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The effect of titanium and zirconium oxides additives on thermal properties of magnesium aluminate spinel

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Magnesium aluminate spinel ($MgAl_2O_4$) composites were prepared by mixing the commercial Alumina and Magnesium Oxide as starting raw materials. Titanium oxide (TiO_2) and Zirconium oxide (ZrO_2) were used as additives. The mixtures were prepared as by milling of five different combinations using zirconia balls for 1 hour each. Then Cold Isostatic Press (CIP) at 200 MPa pressed the batches. The material properties, such as porosity and density, and thermal expansion of the composites were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and the dilatometer measurements. $MgAl_2O_4$ ceramic composites are composed of spinel and garnet structures. The thermal expansion coefficients (CTE) of $MgAl_2O_4$ composites with and without TiO_2 and ZrO_2 additives under different temperature condition (25 °C to 1,300 °C) were characterized for spinel thermal expansion study and it shows that the comparison between the five different sample combinations at 1,300 °C, adding TiO_2 or ZrO_2 by small percentage gives the lowest CTE (9.89E-06, 1.02E-05) respectively, but increasing ZrO_2 increases the CTE.

Keywords: Magnesium aluminate spinel, Thermal expansion, Titanium oxide, Zirconium oxide.

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) has been known as a technologically vital material which has many applications in many different fields, such as in high temperature ceramics [1], fabricating transparent ceramics [2, 3], and catalyst support [4, 5], nuclear waste management applications [6], humidity sensors [7] and cement castables [8].

Magnesium aluminate spinel is an important refractory material because of its excellent properties such as high melting point that reach 2,105 °C, low thermal expansion, high thermal spalling, and corrosion resistance [9]. Synthesis $MgAl_2O_4$ is very challenging from the solid-state reaction route since it needs repetitive grinding and calcination steps. Some common methods, such as plasma spray decomposition of oxide and hydrothermal synthesis can be used to prepare high quality pure material. But these methods do not get a lot of attention in the commercial circle because of the use of expensive raw materials and the requirement of many processing steps [10].

It is important for the side walls, the checker work of glass tank furnace regenerators and the bottom of steel-teeming ladles. Thermal properties are important for all these applications. Increasing the temperature of a material increases the amplitude of vibration of the atoms and results in on overall increase in the volume of the material. This expansion is very critical for the structural integrity and spoiling property of the material [11]. The crystallographic structure of the $MgAl_2O_4$ spinel is simple cubic with eight formula units in one cubic unit cell [12]. The effect of particle size distribution of the spinel on the ceramic mechanical properties and thermal shock performance has been previously studied and mechanical properties of composites decreased significantly with increasing spinel content due to thermal expansion mismatch [13].

The crystallographic structure of the $MgAl_2O_4$ spinel has been reported by Kingrey [14] and illustrated in Fig. 1. The generic formula of this spinel group is AB_2O_4, which "A" represents a divalent metal ion such as magnesium, iron, nickel, manganese and zinc. The "B" represents trivalent metal ions such as aluminum, iron, chromium and/or manganese. In this study, the "A" is the magnesium and "B" is aluminum and the spinel structure is named after the mineral spinel ($MgAl_2O_4$) [15]. The positions of the A ions are nearly identical to the positions occupied by carbon atoms in the diamond structure. This could explain the relatively high hardness and high density typical of this group. The arrangements of the other ions in the structure conform to the symmetry of the diamond structure. However, they disrupt the cleavage as there are no cleavage directions in any member of this group.

The coefficient of thermal expansion (CTE) is a fundamental engineering material property that used to express the dimensional change (volume, length, etc.) of a material in response to temperature change. The

