Effect of $MgAl_2O_4$ Particles on Characterization of Y_2O_3–ZrO_2 System

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ABSTRACT

In this study, four samples composite materials used for manufacturing by using uniaxially technique compressed into cylindrical pellets. The matrix materials of these composites are: yttrium oxide + zirconia (3mol%Y_2O_3+ZrO_2), reinforced with spinel ($MgAl_2O_4$) particles which is added in three percentages (5, 10, 15 % wt) to the matrix. Additionally there are pellet without reinforced and with spinel ($MgAl_2O_4$) particles, then sintering at temperatures 1550 ºC for 2 h.

The density and the apparent porosity of the sintered pellet were measured by the Archimedes drainage method, the microstructure features and the phase identification were examined using SEM and XRD; and the mechanical properties such as hardness and toughness were determined using Vickers indentations.

تأثير أضافة دقائق النبل $MgAl_2O_4$ على خواص النظام $MgAl_2O_4$-ZrO_2

الخلاصة

في هذة الدراسة صنعت اربع نماذج اسطوانية الشكل باستعمال تقنية الكبس الاحادي والمادةالاساس المستخدمة هي (3mol%Y_2O_3+ZrO_2), yttrium oxide + zirconi حيث تم تقويتها بدقائق السبنل spinel ($MgAl_2O_4$) الذي اضيف بثلاث نسب تدعيم مئوية وهي
(5, 10, 15 % wt) الى المادة الاساس بالاضافة الى نموذج غير مدعم بدقائق السبنل وتم التلبيد بدرجة حرارة 1550 ºC لمدة ساعتين

تم قياس الكثافة والمسامية الظاهرية باستخدام طريقة ارخميدس للنماذج الملبدة ومميزات التركيب وتعريف الاطوار المتكونة باستخدام المجهر الاكتروني الماسح والاشعة السينية واما الخواص الميكانيكية مثل الصلادة وقياس متانة الكسرتم قياسها باستخدام طريقة غرز(تثليم) فيكرز .

INTRODUCTION

Zirconia (ZrO_2) based materials exhibit high fracture toughness due to the stress induced martensitic transformation of tetragonal to monoclinic zirconia [1], generally known as transformation toughening. Yttria doped tetragonal zirconia polycrystals (Y-TZP) tend to be the most widely used zirconia ceramic for many applications due to the retention of the ‘‘metastable’’ tetragonal phase, thus maximising the toughening mechanism [2]. Pure zirconia presents the phenomenon of allotropy that is same chemical composition but different atomic arrangement, among the following crystallographic structures as shown in Figure (1) [3]

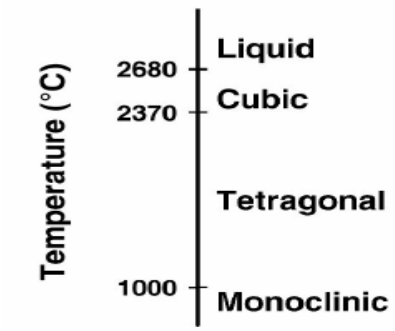

Figure (1) Temperatures in the three phases of Zirconia [4]

The cubic structure is of the fluorite type, with oxygen ions occupying a simple cubic lattice and the zirconium ions occupying the center of half of the anionic cubic cells. Examined upon cooling, the transformation from cubic to tetragonal (c–t) and from tetragonal to monoclinic (t–m) is a thermal and diffusion less (hence the term "martensitic" used to describe this transformation, in analogy to what happens in steel). Furthermore the t–m transformation occurs with a volume expansion (when unconstrained) of about 5 vol. % **[4]** which is sufficient to exceed the material strength and results on its fracture. However, the addition of stabilizers allows maintaining the cubic and tetragonal phases at room temperature **[3]**.

In order to use tetragonal or cubic zirconia, these are doped with oxides such as Yttria (3mol%Y_2O_3), Magnesia (8mol% MgO), Calcium oxide (8mol% CaO), Ceria (12% CeO_2), that stabilize the high-temperature phases at room temperature. This procedure affects both the mechanical and electrical properties. Doping of zirconia results in stabilization of the tetragonal phase at lower dopant concentrations (for mechanical toughness) or the cubic phase at higher dopant concentrations (for high ionic conductivity) at room temperature **[3, 5]**.

