NEW TRENDS IN CERAMIC PROCESSING FOR ARMOR APPLICATIONS

By

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Abstract*:*

Advanced technology efforts towards the development and processing of light weight armor material fitted for personnel protection lead to toughned ceramic materials. Zirconia Toughened Alumina (ZTA) (Al2O3 5 % wt. Y-PSZ reinforced with 10 % wt. of SiC particulates) ceramic matrix composite has been characterized with respect to its densification, room temperature mechanical properties, phase composition and microstructure.

It was found that the composite could be densified at a temperature as low as 1575 ^{o}C by liquid phase sintering. A bending strength of 120 MPa was obtained for 75 % wt. Al_2O_3 , 10 % wt. ZrO_2, 10 % wt. SiC, 5% wt. Y_2O_3 and 1% add on weight MgO composite. Lower sintering temperature was beneficial to the retention of tetragonal ZrO_2 phase at room temperature. The results indicate that liquid phase sintering has a potential advantage in the fabrication cost and room temperature mechanical properties.

A complete protection against 7.62x39 AP (armor piercing projectile) with muzule velocity 740 m/sec was achieved using the above composite with area density 48 kg/m^2, this area density enable this composite to replace armored steel in bothe personnel and light armored vehicles.

Keywords:

Zirconia Toughned Alumina, ZTA, ceramic matrix composite (CMCs), ceramic armor materials, phase transformation toughning mechanisms, phase composition and microstructure.

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1. Introduction*:*

Demand for ceramic armor has spurred innovation in material processing and new material development. Ceramics ,oxide and non-oxide ,offer improved ballistic defense performance relative to melals,particularly where weight saving is desired or necessary [1].

A variety of ceramic materials,oxide, and non-oxide, are currently being manufactured for incorporation into armor systems. The more popular materials are boron carbide (B_4C), tungsten carbide(WC), titanuim diboride(TiB_2), alumina(Al_2O_3), SiC and composites of two or more of these materials[1].

Alumina is one of the most readily available and cost-effective materials. Aluminum oxide possesses strong ionic interatomic bonding giving rise to its desirable material characteristics. However , it has weak points for the bending strength, the fracture toughness and the heat-resistance limit temperature. These weak points restrict their application for structural components [2]. To overcome these weaknesses, there are three methods: toughening with fibers or particles despersion and microstructure control, detection and repair of crack after non-detection testing and inducing a self-crack- healing ability[1,3-5].

Phase transformation strengthening is a traditional and effective method, which utilzes the transformation of metastable tetragonal zirconia from tetragonal phase to monoclinic one by inducing stress to improve alumina ceramics fracture toughness due to formation of unelastic distortion areas around cracking tips[7-8]. The ability of zirconia particles dispersed in an aluminum matrix to undergo the tetragonal to monoclinic (t-m) martensitic phase transformation under an applied load and / or thermal stress is considered to be the basis of the improved mechanical properties induced in zirconia-toughned alumina(ZTA) composites [7].

Deng, et.al [9] investigated the effects of ZrO_2 doping on the fracture mode and toughness of Al_2O_3- 5 vol % SiC composite. They stated that ZrO_2 doping led to a weak Al_2O_3 boundary bonding and an increase in the bodies fracture toughness. Fan, et.al [10] prepared in -situ rod – like Al_2O_3 grains by addition CaO- Al_2O_3-SiO_2(CAS) additives to alumina ceramics containing 3Y-TZP,TiO2 and MgO. They showed that the in –situ rod-like grains,improve Al_2O_3 ceramics mechanical properties. It extends the phase transformation toughening path and prompt the increasing of martensite quantity.

On the other hand, since the pioneer work of Niihara[11], Al_2O_3 –SiC composites have received considerable attention . Research results have shown that the strength increases considerably with the addition of SiC particles to Al_2O_3, but the fracture toughness increases only modestly. Niihara [11] proposed that the intraganular vs intergranular location of the reinforcement phase impacts the mechanical properties by affecting the local tensile and compressive stresses at the boundary between the two phases. For particulate composites with the most improved properties, the authors stated that most of the SiC phase is located within Al_2O_3 grains. Niihara [11] later classified these composites as intragrain type to reflect the unique ditribution of the second phase.   Wang and R.

Steven[12]have found that MgO, as a sintering additive , is important in improving densification and controlling the microstructure of Al2O3-SiC composites.

