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Effect of TiO_2 on the sintering behavior and microstructure of stoichiometric spinel ($MgAl_2O_4$)

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Abstract

In this work, magnesium aluminate spinel (MA) (MgO 28 wt%, Al_2O_3 72 wt%) stoichiometric compound , were synthesized via solid state reaction (SSR) Single firing stage, and the impact of sintering on the physical properties and thermal properties as well as the fine structure and morphology of the ceramic product were examined. The Spinel samples were pressed at of (14 MPa) and sintering soaking time (2h). The effect of adding oxide titania (TiO_2) was studied. The obtained powders were calcined at a temperature range of 1200 and 1400 ˚C. The calcined samples spinel were characterized by XRD, it showed the presence of developed spinel phase end also showed that the best catalyst is titania. The SEM image showed the high sintering temperature increased the regularity of the grain growth, as well as minutes from the acquisition of the spherical shape of the minutes spinel.

Key words

Spinel ($MgAl_2O_4$) ceramics,TiO_2, SSR, thermal properties.

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تأثير TiO_2 على سلوكية التلبيد و التركيب الدقيق للاسبنل المتكافئ كيميائيا $MgAl_2O_4$

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الخلاصة

في هذا البحث دُرس تحضير (الألومينا – منغنيسيا) سبنل (MA) وتم مزج هذه المواد بوزن متكافئ كيميائياً بنسب (MgO 28wt%, Al_2O_3 72wt%) وإضافة أوكسيد التيتانيوم مع السبنل، وتم استخدام طريقة تفاعل الحالة الصلبة ولمرحلة حرق واحدة ودرست الخواص الفيزيائية والحرارية والتركيب الدقيق ومورفولجية السطح. شكلت عينات السبنل بتسليط ضغط مقداره (14 MPa) من مكبس هيدروليكي. لُبدّت عينات السبنل مع إضافة (TiO_2) بدرجات حرق (1200, 1400 °C) وبزمن إنضاج (2h). ومن فحص حيود الأشعة السينية (XRD) اظهر إنّ التيتانيا عامل مساعد في عملية تسريع عملية التلبيد. وأظهرت نتائج فحص (SEM) أنّ ارتفاع درجة حرارة التلبيد تزيد من انتظام النمو الحبيبي والتجانس في تكتل دقائقه فضلا عن اكتساب الشكل الكروي لدقائق السبنل مع أفضلية عند اضافة التيتانيا ودرجة حرق (1400 ˚C). وأظهرت النتائج أنّ زيادة درجات الحرق تزيد من التبلور والنمو الحبيبي للسبنل نتيجة التلبيد الحراري مما ينعكس ايجاباً على خصائصه الفيزيائية و الخواص العزلية.

Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) is one of the most famous oxide ceramic material type with special properties e.g high mechanical strength, low thermal expansion high melting point (2135 ˚C), good thermal shock resistance coefficient, excellent resistance to acid and bases, and also having catalytic and optical properties[1-3]. Due to these desirable properties, it found widely application in optical, electric fields, metallurgical, electrochemical, radiotechnical and chemical industries [4-6]. Thus, the preparation of magnesium aluminate powders with high purity, chemical homogeneity, control of stoichiometry, fine particle size, narrow particle size distribution, and minimum particle agglomeration with high sinter activity has received considerable attention in order to improve the material properties [7]. A number of techniques such as conventional solid state reaction (SSR), sol-gel method, wet chemical method, self-heat-sustained (SHS) technique and spray drying (atomization) have been employed for the preparation of spinel ($MgAl_2O_4$) [8, 9]. The conventional solid state reaction (SSR) method is one of the method for preparation of spinel oxides. To reduce the sintering temperature of the spinal ceramics, sintering additives should be introduced. Effects of additives on the sintering of stoichiometric or nonstoichiometric spinel are reported for various additives [10]. Managed to obtain well-densified spinal body with a single – stage firing using calcined Al_2O_3, sintered MgO as starting material and $MgCl_2$ as sintering aid. Other studies have shown that the presence of additives such as B_2O_3, V_2O_5, Y_2O_3 and $MgCl_2$ help to produce a more densified spinel. Kim et al. [11] investigated the effect of SiO_2, $CaCO_3$ and TiO_2 on the sintering of spinel, and found that in case of SiO_2 and $CaCO_3$, the densification was enhanced with SiO_2 and $CaCO_3$ additives by forming glassy phases in grain boundaries; whereas the additives of TiO_2 resulted in the formation of secondary phase at grain boundaries and inside grains a long with enhanced densification. Sarker et al. [12] found that the addition of TiO_2 enhanced densification by exsolution of alumina and dissolution of TiO_2. Zagrafou et al. [13] study the effect of dopants such as Al_2O_3, MgO and SiO_2 on the sintering behavior of spinel [10]. Their study showed that the densification of spinel was highly influenced by variation in composition. Ganesh et al. [14] prepared different grades of stoichiometric and nonstoichiometric dense spinel ($MgAl_2O_4$) by conventional double-stage firing process. They found that TiO_2 and moisture present in the precursor oxides highly influence the spinel formation. Used the present study, used TiO_2 as sintering aid, stoichiometric spinel was prepared form magnesia and alumina. Sintered samples were characterized for densification, phase analysis and microstructure studies. The effect of TiO_2 addition on the thermal conductivity of sintered samples was also studied.