The 3Y- ZrO_2 consists of an array of stabilized zirconia with a (2-4mol %) yttrium oxide. In 1977, it was reported that ZrO_2 fine grain (usually <0.5 μm) with small concentrations of Y_2O_3 stabilizers could contain up to 98% of the metastable tetragonal phase after sintering. The main feature of this microstructure is to be formed by tetragonal grains of uniform diameter in the order of nano meters, sometimes combined with a small fraction of the cubic phase.

The most important feature of the ZrO_2-Y_2O_3, phase diagram is the decrease in temperature of the tetragonal monoclinic transformation with increase in Yttria content, a phenomenon which does not occur with MgO and CaO additions. It would be noted that HfO_2 additions increase the transformation temperature. This behaviour has important implications for both the design and use of toughened ceramics produced as either partially stabilized zirconia or as heterogeneous two phase systems, since the upper temperature limit for any application is determined by the monoclinic tetragonal transformation temperature. **[2]**

The 3 mol % Y_2O_3 ceramic provides insurance against under stabilization due to chemical homogeneity, when spontaneous transformation to the monoclinic form would lead to degradation in mechanical properties. The over stabilization also allows a larger critical particle size to remain metastable

When 'constraint' is removed by heating in a water containing atmosphere at ~ 2000 °C

Fully Yttria stabilized zirconia (YSZ) has a number of applications:

1. For its hardness and chemical inertness (e.g., tooth crowns).
2. As a refractory (e.g., in jet engines).
3. As a thermal barrier coating in gas turbines
4. As an electro ceramic due to its ion-conducting properties (e.g., to determine oxygen content in exhaust gases, to measure pH in high-temperature water, in fuel cells).
5. Tetragonal Zirconia Polycrystal (3Y-TZP) was first applied in the medical field of orthopaedics, with significant success due to its good mechanical properties and biocompatibility **[6]**.

Specimen preparation

The material used in this study as matrix was zirconia, which is stabilized by adding yttrium oxide (3% mol Y_2O_3+ZrO_2) (ferak company-Germany) the additive used in this work is spinel ($MgAl_2O_4$) which is added in three percentages (5, 10, 15 % wt) to the matrixes.

The resulting Po

wders are usually pressed damp in metal dies; the powder contains binder were formed by pressing uniaxially at pressure of 624 Mpa in the metal-die cylindrical to form pellets have 10mm diameter.

The process of sintering applied to all samples was completed in an electrical programmable furnace at temperatures 1550 $^{\circ}$C for 2 hours, the rate of heating and cooling was 15 ° C / min.

The physical testes

The bulk density (B.D)

This is representing the ratio between the weight to the total volume (volume of material grain + volume of open &close porosity). The test was applied according to ASTM (C 373 – 08). That's Calculate from the relationship:

$$(B.D) = \frac{W_d}{W_s - W_n} \times D \qquad \ldots (1)$$

Where:

W_d : weight of the dry sample.
W_s : weight of sample being infiltrated with water.
W_n : weight of sample being immersed in water **[7]**.
D : density of water (1g/cm^3).

the apparent porosity (A.P)

The apparent porosity of such samples was measured using traditional Archimedes method; it was calculated using the following equation

$$(A.P)\% = \frac{W_s - W_d}{W_s - W_n} \times 100 \qquad \ldots . (2)$$

The liner shrinkage (L.S)

The length variation of the specimens before and after the sintering was measured with a vernier calliper, and the linear contraction was tested.

$$(L.Sh)\% = \frac{L_\circ - L}{L_\circ} \times 100 \quad \text{.... (3)}$$

Where:

L.S:- The liner shrinkage of samples.
L_o : - the length of samples before the sintering process.
L : - the length of samples after the sintering process.

The mechanical testes

Vickers micro Hardness

It is defined as the resistance to penetration Displayed by a material by hard indenter of defined geometry and forced into the test surface in a prescribed manner; the test is applied as ASTM (C 1327 – 99).