The objective of the present study is to determine the effect of substituting Al_2O_3 (in the Al_2O_3 -10 wt. % SiC composites) by up to 20 wt.% ZrO_2 on the densification behaviour of the composites, as well as their phase composition , microstructure and mechanical properties.

2. Materials and methods:

2.1.Materials:

The materials used in this study are : α- alumina,silicon carbide, partially stabilized ZrO_2 (TZ-3Y, Tososh corporation, Japan) powders and chemically pure $Y_2O_3$and MgO.

a) Batch formulation

The compositions of different mixes are shown in table 1.

Table 1 Different Batches composition.

Batch No.	Al_2O_3 %	ZrO_2 %	SiC %	Y_2O_3 %	MgO (gm add on weight)
1	85	0	10	5	1
2	80	5	10	5	1
3	75	10	10	5	1
4	70	15	10	5	1
5	65	20	10	5	1

b) Forming of ceramic composite specimens:

The powder mixtures were pressed into discs of 15 mm diameter and 5 mm thickness and beams of 10x35x7 mm using uniaxial press at 60 Mpa.

c) Sintering of ceramic composite specimens:

Four complete sets of all composition were fired between 1500 ^{o}C -1600 ^{o}C one by one with 25 ^{o}C intervals. The temperature of the samples was raised at a rate of 5 ^{o}C/min, followed by 1h   soaking (holding) time at the peak temperature, then cooled down to room temperature. Figure (1) shows the heat treatment cycle of the samples.
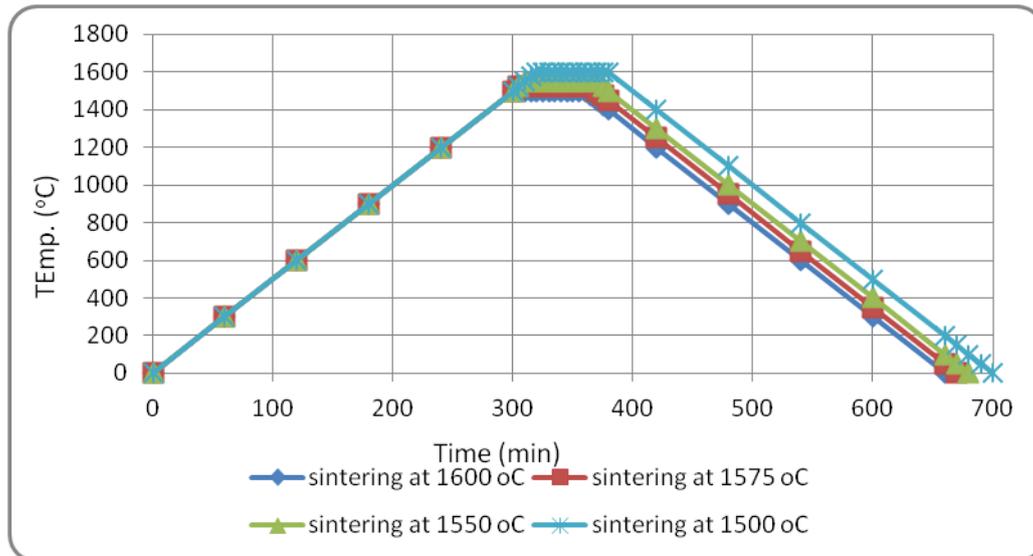
Figure (1): Sintering *cycles of different ceramic composites batches.*

2.2.Characterizatio:

In the present work, material characterization was conducted to evaluate the physical and mechanical properties of the ceramic composite specimens. The results obtained from physical properties tests of ceramic composite specimens are considered as preliminary investigations for selection of the ceramic composite specimens for phase composition, microstructure examination, and mechanical properties evaluation.

-The bulk density and the apparent porosity of the fired ceramic composites were tested according to the ASTM specification C373 (ASTM C373 1999).

-The different phases developed during firing were identified by X-ray analysis (XRD)using Siemens apparatus type D500 with a Cu target and Ni filter.

-Microstructure of selected fracture surfaces was examined using Philips XL 30 SEM apparatus.

-Three–point bending test was carried out to determine the flexural bending strength of the manufactured composites according to ASTM C1161 (1990).

-Hardness was measured by means of Vickers indentation method by using micro hardness tester (Model HVS-50, Laizhou Huayin Testing Instrument Co., Ltd. China) with a Vickers diamond indenter and a 20X objective lens, according to ASTM C1327-97 (1996).

