

Synthesis and Characterization of the Mullite-Zirconia Composite Material

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ABSTRACT

Mullite- Zirconia ($3Al_2O_3 \cdot 2SiO_2 \cdot ZrO_2$) composite was an important industrial material, which has been synthesized by a solid state reaction method from its constituent ($3Al_2O_3 \cdot 2SiO_2$) and zirconia (ZrO_2). Mullite has been synthesized by sol-gel method from raw materials, pure aluminum (98-100%), pure silica foam (99.9-100%), and aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and calcined at $1200^\circ C$ for 2 hr. mullite has been a matrix and the reinforced component addition were 5 %, 10 %, and 15% zirconia. The phase and microstructure evolutions of the composite synthesized at desired temperature of 1150, 1350, and $1450^\circ C$ were characterized by x-ray diffractometry and scanning electronic microscopy, respectively. The influences of sintering temperature on shrinkage ratio, apparent porosity and bulk density. The formation process of the composites were examined in detail. The results show that the zirconia-mullite composites with good sintering properties can be prepared at $1450^\circ C$ for 2 hr.

Key words :- Zirconia , Mullite, Sol-Gel, Composite Material, solid –state , composite properties

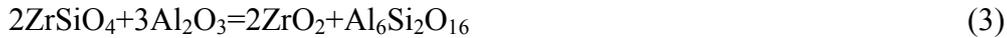
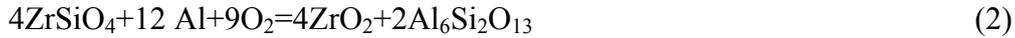
الخلاصة

المولاييت- زركونيا هو مادة صناعية مهمة تم تحضيرها بطريقة تفاعل الحالة الصلبة من مكوناتها الأساسية المولاييت وزركونيا. عندما يضاف المولاييت الى زركونيا لتحسين الاستقرار الحراري وتقليل معامل التمدد الحراري التي تستخدم في تطبيقات طب الأسنان. أما، المولاييت فيتم تحضيره بطريقة سول- جيل من المواد الأولية: الالمنيوم النقي (98-100%) و سيلكا النقية (99.9-100%) وكلوريد الالمنيوم السداسي وتم حرقه في درجة حرارة ($1200^\circ C$ لمدة ساعتين. زركونيا كانت المادة الاساس ومادة التقوية هي المولاييت وكانت نسبة اضافة مادة تقوية هي (5%، 10%، 15%). و تم حرق المادة المركبة في درجات حرارة مختلفة : (1150، 1350، $1450^\circ C$ درجة مئوية) و بمعدل تسخين $5^\circ C/min$ ولمدة ساعتين. وتم التحقق من النماذج المحروقة باستخدام تقنيات XRD و SEM. وجد ان الزركونيا المستخدمة في تحضير المادة المركبة يكون بطور الرباعي (Tetragonal) المستقر بواسطة اضافة 1% من MgO وتبدأ بالتحويل تدريجياً الى طور الاكثر استقراراً وهو طور (monoclinic) من الغلاف الخارجي الى داخل الحبيبة مع زيادة درجة حرارة الحرق. بزيادة درجة حرارة الحرق اكثر من $1350^\circ C$ درجة مئوية سوف تبدأ بظهور بلورات الالومينا والكوارتز ناتجة من تفكك مكونات المولاييت في المركب. الخواص الفيزيائية، الميكانيكية، والحرارية ايضا تم التحقق منها لكلا المركبين. ان كثافات كلا المركبين تزداد بزيادة درجة حرارة التليد وكمية اضافة مادة التقوية، وصلت الى اعظم قيمه لها وهي ($5.9 g/cm^3$) عند درجة حرارة ($1450^\circ C$) بينما قيم المسامية للمركبين تقل مع زيادة درجة الحرارة التليد وكمية مادة التقوية المضافة بعد ذلك تصل الى اقل قيمة لها وهي 10.4%. الانكماش الخطي للعينات المحروقة لكلا المركبين يزداد بزيادة درجة حرارة التليد ويقل بزيادة كمية مادة التقوية. كلا الصلادة ومقاومة الانحناء يزدادان مع زيادة درجة حرارة التليد وكمية اضافة الزركونيا وتقلان بزيادة كمية المولاييت لكلا المركبين. معامل التمدد الحراري قل مع زيادة درجة الحرارة التليد. بينت النتائج ان افضل تبلور لكلا المركبين يكون في درجة حرارة $1450^\circ C$.