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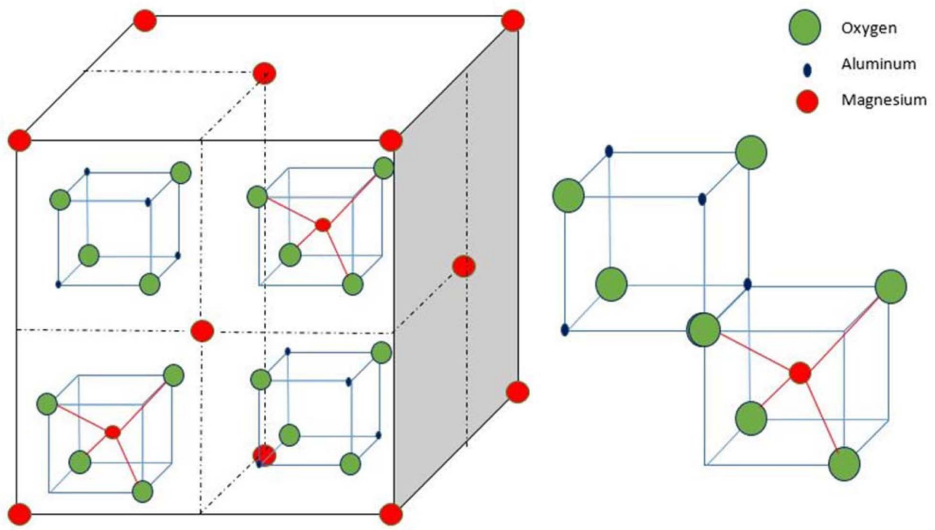


Fig. 1. Crystallographic structure of $MgAl_2O_4$ spinel (Redrawn from Kingrey [14]).

thermal expansion/ contraction behavior due to daily and seasonal temperature changes plays an important role on the degree of opening/closing of transverse cracks in concrete structures [16].

The objective of this study is the investigation the influence of TiO_2 and ZrO_2 additives on the spinel material properties and the thermal expansion. The $MgAl_2O_4$ spinel without additives will be set as a baseline composite that will be compared with the spinel with TiO_2 and ZrO_2 additives. Spinel has high melting points that allow measurements to be made over wide temperature ranges. Five different spinel compositions, were tested for thermal expansion characteristics.

Materials and Experiment Method

Commercial Alumina (Al_2O_3 with 94% purity) and Magnesium Oxide (MgO with 99% purity) were used as raw materials of the $MgAl_2O_4$ spinel. Titanium oxide (TiO_2 with 99% purity) and Zirconium oxide (ZrO_2 with 99% purity) were used as additives. Five samples were prepared for this study, sample A is a mixture of Al_2O_3 and MgO without any additives, sample B is a mixture of the $MgAl_2O_4$ spinel adding 2.44% Titanium oxide of the mixture weight, sample C is a mixture of the $MgAl_2O_4$ spinel adding 4.76% Titanium oxide of the mixture weight, sample D is a mixture of the $MgAl_2O_4$ spinel adding 2.44% Zirconium oxide of the mixture weight, and sample E is a mixture of the $MgAl_2O_4$ spinel adding 4.76% Zirconium oxide of the mixture weight. Table 1 shows the particle size analysis for MgO, Al_2O_3 and the mixture after milling for 1 h. Table 2 shows all samples with their specific weights. The five batches of 250 gm powder was prepared by milling of five different combinations using 10 small ZrO_2 balls for one hour each. Then, the batches were pressed by Cold Isostatic Press (CIP) at 200 MPa.

Table 1. Results of particle size analysis

	25%D (μm)	50%D (μm)	75%D (μm)	Mean V
MgO	2.154	4.073	6.890	3.883
Al_2O_3	4.541	13.223	115.913	18.629
Mixture	2.945	7.233	19.746	7.367

Table 2. Batch composition of samples (Raw materials and additives)

Composites Samples	Al_2O_3 Wt.%	MgO Wt.%	TiO_2 Wt.%	ZrO_2 Wt.%
A	69	31	0	0
B	67.32	30.24	2.44	0
C	65.71	29.52	4.76	0
D	67.32	30.24	0	2.44
E	65.71	29.52	0	4.76

All prepared samples then were slowly heated with the rate of 1 ºC per minute to 100 ºC with holding time 60 minutes, then to 1,750 ºC with rate of 5 ºC per minute and holding time 60 min.

For particle size analysis, MgO and Al_2O_3 powders were analyzed before and after milling the mixtures for one hour using "Shimadzu SALD-2300". The porosity (ϕ) and density (ρ) of the sintered samples was determined by the Archimedes method with water as liquid media. The following equations used to calculate the porosity and the permeability for the spinel:

$$\phi(\%) = \frac{(W_W - W_D)}{(W_W - W_S)} \times 100$$

$$\rho\left(\frac{gm}{cc}\right) = \frac{W_D}{(W_W - W_S)}$$

where:

W_D = is the wt. of dried sample (g).