3. Results and discussions:
3.1. Effect of Zirconia content on the composites physical properties:

The vitrification parameters of the studied composites in terms of bulk density and apparent porosity as functions of firing temperature and zirconia content were studied. Figures 2 and 3 illustrate the vitrification parameters of the samples fired at 1500 ^{o} up to 1600 ^{o}C for 1 hr. As the firing temperature increases from 1500 ^{o}C up to1600 ^{o}C, the bulk density is sharply increased. On firing at 1575 ^{o}C the samples reached about 95% of their theoretical density values. Further increase in the firing temperature decreases the density to reach about 93% of its theoritical density value. On the other hand the apparent porosity decreases with increasing the sintering temperature and reaches its minimum value (about 0.1 %) at 1575 ^{o}C. From the study of the two figures 2 and 3, it was found that the optimum sintering temperature was 1575 ^{o}C where the porosity was minimum and density more close to the theoritical value specially for 10% zirconia composition.

The results show that the increase in the ZrO_2 content increases the bulk density, figure 2. Such increase is related to the zirconia density (ZrO_2 theoretical density 5.6 gm/cm3). We believe that the bodies were densified at relatively low temperature, 1575 ^oC, due to the the presence of MgO, which acts as a fluxing agent [15]. It has been observed that in case of MgO- containing samples the reaction rate is high.

The decrease in sample density with firing temperature above 1575 ^oC, may be due to glass formation in the Al_2O_3, Y_2O_3, SiC system. At high temperature Y_2O_3 might dissolve into the glass and the glass content would increase.A small amount of glass promoted the composites densification, but more glass lead to a decrease in density, since glass usually has a lower density than solid crystals [13].
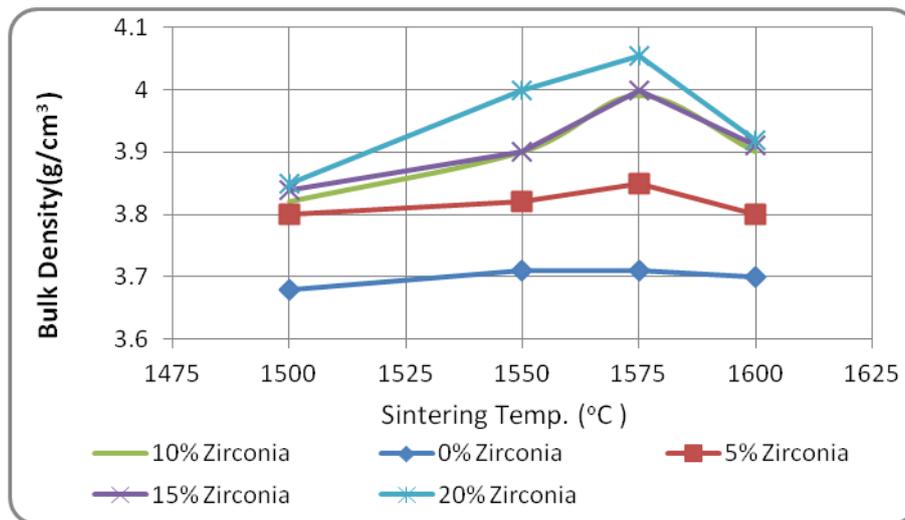

Figure (2): Bulk density of ceramic composites,fired at different firing temperatures.