Experimental

A commercially available materials, magnesia (Espana source, 99% pure, polycrystalline materials with grain size 30-40micron) and fine powdered alumina (Switzeriand supplied, 99.9% pure) powdered titania (TiO_2) (India, 99% pure grain size 20-30 micron) were used as starting materials. The spinel compositions was prepared using these materials with MgO: Al_2O_3 weight ratio (MgO 28wt%, Al_2O_3 72 wt%) (stoichiometric spinel composition). The amount of TiO_2 added to the starting powder mixture varied from (0 to 8 wt%) at the interval of (2wt%). The powder mixtures were initially mixed for 5hr. in planetary ball mill (Model #8000 M, USA) using alumina balls. The powder mixtures were compacted by semi dry pressing into cylinder (50mm in height and 12mm in diameter) under a pressure of 14 MPa using 4% PVA solution as binder. The green compacts were dried at 110 $^{\circ}$C (0.5 h) and then heating at

1200 and 1400 °C for 2h in an electric furnace. During sintering process, the compacts have undergone phase transition forming ($MgAl_2O_4$) spinel. The density of the green and sintered compacts was calculated by measuring weight and volume of the compact samples. The porosity and apparent absorption of the samples was calculated by liquid absorption technique. The XRD studies were carried out by the (D2 PHASER, Bruker, USA) X-ray deffractometer (Cu Ka irradiation). The morphological studies were carried out using a scanning electron microscopy (SEM) have number (9922650, model INSPECT S50, 2013 Dutch).

Results and discussion

1. Phase analysis

XRD diffraction patterns for the produced magnesium aluminate spinel products synthesized by solid state reaction at 1200 °C firing temperature for all composition are shown in Fig.1. It was found that the strongest four peaks of the produced samples appeared at 2θ values (31.7°, 37.3°, 65.6° and 77.2°). These peaks correspond to (202), (311), (404) and (533) diffraction planes of the magnesium aluminate phase as shown in Tables 1 and 2. The peak intensities in 1200°C sintered for all compositions were found to be strong due to starting of spinel reaction, which confirms that the crystalline spinel phase formation starts below 1200 °C. At 1200 °C, spinel phase is present with the reactant Al_2O_3 and MgO phases and with increasing TiO_2 amount and firing temperature spinel phase, peak intensity has increased with a decrease in peak intensities of the reactant phases. Complete spinel formation was observed in the 1400 °C fired compositions as shown in Fig. 2. Complete spinellisation of $MgAl_2O_4$ spinel samples in the 1400 °C firing compositions occurred due to increase in surface area leading to increase in reactivity of the reactants.

The crystalline phase of $MgAl_2O_4$ spinel was identified by an (XRD). Crystallite sizes were estimated from XRD peak widths using the Scherrer equation after correction for instrumental broadening [15]:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystallite size, K is a shape factor with a value of 0.9-1.4, λ is the wavelength of the X-rays (1.54056 Å), θ is the Bragg angle and β is the value of the full width at half maximum (FWHM).