The equation from which the Vickers micro hardness is derived is shown below **[8]:**

$$H_v = 1.854 * P/a^2 \quad \text{…(4)}$$

Where:

H_v is the Vickers micro hardness (Mpa);

P is the indentation load (N);

(**a)** Is half the indentation diagonal (mm). And **1.854** is a geometrical Constant of the diamond pyramid.

Indentation Fracture Toughness

To evaluate fracture toughness, indentation by Vickers was used at which the crack length was measured at a load (5kg)

$$K_{Ic} = 0.0889 (HP/4L)^{0.5} \quad \text{.... (5)}$$

Where

K_{Ic} is fracture toughness (Mpa);

H and **P** is the Vickers hardness and indentation load respectively,

L **= c –a**; **2a** the indentation diagonal and **2c** the length of the full crack (both in mm) **[9]**

Results section

X-ray Diffraction

The x-ray diffraction analysis was performed in order to study phase present in the samples.

Phase analysis of different samples was carried out by XRD using Cu Ka radiation with a wavelength of 0.154 nm.

In Figure (2) and Figure (3) the phase assemblages of $MgAl_2O_4$-3mol%Y_2O_3-ZrO_2 composites containing 10wt % $MgAl_2O_4$ sintered at 1550°C are shown, there is minor intensity of XRD peaks at 36.9° and 65.3° of $MgAl_2O_4$ and, In the $MgAl_2O_4$-3mol%Y_2O_3- ZrO_2 at 30°, 34.6°(2θ), another two at 50° And 60 ° (2θ) is noted with added amounts of spinel to the zirconia matrix

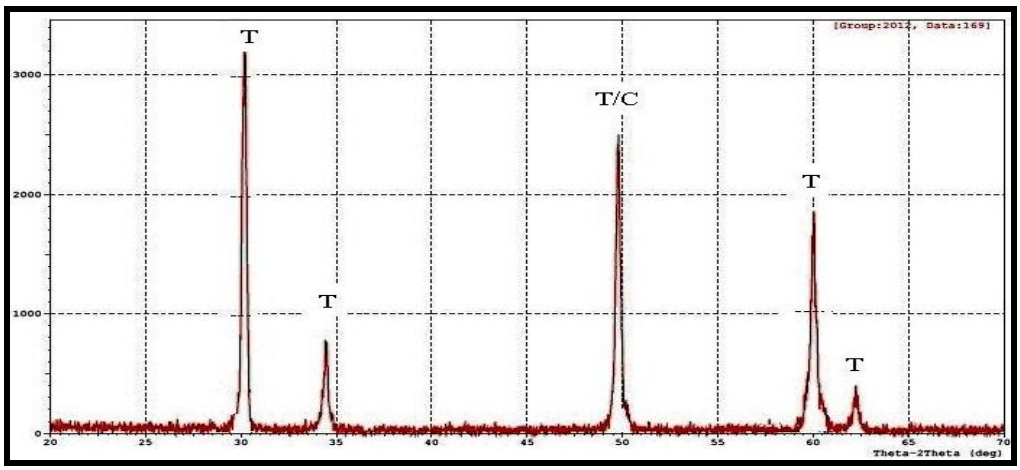

Figure (2) XRD pattern of ZrO_2 doped with 3 mol % Y_2O_3 sintered at 1550°C. T- Tetragonal phase.