The formation of a glassy phase prompts the growth of Al_2O_3 grains and increases the relative density of the materials. But too much glassy phase formed when ZrO_2 content increases can lead to the formation of big size grains. This hampers the flow of liquid phase. With the grains growing and macrocrystals increasing, the interlayering and bridging of the grains increase, which results in more vacancies associated with further increase in porosity and reduction in density. Figure (3) shows the effect of firing temperature on apparent porosity.
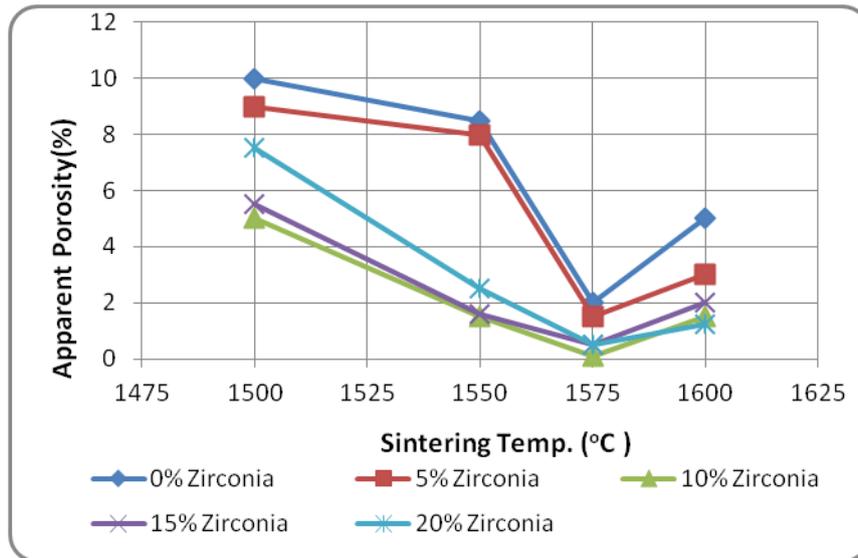
Figure (3): Apparent porosity of ceramic composites fired at different firing temperatures.

3.2.Phase composition test results:

Figure (4) shows the plots of XRD spectra of the sintered composite bodies. The crystalline phases content vary with batch composition, Corundum, t-ZrO_2, m-ZrO_2, SiC and SiC-2H were detected in the samples containing ZrO_2 . The two strongest m-ZrO_2 peaks, (111) and (101) appearing at N28.2^o and N31.5^o, respectively, become stronger with the increase in ZrO_2 content. The stability of the t -ZrO_2 phase, is generally controlled by its grain size. Tetragonal phase can be stable at ambient temperature even without stabilizer if its particle size is finer than about 30 nm, i.e. the surface energy of the t-phase is smaller than that of the m-phase [18]. But instead, Mitsuhashi, et.al [16] reported that grain growth provides active nucleation sites for phase transformations.

The possible reasons for the destabilization of the t-phase in the present study are not only the ZrO_2 grain size but also the internal stresses which develop in during cooling, resulting from thermal expansion mismatch between alumina, SiC and ZrO_2. The large difference in thermal expansion coefficient between alumina, SiC and ZrO_2 inclusions would introduce thermal stresses in the ZrO_2 grains during cooling from sintering temperature (10,5,12 µm/m-°C) respectively. The stability of t-ZrO_2 phase relies also on the content of stabilizer in solid solution because the yttria stabilizer, for instance, has been known to posess a tendency to react with other oxides such as, in this study, SiO_2 present as a product of SiC oxidation at the sintering temperature, resulting in t-ZrO_2 with lack in yttria solid solution as shown in the SEM pictures. The XRD profiles of the studied composites show that there no reaction between Al_2O_3 , ZrO_2 and SiC was detected.
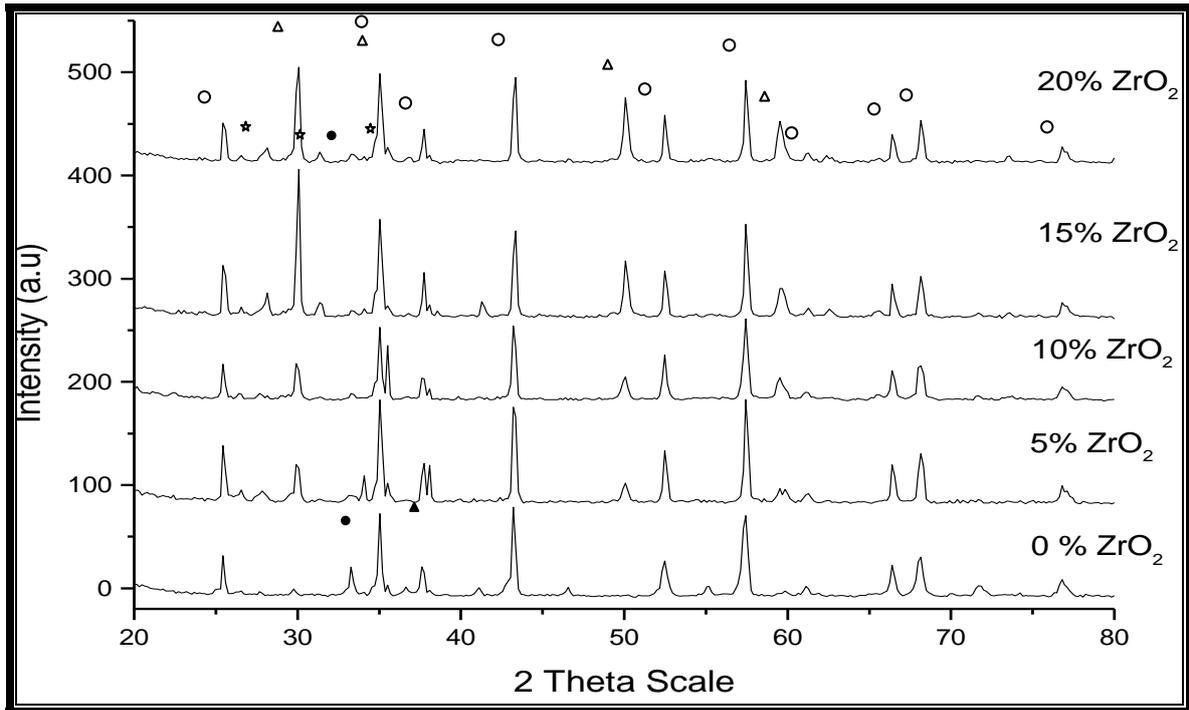
Figure (4): XRD patterns of the tested composite specimens,
where   : Corundum ○, t-ZrO₂ ▵, m-ZrO₂☆ ,   SiC• and SiC-2H