Ws = is the wt. of sample measured in water (g).

W_w= is the wt. of water soaked after 24 h (g).

Thermal expansion was investigated using dilatometer (DIL 402 PC, NETZSCH Geratebau GmbH, Germany) with temperature range 25-1,300 ºC [17].

To calculate the Coefficient of Thermal Expansion (CTE) the following equation were used [18]:

$$\alpha_l = \frac{\varepsilon_l}{dT} = \frac{d_l/l}{dT}$$

where:

α_l = thermal expansion coefficient for the parameter l, K^{-1}

ε_l = dl/l is the strain for the parameter l, and,

T = is the temperature, K.

The effect of adding TiO_2 and ZrO_2 to the spinel mixture on the coefficient of thermal expansion can be calculated using equation (X) by setting sample A (when we have $MgAl_2O_4$ spinel without any additives) as a baseline to compare it with the other samples.

$$Effect\ \% = \frac{CTE(sample\ A) - CTE(x)}{CTE(sample\ A)} \times (-100)$$

For thermal shock resistance study, the samples were exposed to a temperature of 1,000 ºC for 15 min, each thermal shock cycle involved heating of the sample to 1,000 ºC for 15 min in an electric furnace, the first two cycles quenched at room temperature for 15 min, and the third cycle quenched in cold water [19].

Finally, for the X-ray analysis, the sintered samples were ground into powder using milling. The powder was placed on a sample holder and was irradiated by a monochromatic X-ray beam from an X-ray tube. The samples were examined using scanning electron microscopy (SEM) (MiniFlex 600, Rigaku, Japan) operated at 20 KV. Cu-Kα radiation passed through nickel filter was used. The range of scanning angle (2θ) used was 0º-70º. XRD of 1,750 ºC for one hour sintered sample was done to see the spinel phase.

Results and Discussion

The results of XRD, porosity and density, thermal shock resistance, scanning electron microscopy (SEM), and the thermal expansion of the spinel mixtures are presented in this section. All the analysis and integration of the results obtained previously discussed also in this section.

Phase composition by X-Ray Diffraction (XRD)

Fig. 2 shows the XRD patterns of the samples after sintering at 1,750 ºC for 1 h and milling for 1 h. In the first combination, Al_2O_3 was transformed completely to the magnesium aluminate spinel but there are still small patterns of MgO, and the same happened in the second combination when TiO_2 added but the MgO patterns were smaller than what happened in the first combination.

X-Ray Diffraction (XRD) patterns of non-additive and additive contained batches are shown in Fig. 2. The XRD pattern of 1,750 ºC sintered compositions shows the presence of spinel in both non-additive and additive contained batches. As the percentage of TiO_2 was increased, amount of spinel formation was also increased in all batches, compared to that of no additives and ZrO_2 contained batches. The highest spinel peak intensity was observed in TiO_2 containing compositions. This clearly indicates a higher rate of spinel formation occurring in these compositions. The presence of only spinel phase was observed in 5% TiO_2 containing sample, this observation of complete solid solubility of free MgO in spinel phase with TiO_2 finds similarity with the work of Sarkar and Bannerjee [20]. However, small peaks of unreacted phases were detected in all the other samples, indicating incompletion of spinel formation reaction in the batch.

This is supported by comparing with the work of Quénard et al. [21]. In addition to the spinel and ZrO_2 phases, the presence of a small amount of MgO. The relative intensity of the (200) MgO peak is similar whatever the ZrO_2 content.

When TiO_2 was increased in the third combination, MgO and Al_2O_3 were completely transformed to magnesium aluminate spinel and there was small pattern of TiO_2. When ZrO_2 was added, Al_2O_3 was transformed completely to the magnesium aluminate spinel but there are still small patterns of MgO and ZrO_2, and when the ZrO_2 percentage was increased in the fifth combination the patterns of MgO and ZrO_2 were even bigger than what happened in the fourth combination.