الكلمات المفتاحية :- زركونيا، مولاييت ، سول - جيل ، المادة المركبة ، الحالة- الصلبة ، خواص المركب .

Introduction

Zirconia-mullite composite have been found widespread applications due to their excellent properties such as high melting point, strength and fracture toughness as well as good wear point, chemical stability, high-creep resistance, and fracture toughness, as well as good wear, and thermal shock resistance. In recent years, some researchers have focused on using various raw materials to fabricate the Zirconia-mullite composites with low cost by reaction sintering process. The raw materials mainly involve zirconia, alumina (Al_2O_3) and silica (SiO_2), aluminum dross (Al) and zircon ($ZrSiO_4$). During the preparation process of zirconia-mullite composites from above raw materials, the following chemical reactions may be occur :



Preparation of Zirconia-mullite composite has been developed in order to achieve high thermo-mechanical properties. Mullite-zirconia composite have been prepared by various routes mainly including colloidal technique, and liquid infiltration technology (Bei-yue *et.al.*, 2010). The reaction sintering process (IBARRA *et.al.*, 2009)(ZHAO *et.al.*, 2003) is considered a promising technology for preparing zirconia-mullite composites because it has some advantages such as using cheap raw materials, simple production technology and low manufacturing cost ^[1], reaction sintering of alumina and zircon, reaction sintering of alumina, silica, and zirconia (Koyama *et.al.*,1996)., sol-gel method (YUAN *et.al.*,1986), microwave sintering method (RAABE *et.al.*, 2001), thermal plasma method (BHATTA *et.al.*, 2000), semi-colloidal technique(MAITRA *et.al.*, 2006), liquid infiltration technology (PARK *et. al.*, 2005).The hydration resistance of zirconia is improved by the incorporation of mullite. It is found that the element (Si) is promising for the future denture cementation property and the combination of a veneer porcelain. mullite was used to modify zirconia for dental application based on the following demands in the dental clinical community. Based on the appealing particularity of mullite and imperative advancement of zirconia, the purpose of the present investigation is to introduce the elastic gradients of mullite to modify zirconia (Limin. *et.al.*, 2011).

Experimental Procedure

Preparation of specimens

Mullite- zirconia composite has been synthesized by solid state method. Mullite was a reinforce member in the composite, while the zirconia was a matrix the reinforced component addition was 5, 10, and 15 %. So, three batches of composite were wet mixed with distilled water using a planetary ball mill which runs 300 rpm. The obtained solution was dried in an electric oven at 105°C for 24 hr. Table 1 show the weight percentages of zirconia and mullite in the composite batch. Particle size analysis was measured using laser particle size analyzer (Bettersize 2000) to give average particle size 7.453 μm as shown in fig.1

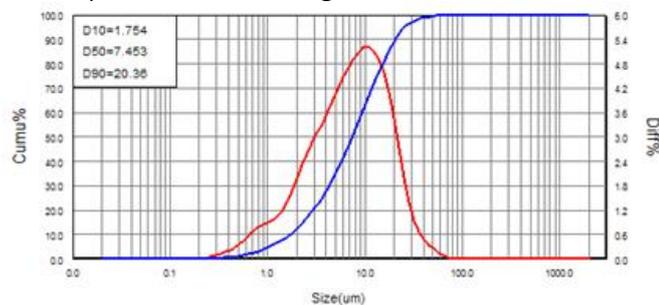


Figure.1. Particle size analysis of the mixed powder.

Table (1) Zirconia/mullite composite weight percentage.

Batch type	Zirconia %	Mullite %
	95%	5%
	90%	10%
	85%	15%

Characterizations

All samples obtained from the sintering batches were finely ground and scanned by x-ray diffractometer (Shimadzu, 6000) at room temperature using $\text{CuK}\alpha$ radiation with Ni filter. The microstructure were observed using the scanning electron microscope(VegaII XMV). The final sintered bulk density and porosity were measured by Archimedes method with an average of three samples of cylinder shape for each batch. A three- point bending test was carried by using rectangular bar samples prepared with dimensions $(50 \times 10 \times 5) \text{ mm}^3$. Vickers hardness test was carried out by using digital microvickers hardness tested (TH-717). The linear thermal expansion coefficient (α) of sintered samples was measured at temperature rang 25-800°C by dilatometer (Quick line-10).