3.3.Microstructure Analysis:

The microstructure of batch 1 sample fired at 1575 ^{o}C without zirconia addition is shown in Fig5. The figure indicates that there is no interface reaction between SiC particles and alumina matrix. The SiC particle surface was covered with a very thin layer of glassy phase, which contains fine crystals of mullite. The spectra of EDX- point analysis confirmed the existance of Al_2O_3 rich glassy phase and mullite as shown in Fig. (5), because of the mullite content of the sample is less than 5%, its peak is absent in the XRD pattern of the samples. Figure 6 in the same sample showed an alumina matrix grain growth and small white particles of yttrium aluminum garnet (YAG) phase. The YAG particles are uniformly distributed in the Al_2O_3 matrix, most of them, however , located within the Al_2O_3 grains rather than at the grain boundaries. SEM-EDX element analysis Fig. 5 revealed that no elements other than Al_2O_3 and Y_2O_3 were present within the YAG white particles.

The pinning effect of ZrO_2 on the grain growth of Al_2O_3 is shown in Fig.7. The presence of ZrO_2 changed the alumina grain morpology from abnormal to equiaxied grains. The suppressing effect of ZrO_2 on the formation of abnormal Al_2O_3 is great. Some ZrO_2 particles are trapped into alumina grains. Hirlinger [15] reported that abnormal growth of Al_2O_3 was prevented by the ZrO_2 inclusions. Figure 8 illustrates the presence of cluters of fine-grained ZrO_2 particles. ZrO_2 grains have a spheroidal shape, it tends to possess convex boundary segments. Small particles of YAG are located at the grain boundary triple point of zirconia grains.

Figure (5): EDAX microanalysis and SEM of alumina with out zirconia.
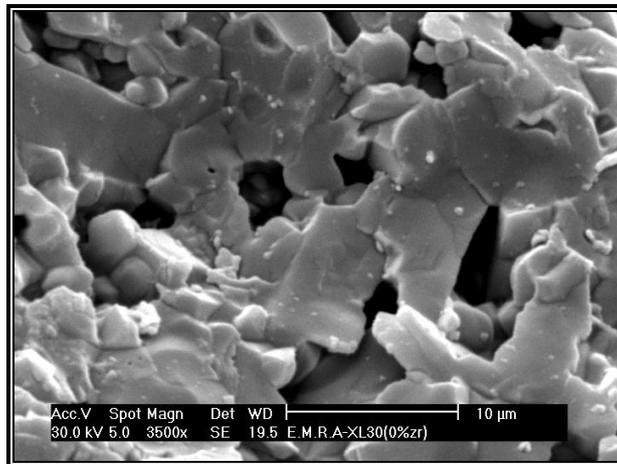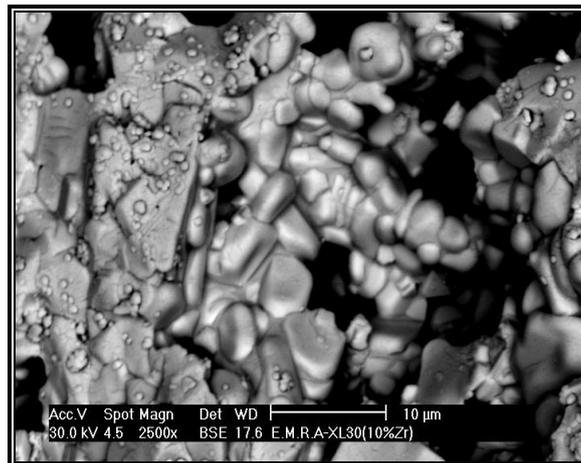