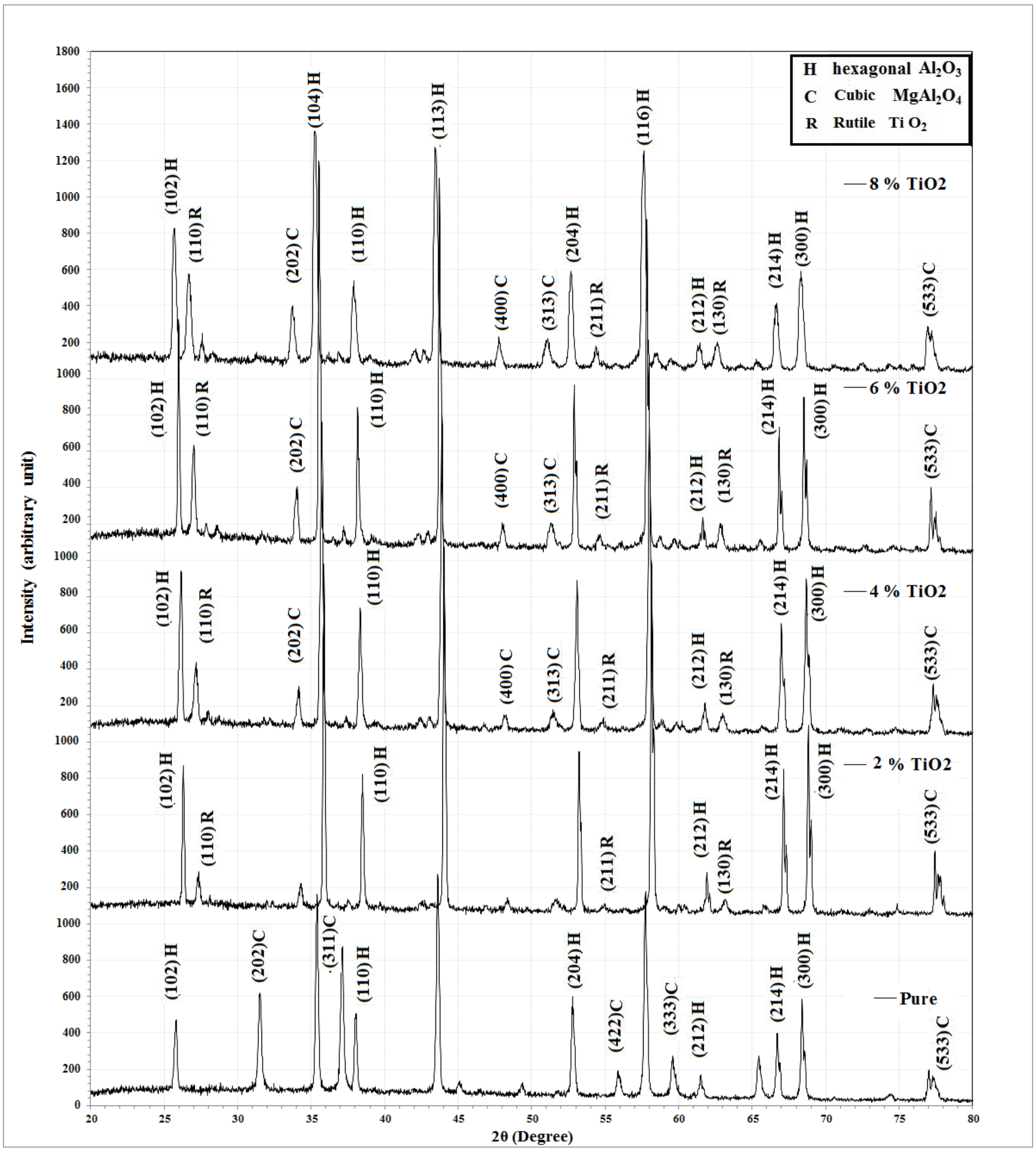

Fig. 1: XRD patterns of sintered specimens at 1200 °C with different TiO_2 content.