Results and Discussion

X-Ray Diffraction (XRD)

Fig.2 shows the XRD patterns of the crystallization behavior of powder sintered at different temperature (1150, 1350, 1450 °C) and the reinforced component addition was 5, 10, and 15 % of mullite. Figure.(2.A) shows the x-ray diffraction patterns of mullite reinforced zirconia which are sintered at 1150°C. It is previously stated that the raw zirconia used to prepare the composite was a metastable tetragonal phase which is stabilized by adding 1 % of MgO. The fact as mentioned in literature that zirconia undergoes phase transformations with respect to change in temperature. It is clear that there are a principal tetragonal phase as a major and the commence crystallization of monoclinic zirconia as a minor. The presence of sub-amorphous mullite components up to 15 % does not appears as a well crystallized phase in the composite batches. On the other hand, it is located in the three batches as amorphous media between the zirconia particles. The existence of these phases without any transformation or reaction between them provides the stability state of zirconia when sub-amorphous mullite components is added to the composite. Sintering at the temperature of 1350°C, figure (2.B). It is clearly noted that a tetragonal zirconia phase is still the main phase in the composite. But, the increasing in sintering temperature up to 1350°C was caused to appear the commence of crystalline of alumina and quartz phases from the dispersed of sub amorphous mullite components in the composite as mention (PARK and YOON *et.al.*,2005) On the other hand, the crystalline mullite phase was detected in its early stage of growing. In the same time, the metastable phase of tetragonal zirconia starts to transform gradually to the monoclinic zirconia phase from the outer rims toward inside the grains. The excess of mullite components addition up to 10 % in the composite were enhanced the growth of both alumina and quartz phase. Also, the monoclinic zirconia phase was progressed in buildup at the expense of tetragonal zirconia phase. Ten percentage of sub-amorphous mullite components addition exemplify the ultimate range of growing both alumina and quartz phases, and transformation of metastable tetragonal zirconia phase to more stable of monoclinic zirconia phase, where any excess back in crystallization of both alumina and quartz, and degenerate of monoclinic zirconia phase development. Sintering at 1450 °C, figure (2.C) shows the same resulting in the sintering at 1350°C excluding the peaks are more stability and stopped in the growth.