Figure (6): SEM of Alumina grain growth

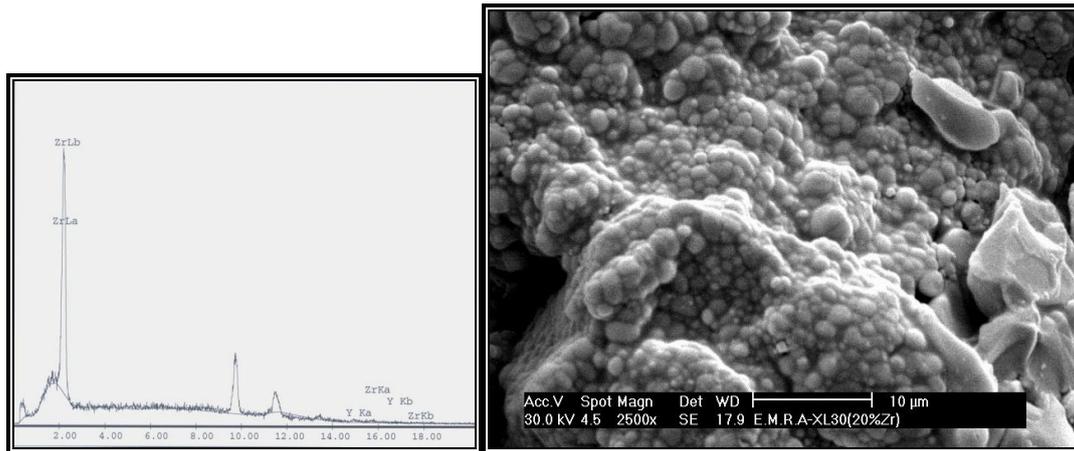**Figure (7):** The pinning effect of ZrO2 on the grain growth of Al_2O_3

Figure (8): EDX of clusters of fine-grained ZrO_2 particles
ZrO_2 grains have a spheroidal shape

3.4.Mechanical properties test results:

A three point bending test was carried out according to ASTM C1161 (1990) on different batches compositions starting from 0% zirconia up to 20% zirconia. The weight percentage of zirconia affects the mechanical properties of ceramic composites specimens. Figure 10 illustrates that the addition of zirconia improves the flexural bending strength of the ceramic composite specimens. Recent experimental results [13] show that, if just a trace of dopant Zr 4+ ions and Si4+ ions segregates at the Al2O3 grain boundary, the Al2O3 boundary bonding strength increases relative to that of the clean Al2O3 boundary. Deng,et al [13] showed in their study that Zr 4+ doping in alumina – siliconcarbide composite led to a weak Al2O3 boundary bonding , so that the fracture mode of Zr 4+ - doped composite becomes intergranular, and the fracture toughness increased relative to that of undoped composite. The weak Al_2O_3 boundary bonding is caused by the action of boundary segregated Zr^{4+} ions and Si^{4+} ions dissolved from the SiC particle surfaces. 10% Zirconia addition showed the best flexural bending strength results. Further increase of Zirconia percentage decreases the flexural bending strength of the whole composites. This decrease in flexural bending strength over 10 wt% may be attributed to the occurence of excessive grain growth. The transformation of larger ZrO_2 grains from tetragonal phase to monoclinic phase leads to the formation of microcracks in the sintered body. As a result the flexural bending strength decreased.
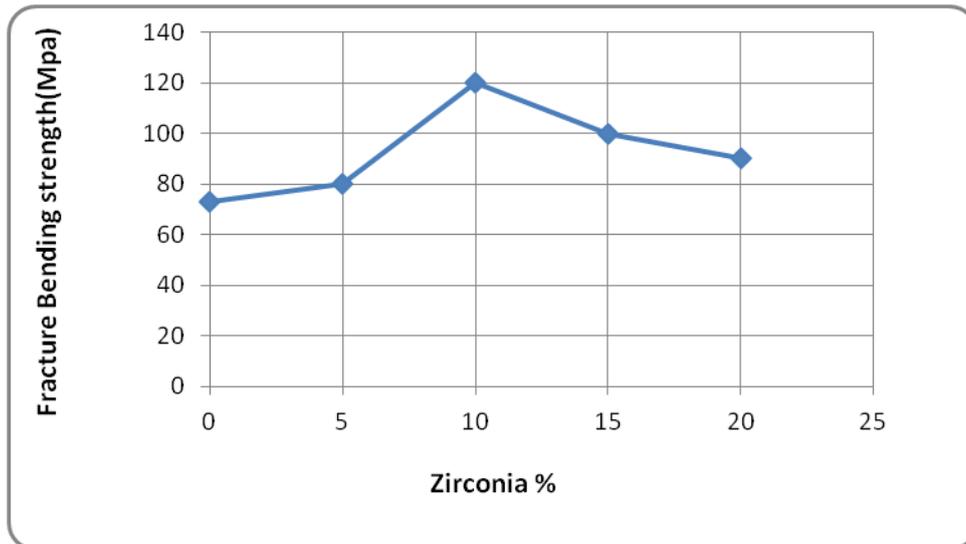
Figure (9): Effect of weight percent of Zirconia
on flexural bending strength of the ceramic composite.