Porosity and density

Porosity and Density of all the sintered samples at 1,750 ºC for 1 h and 200 MPa are given in Table 3 and shown in Fig. 3. In first combination, which is without any additives, the porosity has the lowest value (0.36%). When TiO_2 added to the mixture, the porosity increased (2.30%), but when the percentage of TiO_2 increased the porosity decreased (1.23%). For ZrO_2, the porosity increases with higher percentage of ZrO_2 (0.66 at 2.5% ZrO_2 and 0.92% at 5% ZrO_2), but overall ZrO_2 gives less porosity than TiO_2 as additives.

For Density, there isn't much different with additives at different percentages, but using TiO_2 gives a lower value of density than using ZrO_2.

Thermal shock resistance and thermal expansion

No visible cracks or damaged surface of the samples were found as a results of thermal shock resistance test.

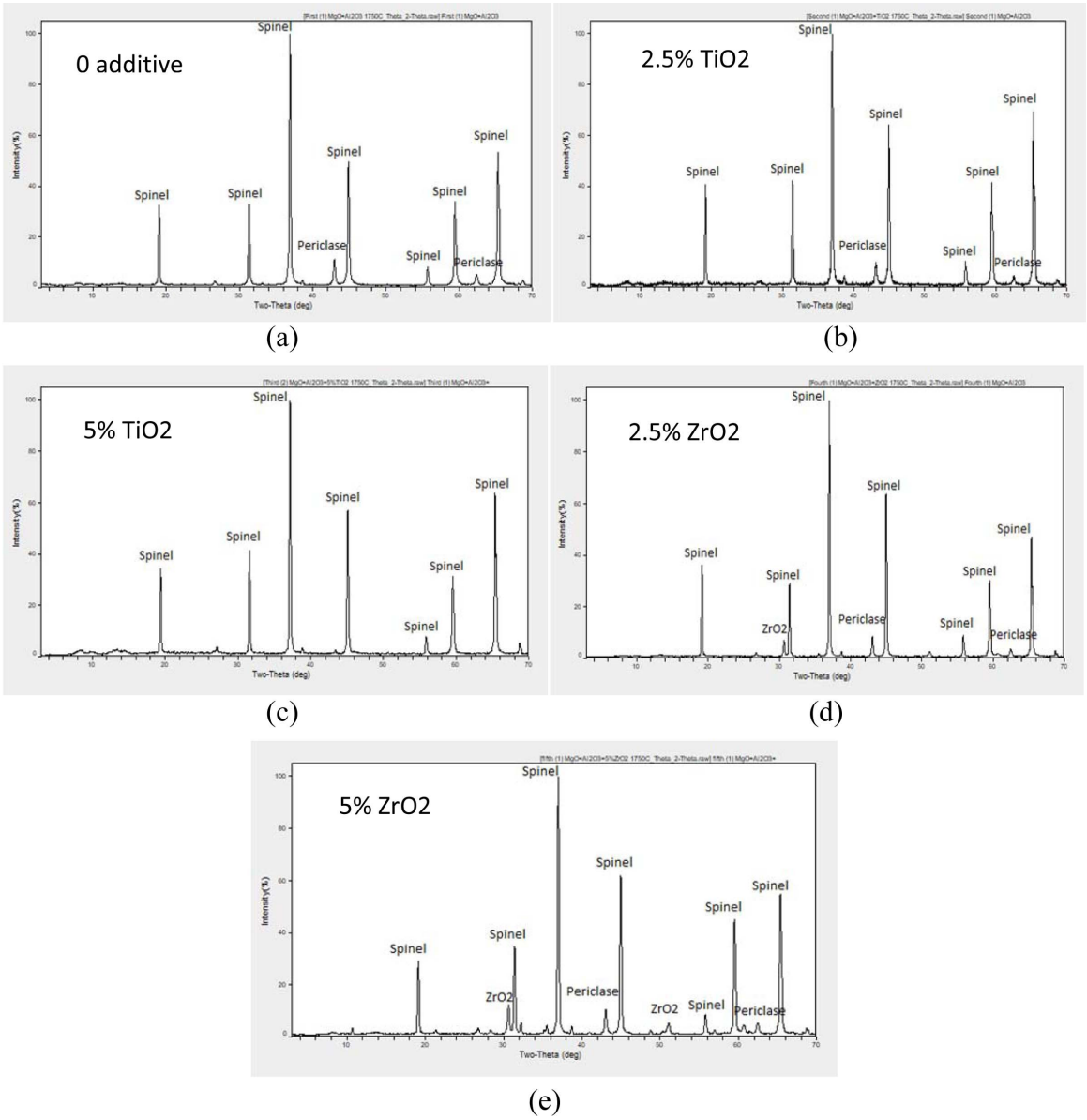


Fig. 2. Phase analysis study (XRD) of (200 MPa, 1,750 °C-1 h) sintered samples: (a) First Combination: Sample A, (b) Second Combination: Sample B, (c) Third Combination: Sample C, (d) Fourth Combination: Sample D, (e) Fifth Combination: Sample E.