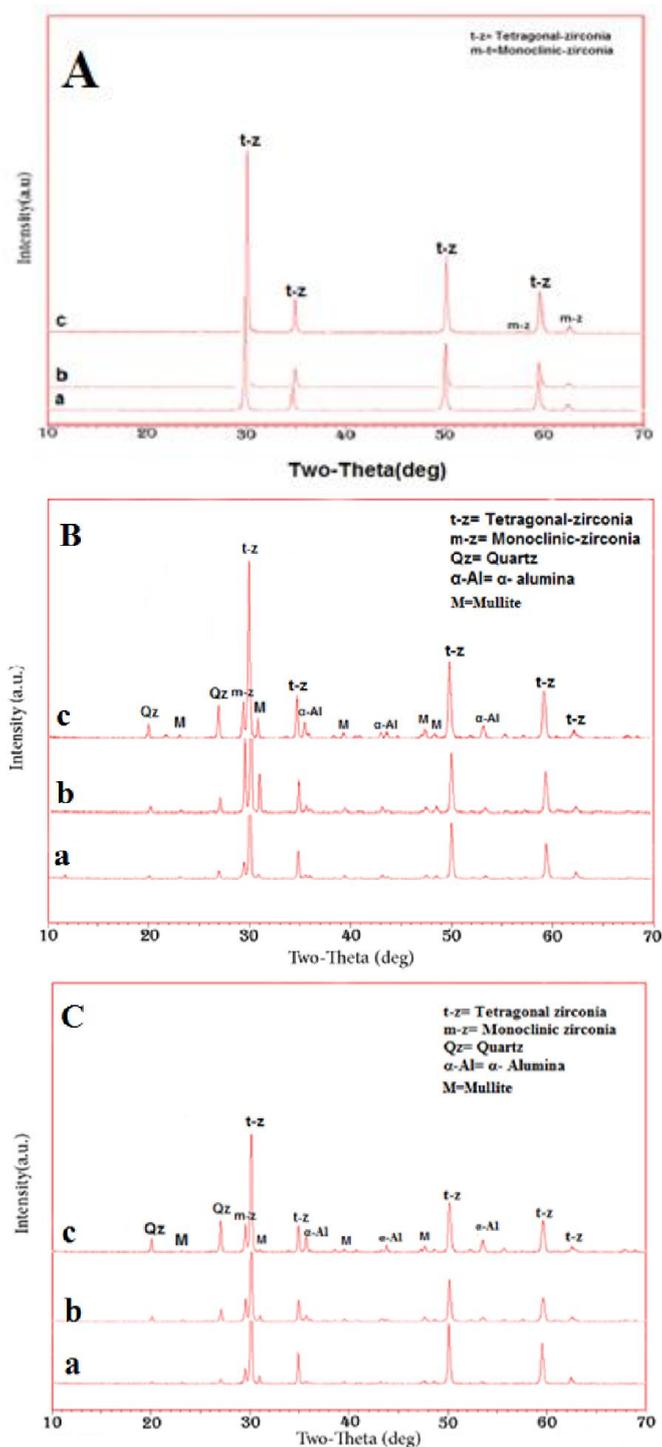
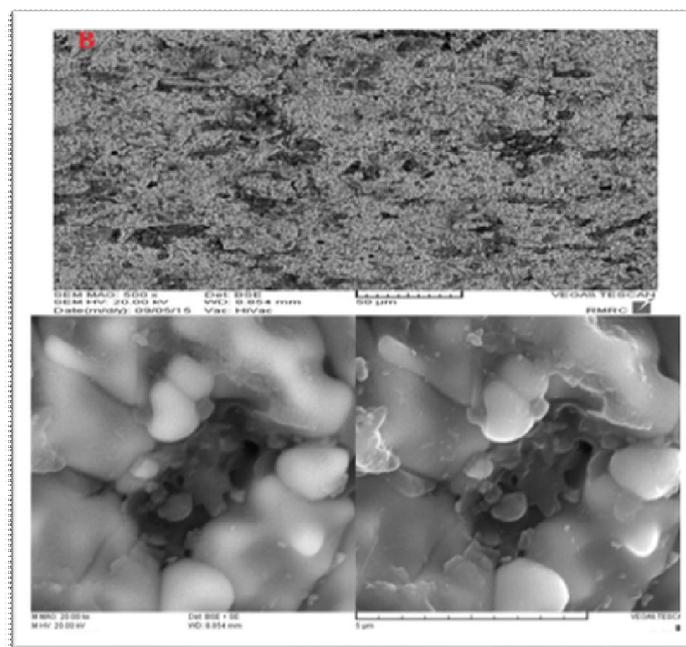
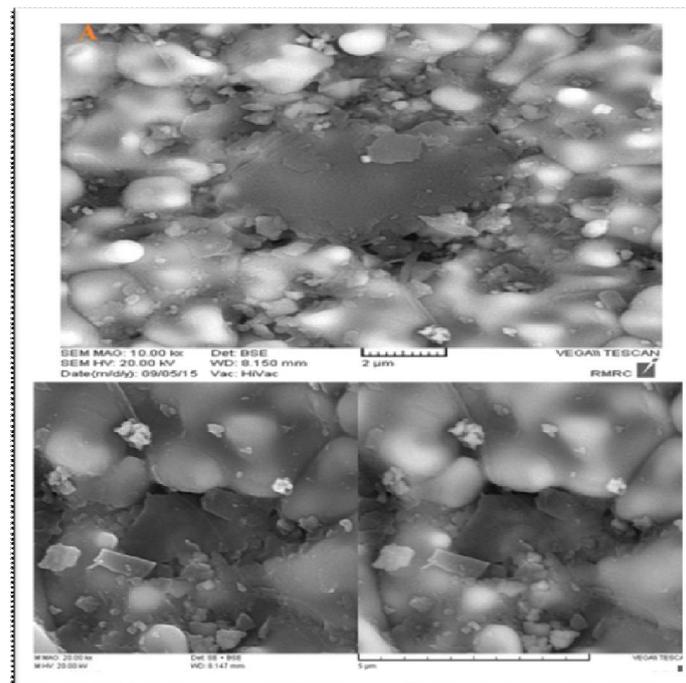


Figure.2. XRD analysis of mullite-zirconia composite sintered at 1150°C(A), 1350°C(B), 1450°C(C) of (a) 5 % mullite , (b) 10 % mullite, and (c) 15% mullite. SEM Micrographs