The Hardness was measured by means of Vickers indentation method by using micro hardness tester (Model HVS-50, Laizhou Huayin Testing Instrument Co., Ltd. China) with a Vickers diamond indenter and a 20X objective lens, according to ASTM C1327-97 (1996).

Figure. 11 illustrates the effect of ziconia percentage on the hardness of the material, with the addition of zirconia improves the vickers hardness of the ceramic composite specimens until 10% Zirconia. Further increase of Zirconia percentage decreases the vickers hardness of the resulting composites.
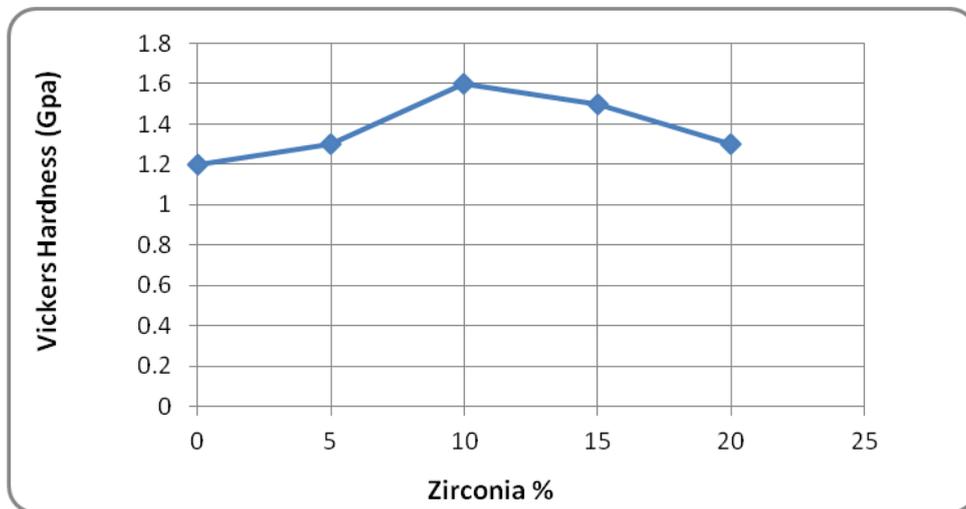

Figure (10): Effect of weight percent of Zirconia
on vickers hardness of the ceramic composite.

4. Conclusion:

1- The presence of up to 10 wt. % Zirconia improves the sintering behavior of the alumina-Zirconia composites. It also imparted better physical and mechanical properties.

2- In all batches the minor phases predominantly are $t-ZrO_2$, $m-ZrO_2$, SiC and SiC-2H phase.

3- Increasing the Zirconia content over 10% decreases the bending strength and the Vickers hardness of the composites

4- The 10 wt. % Zirconia batch was utilized in armor module as a facing material with glass fiber backing and ested as an armor with real firing with 7.62x39 AP projectile with 750 m/sec impact velosity, it did make protection with areal density 48.5 kg/m2, which means about 35% weight saving compared with compatable rolled homogenous armred steel (RHA).

5. References:

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