Thermal expansion coefficient depends mainly on its component materials. Spinel compositions (Table 4) shows no significant spinalization reaction up to 1,000 °C. Only a small, gradual increase in expansion values is observed with increasing temperature. Above 1,000 °C, expansion values improve sharply, which marks the starting of spinel formation reaction.

The addition of TiO_2 and ZrO_2 above 1,000 °C gives a better homogeneous spinel. On increase in its growth, spherical shape particles are formed which help to achieve the crystallization of those compositions at temperatures lower than that of model spinel without adding these oxides. The fluctuation in the thermal expansion coefficient value, when the temperature is below 1,000 °C, it believes to be a result of temperature variation and rearrangement of grains.

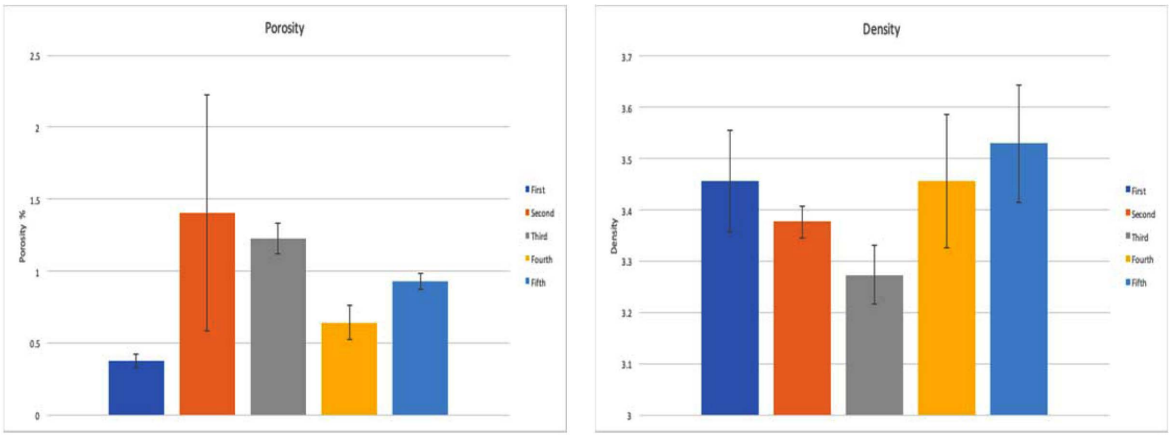
Fig. 4 shows the comparison between the five different sample combinations at 1,300 °C, adding TiO_2 or ZrO_2 by small percentage gives the lowest CTE (9.89E-06, 1.02E-05) respectively, but increasing ZrO_2 increases the CTE.

Scanning Electron Microscopy (SEM) results

The morphology of the surface of the magnesium aluminate spinel - with and without additives -are analyzed by SEM observations as shown in Fig. 5. As can be seen from this figure, the baseline sample which is the $MgAl_2O_4$ spinel without additives have smallest crystals particles (see Fig. 5(a)) that maybe contributed to that milling grind the particles and made homogenous small size particle. With adding a TiO_2 to the spinel (see Fig. 5(b)), the porosity increased because of the

Table 3. Experimental values of Porosity and Density with the theoretical density values

Sample	Dried weight (W_D) g	Soaked water (Ws) g	Sample measured in water (Ww) g	Porosity (%)	Density (g/cm^3)	Theoretical Density (g/cm3)
A	13.47	9.58	13.48	0.36	3.43	3.67
B	12.20	8.64	12.25	1. 41	3.39	3.68
C	14.74	10.29	14.80	1.23	3.27	3.68
D	11.66	8.31	11.68	0.64	3.47	3.79
E	16.19	11.64	16.23	0.93	3.52	3.73



(a) (b)

Fig. 3. Comparison between different combinations: (a) Porosity (b) Density.