Scanning electron micrographs of the three batches of MRZ that sintered at 1450°C shown in figure (4). All the samples have a dense microstructure with low residual porosity. There is no preferential direction or orientation of the sub-amorphous mullite components grains in the microstructure of these materials. White

color grains are zirconia which can be observed in all cases, gray tint grains of mullite/zirconia composites, and dark gray grains of sub-amorphous mullite components. The small black area is the gas pores. Image A represents the scanning of batch 5 % sub-amorphous mullite components, the grains of sub-amorphous mullite components and zirconia separated by small pores. The morphology of the zirconia grains is spherical shapes. Image B and C represent the scanning sintered surface of batches 10 % and 15 % sub-amorphous mullite components respectively. Both of B and C image expose the same phases present in image A excluding observed two shape of zirconia particles, spherical and ellipse shapes with low residual porosity as shown in figure (3B,C) as shown in the reference (PARK *et. al.*, 2005)



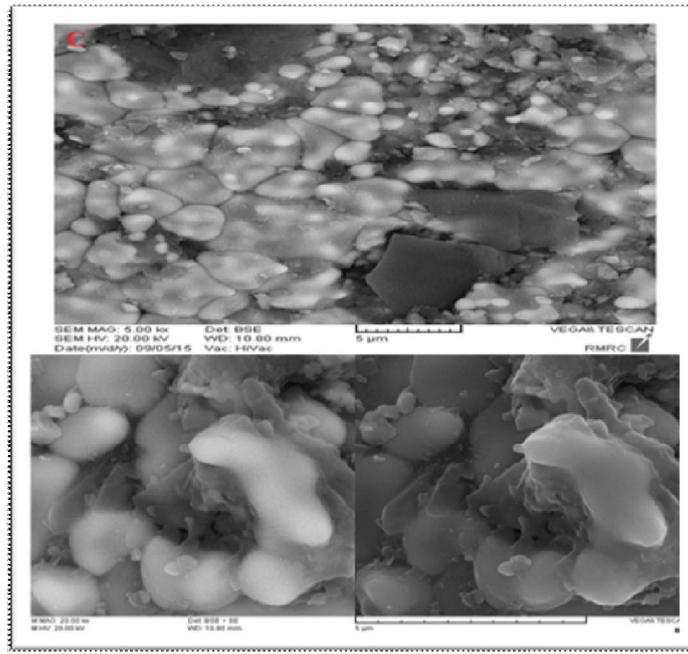


Figure (3) SEM Micrographs of mullite /zirconia composite A (5%) Mullite, B (10%) Mullite, C (15%) Mullite.

Physical Characterization

Figure (4) shows the relation between the compact samples with different weight percent of mullite and porosity. It is evident that the increase of mullite content in the compact sample caused decrement in porosity value of the compact sample. In the contrast, the increase in sintering temperature will reduce the porosity values. Figure (5) the relationship between mullite versus bulk density. It is evident that the increasing of mullite content in the compact sample will cause increment in bulk density value of the compact sample. In the contrast, the increase in sintering temperature will increases the bulk density values. It is interesting to know that the density varies as a function of porosity in these samples in which lower porosity shows a higher amount of density. Figure (6) represent the relation between linear shrinkage against mullite content. The increase of mullite content in the compact sample causes decrement in linear shrinkage value of the compact sample. In the contrast, the increase in sintering temperature increase the sintering shrinkage values.

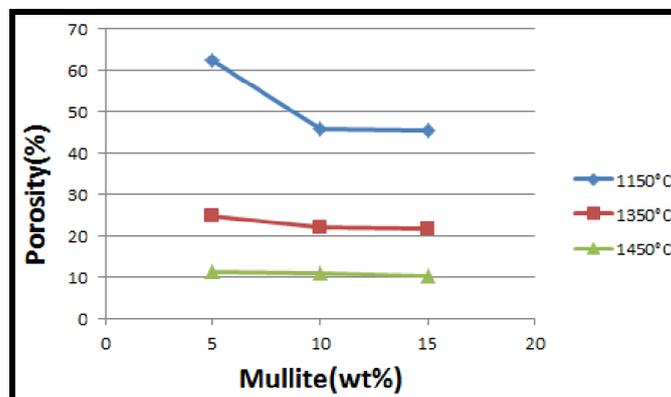


Figure (4) Variation of Apparent Porosity Compacts with Mullite Percentage.