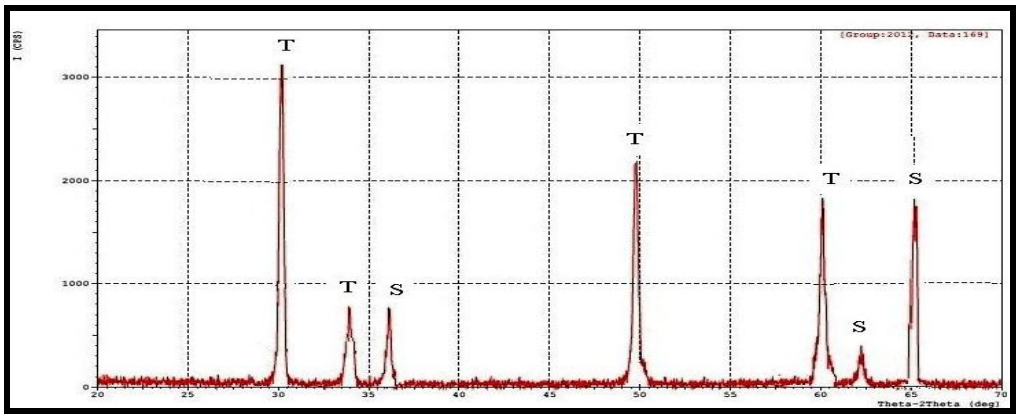

Figure (3) XRD pattern of 3 mol % Y_2O_3 -ZrO_2 doped with 10 % wt $MgAl_2O_4$ sintered at 1550°C. T- Tetragonal phase. S- Spinel powder ($MgAl_2O_4$).

So sintered 3mol%Y_2O_3-ZrO_2 samples contained two phases, predominantly consisting of a tetragonal phase with cubic phase, this result agrees with the phase diagram of a previous study that 3mol% Y-ZrO_2 at sintering temperature 1400-1550°C should present two phases which are tetragonal and cubic phases. . [11]

Density and Porosity

As show in the figures (4) which is represent the value of the density of theY-ZrO_2-$MgAl_2O_4$ composites, the maximum values of density can be noted at (5% $MgAl_2O_4$), followed by a decreasing trend beyond this percentage.

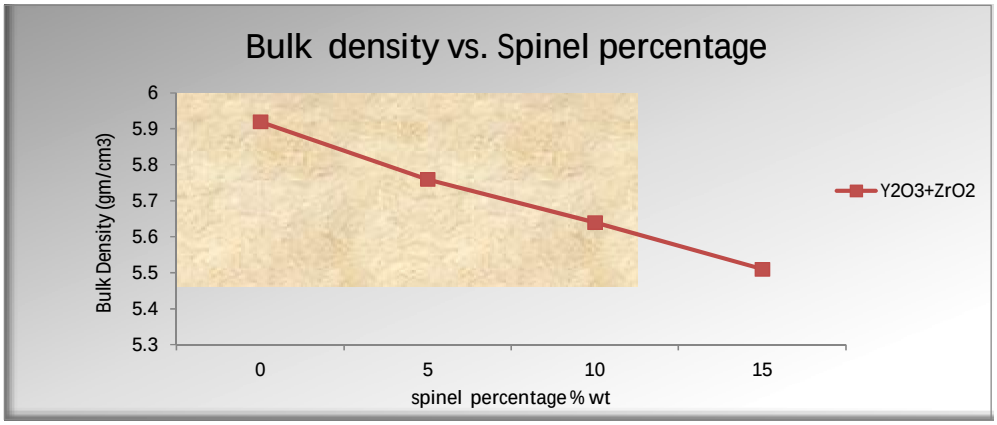

Figure (4) Variation of bulk Density with Spinel percentage

The highest density may have resulted from incorporation of heavier ZrO_2 into the $MgAl_2O_4$ than from densification.

The decreasing bulk density in (10%, 15%)wt $MgAl_2O_4$ of sintered materials beyond certain percentage is a well-known phenomenon Related to the grain coarsening and pore coalescence, and increase the low density of $MgAl_2O_4$.

All Y_2O_3-ZrO_2-$MgAl_2O_4$ composite exhibited apparent porosity values almost approximate to zero when sintered at 1550 ˚C for 2 h, so the apparent porosity behaves in the opposite direction of the density. As show in figure (5)