Table 4. Results of CTE at different temperatures and effect % of adding TiO_2 and ZrO_2

Temperature \ Sample		A	B	C	D	E
25 °C	CTE (Mean Value) Effect %	1.58E-06	1.68E-06 6.00%	1.73E-06 9.59%	1.81E-06 14.80%	1.48E-06 -6.60%
500 °C	CTE (Mean Value) Effect %	8.50E-06	8.14E-06 -4.20%	8.38E-06 -1.36%	8.36E-06 -1.62%	8.51E-06 0.10%
1000 °C	CTE (Mean Value) Effect %	9.64E-06	9.17E-06 -4.92%	9.23E-06 -4.23%	9.31E-06 -3.39%	9.73E-06 0.91%
1300 °C	CTE (Mean Value) Effect %	1.05E-05	9.89E-06 -5.75%	1.03E-05 -1.41%	1.02E-05 -2.96%	1.06E-05 0.71%

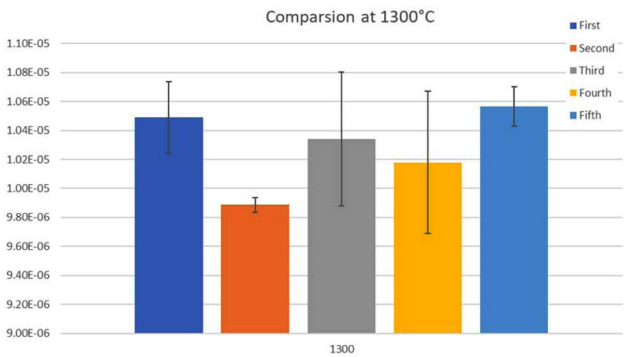


Fig. 4. Comparison of CTE for the five combinations at 1,300 °C.

excessing of the fractures that induces which led to more connected accessible channels that led the fluid to occupied that space. In Fig. 5(c), the amount of TiO_2 has been doubled and the porosity has been increased due to the induced fractured and air bubbles that is generated as a results of liberated gases from adding the TiO_2 to the mixture similar behavior has been reported by Saleh and Hassen [22]. Not that far from adding TiO_2, ZrO_2 has been added to the spinel mixture to form the sample D as we can see in Fig. 5(d). It shows an increase in porosity and fractures was clearly presented in the structure. By doubling the amount of ZrO_2 (Fig. 5(e)), the porosity has been increased allowing more isolation property and more fluid can be stored in this pours. Furthermore, it is clear that the adding TiO_2 provided more homogenous dispersion and distribution of the metal oxide particle than ZrO_2. This homogeneity agrees with thermal expansion values