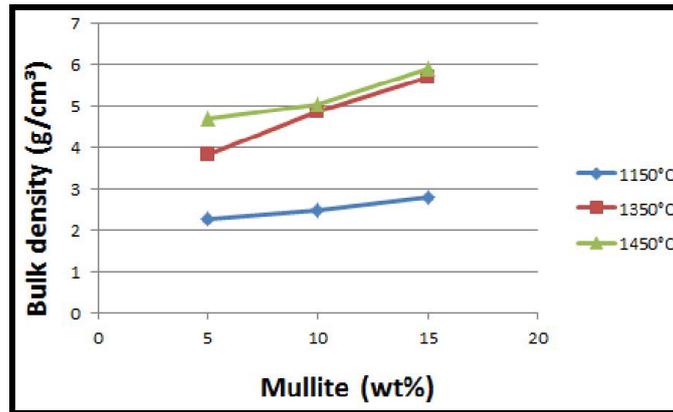


Figure (5) Variation of Bulk Density with Mullite Percentage.

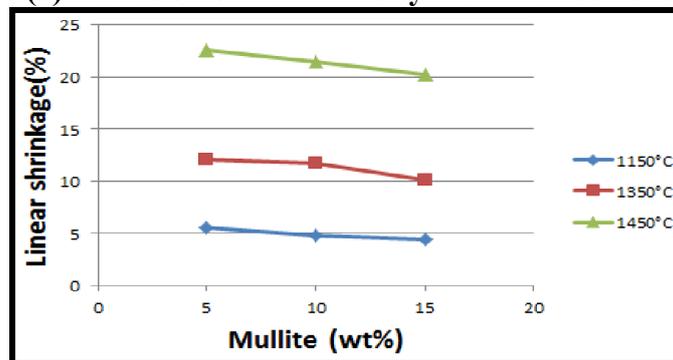


Figure (6) Variation of Sintering Shrinkage with Mullite Percentage.

Mechanical Characterization

Figure (7), (8) show the relation between the compact samples with different weight percent of sub-amorphous mullite components and bending strength, and Vickers hardness. It is evident that the increase of sub-amorphous mullite components content in the compact sample causes decrement in the mechanical properties values. In the contrast, the increase in sintering temperature increases the mechanical properties values.

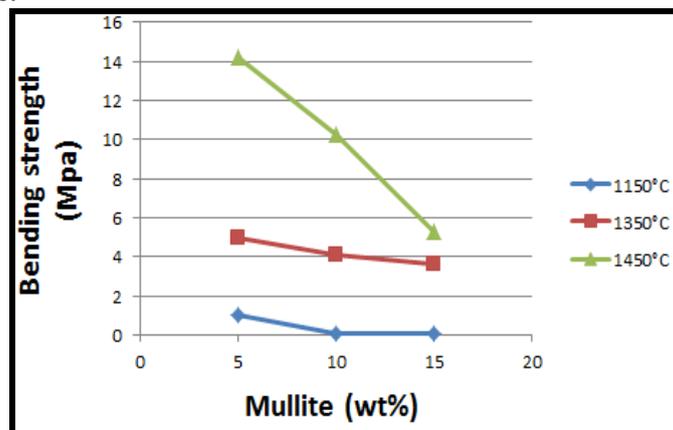


Figure (7) Variation of Bending Strength with Mullite Percentage

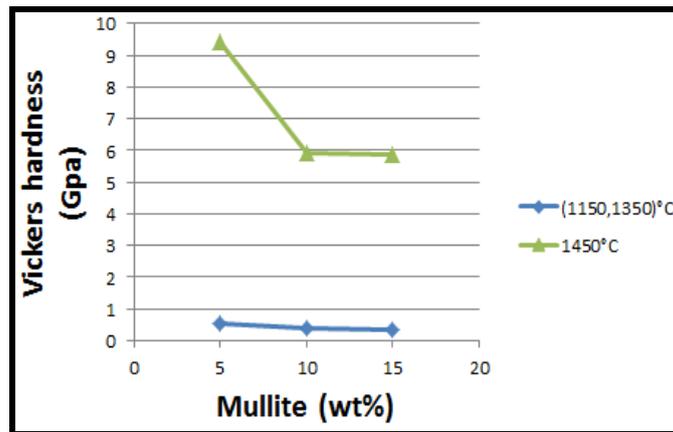


Figure (8) Variation of Vickers Hardness with Mullite Percentage.