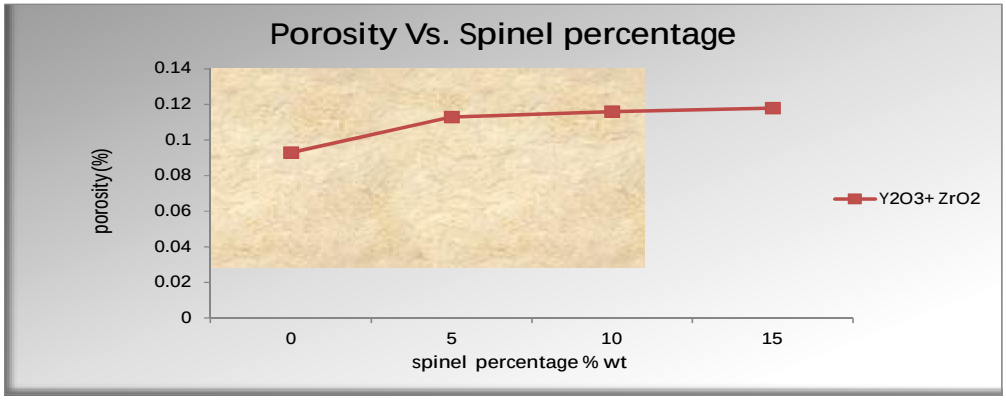

Figure (5) Variation of porosity with Spinel percentage

Figure (6) gives the shrinkage values for various composites substantiate the information obtained from their bulk density values. There is decreasing in the liner shrinkage value due to increasing the spinel particles percentage.

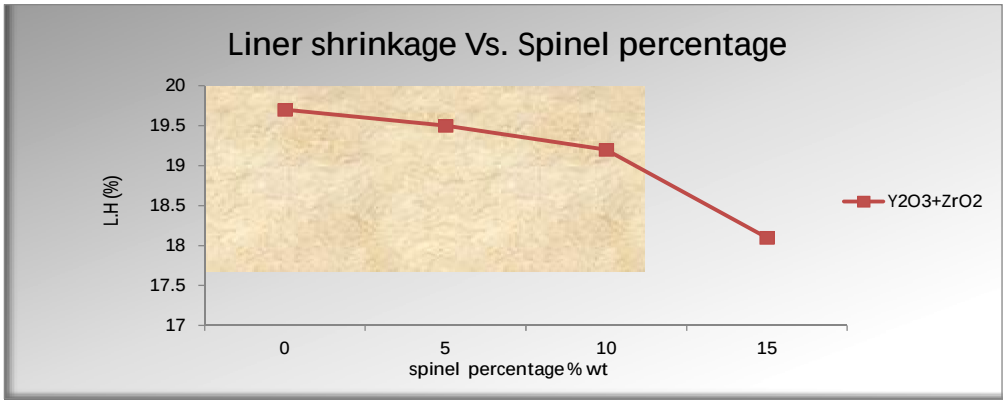

Figure (6) Variation of L.S with Spinel percentage

Vickers hardness test

As show in the Figure (7) which is represent the relation between the Vickers hardness and spinel percentages.

In our system $MgAl_2O_4$-ZrO_2-Y_2O_3 , We find the 15% $MgAl_2O_4$-Y_2O_3-ZrO_2 system have the maximum values which are reaching to 1327.2 H_v

This is due to the presences of ($MgAl_2O_4$) particles with zirconia matrix increase the hardness due to ability of these particles to hinder the crack propagation, in addition to the strong bonding of zirconia matrix with the reinforcement.

Although the variation in hardness could be attributed to the presence of the porosity, due to presence spinel ($MgAl_2O_4$)particles, the marked variation in toughness suggest that is responsible of this variation is the generation of micro cracks.

It is important to note that these samples show the best properties, possibly coming from the better spreading of the glassy phase formed during sintering and its penetration around the ZrO_2 particles. This phenomenon's facilitates the elimination of pores and reduce accumulation of glass triple joints, minimizing the generation of stress fields during cooling and therefore points in favour of crack propagation

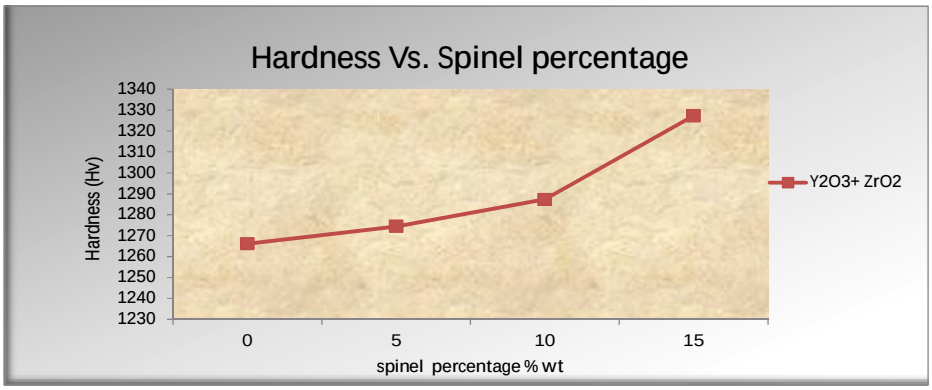

Figure (7) Variation of Vickers hardness with Spinel percentage

Indentation Fracture Toughness

From the Indentation Vickers hardness test we calculate the fracture toughness value for each sample in dentations.