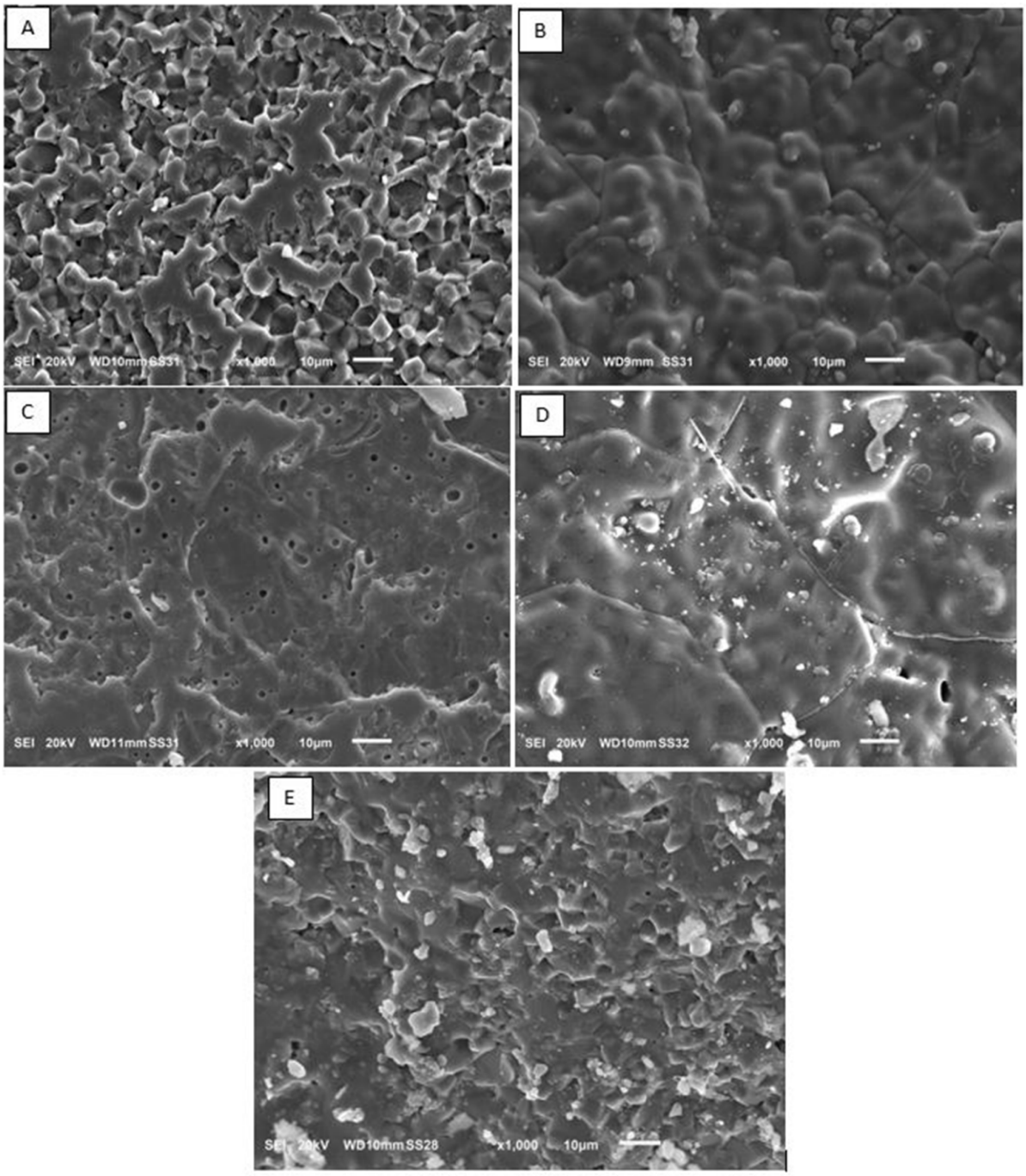


Fig. 5. SEM photograph of $MgAl_2O_4$ samples: (A) $MgAl_2O_4$ without additives (baseline sample); (B) $MgAl_2O_4$ with 2.44% TiO_2; (C) $MgAl_2O_4$ with 4.76% TiO_2; (D) $MgAl_2O_4$ with 2.44% ZrO_2; (E) $MgAl_2O_4$ with 4.76% ZrO_2.

where the reduction has been noticed in the case of adding TiO_2. At 2.44%, however, farther addition slightly improve the thermal expansion this could be due to agglomeration of the particle inside the spinel. In the other hand, this mechanism and behavior of agglomeration has been noticed in the case of ZrO_2 even at 2.44% weigh. These results indicate the advantage of adding TiO_2 and ZrO_2 for improve the thermal properties of $MgAl_2O_4$ spinel. The optimal loading of TiO_2 is 2.44% in this study.

Conclusion

In this study, different loading titanium oxide (TiO_2) and zirconium oxide (ZrO_2) were used as additives to fabricate magnesium aluminate spinel composites. The thermal expansion coefficients of these composites and porosity were analyzed. For pure spinel (without any additives), the porosity has the lowest value. However, adding TiO_2 to the mixture increases the porosity, but when the percentage of TiO_2 increased the porosity appeared to be decreasing. In other hand, increasing

loading of ZrO_2 leads to the increase in the porosity. Generally, ZrO_2 gives less porosity than TiO_2 when they added to the mixture.

In all compositions there are no significant spinalization reaction up to 1,000 ºC, but above 1,000 ºC expansion values improve sharply, which marks the starting of spinel formation reaction. The addition of TiO_2 and ZrO_2 above 1,000 ºC gives a better homogeneous spinel. At 1,300 ºC, adding TiO_2 or ZrO_2 by small percentage gives the lowest CTE.

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