Thermal properties

The thermal expansion coefficient is defined as the fractional change in length with change in temperature at constant pressure. The changes in the thermal expansion coefficient with respect to temperatures with different mullite content and sintered at 1150, 1350, and 1450°C shown in figure(9), figure (10), and figure (11). Generally, the thermal expansion coefficient increases in its value with increasing the temperature from 50 °C up to 800 °C. But the specimens with higher mullite content show the lowest values of thermal expansion coefficient in comparison with those specimens have lower mullite content.

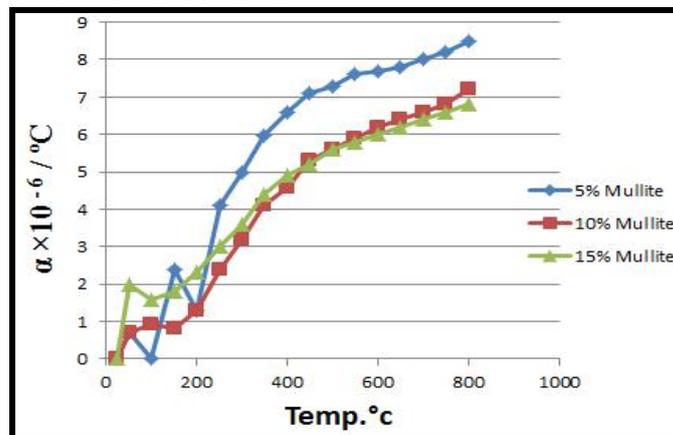


Figure (9) Thermal Expansion Coefficient of mullite-zirconia composite Sintered at 1150°C.

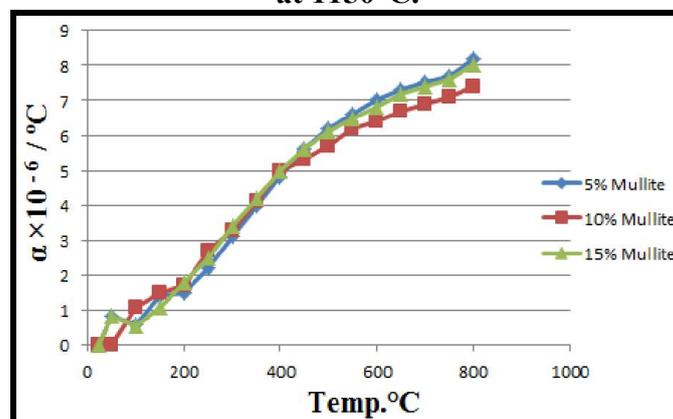


Figure (10) Thermal Expansion Coefficient of mullite-zirconia composite Sintered at 1350°C.

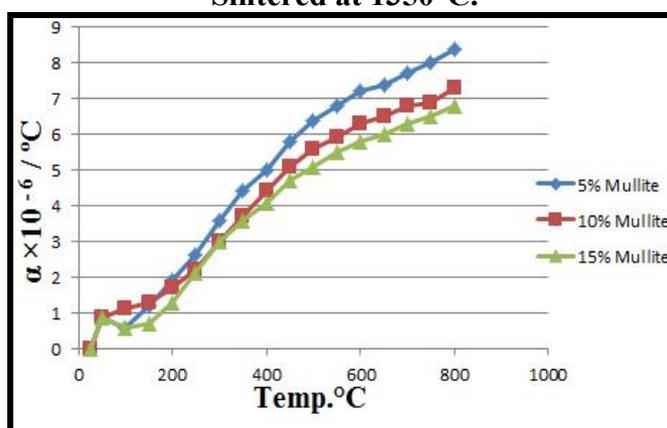


Figure (11) Thermal Expansion Coefficient of mullite-zirconia composite Sintered at 1450°C.

Conclusions

Mullite was prepared from (Aluminum powder, silica foam, and chloride hexahydrate) raw materials by sol-gel method. Prepared mullite was formed at sintering temperatures 1200 °C for 2 hr. Tetragonal –zirconia which transformation to monoclinic –zirconia after sintering at 1150°C for 2 hr. The increasing in sintering temperature up to 1350°C was caused to appear the commence of crystalline of alumina and quartz phases from the dispersed of sub-amorphous mullite components in both composite. SEM micrographs are highly confirmed the densification characteristic of mullite-zirconia composite. Physical properties (porosity, water absorption and density) of mullite-zirconia composite showed a rational behavior with the sintering temperatures as usual done of ceramic materials. Bending strength and micro-hardness for both composite were increased linearly with sintered temperatures to record the maximum values of 14.19 MPa and 9.404 GPa respectively at 1450 °C

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