown in XRD analysis can enhance toughness of composite via phase transformation mechanism. These composites seem to be an adequate material to be

used in the manufacture of implant abutments instead of the pure oxides actually in use. The relatively lower microhardness values can be suitable for ceramic abutments in the attainment of their final form by machining. The approach adopted in the present study may provide an alternative to design Al_2O_3- ZrO_2 composites with improved mechanical properties.

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