As show in the Figure (8) represents the relation between the fracture toughness as a function of the spinel additive to the matrix Y_2O_3- ZrO_2

In the 5% wt $MgAl_2O_4$-ZrO_2-Y_2O_3 system, the samples sintered at 1550°C may contain the semi ideal microstructure is the tetragonal phase and cubic phase as discovered by *Lange and Gupta* **[5]** reported that fine grain ZrO_2 with small concentrations of stabilizing Y_2O_3 could contain up to 98% of the metastable *t* phase following sintering

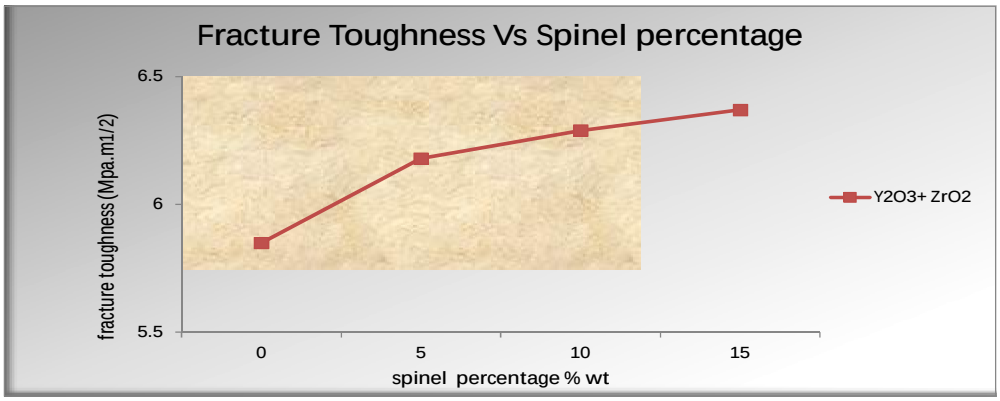

Figure (8) Variation of Fracture Toughness with Spinel percentage

In the (10% wt and 15%wt $MgAl_2O_4$) in ZrO_2-Y_2O_3 samples there is increasing in fracture toughness value, due to incorporation of ($MgAl_2O_4$) particles improved strength, because crack propagation was hindered at the boundary of the second phase ($MgAl_2O_4$) much harder than the ZrO_2 particles **[10],** Figure (9) represent Vickers indentation of 10% $MgAl_2O_4$ - 3%Y_2O_3- ZrO_2 samples Sintered at 1550°C (2 hour) also may be the toughness and limited crack extension of ZrO_2 by the incorporation of $MgAl_2O_4$ is due to a combination of several toughening mechanisms including stress-induced t → m phase transformation toughening, micro crack toughening and crack deflection

Figure (9) Vickers indentation of 10% $MgAl_2O_4$ - 3%Y_2O_3- ZrO_2 samples Sintered at 1550°C (2 hour) by Scanning electron micrographs (SEM) (200µm)

Microstructure Analysis of sintered samples SEM

All samples ($MgAl_2O_4$–3mol %Y_2O_3-ZrO_2) sintered at 1550°C for 2 h were tested using scanning electron microscopy (SEM).

Are shown in Figures (10), wherein the brighter portions correspond to ZrO_2 and darker zones are corresponding to $MgAl_2O_4$ phase and porosity.
The microstructures of the other samples presented similar features, but with the dark portions increasing with the $MgAl_2O_4$ particles
There is evidence of $MgAl_2O_4$ particles associated with porosity at the grain boundaries of the ZrO_2grains.

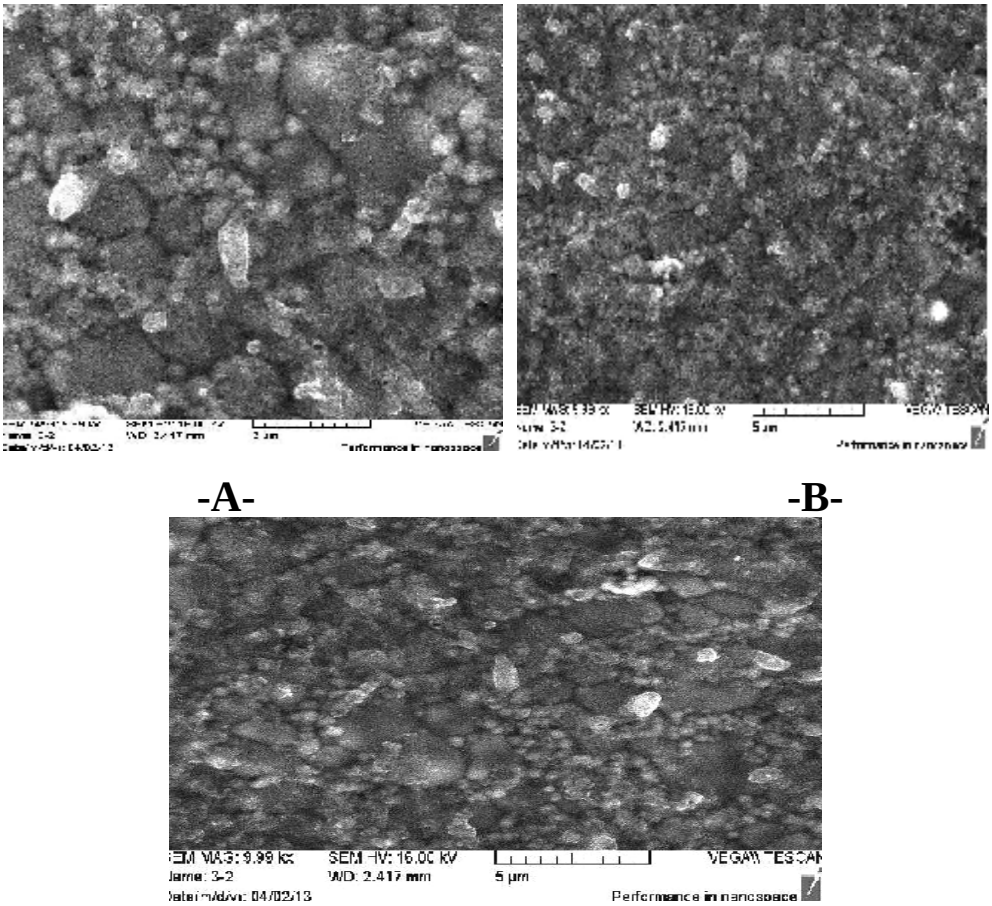

Figure (10) Scanning electron micrographs (SEM) of 3%mol Y_2O_3- ZrO_2 samples Sintered at 1550°C (2 hour), At Scale bar 5µm.
(A) 5 % $MgAl_2O_4$ (B) 10% $MgAl_2O_4$ (C) 15% $MgAl_2O_4$

CONCLUSIONS

1- the maximum values of densities can be noted at (5% $MgAl_2O_4$); In the case of Y-ZrO_2-$MgAl_2O_4$,All Y_2O_3-ZrO_2-$MgAl_2O_4$ system exhibited apparent porosity values almost close to zero when sintered at 1550 ˚C for 2 h,

2- The maximum values of the Vickers hardness find at 15% $MgAl_2O_4$-3mol%Y_2O_3-ZrO_2 system so which it take increasing the wear resistance

3- The maximum fracture toughness is obtained in 15% $MgAl_2O_4$-3mol%Y_2O_3-ZrO_2 system which it take improved strength, because crack propagation was hindered at the boundary of the spinel ($MgAl_2O_4$) particles .

4- Spinel ($MgAl_2O_4$) enhances the sinterability of ZrO_2 so could be sintered at a lower temperature

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