Table 1: The results (XRD) of the samples spinel ($MgAl_2O_4$) the addition oxide (TiO_2) in different proportions at a temperature (1200 °C).

TiO_2 %	2θ (Deg.)	FWHM (Deg.)	Intensity	d_{hkl} Exp.(Å)	C.S (nm)	d_{hkl} Std.(Å)	hkl	Phase
pure	31.4994	0.2706	549	2.8379	30.5	2.824	(202)	$MgAl_2O_4$
	37.1139	0.3383	790	2.4204	24.8	2.4083	(311)	$MgAl_2O_4$
	55.8512	0.3383	150	1.6448	26.6	1.6304	(422)	$MgAl_2O_4$
	77.0237	0.4735	175	1.2371	21.4	1.2181	(533)	$MgAl_2O_4$
2	77.4295	0.4735	367	1.2316	21.5	1.2181	(533)	$MgAl_2O_4$
4	77.2943	0.4058	314	1.2334	25.1	1.2181	(533)	$MgAl_2O_4$
6	77.1590	0.4058	389	1.2352	25.0	1.2181	(533)	$MgAl_2O_4$
8	76.9560	0.4736	247	1.2380	21.4	1.2181	(533)	$MgAl_2O_4$

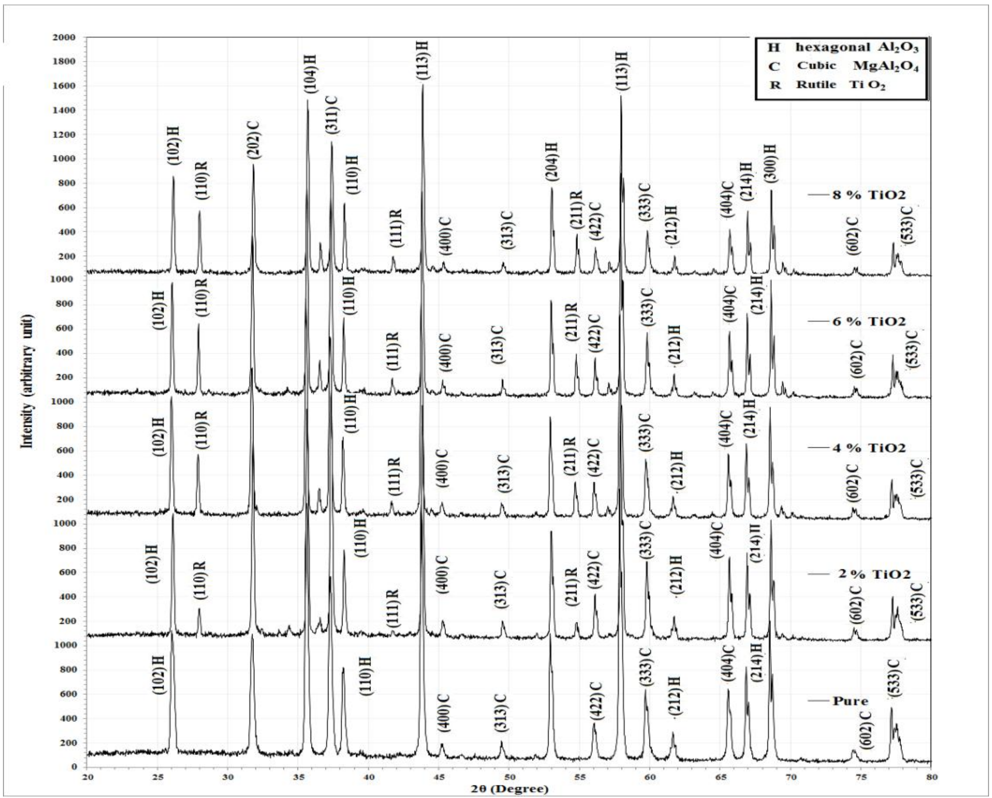

Fig. 2: XRD Patterns of sintered specimens at 1400 °C with different TiO_2 content.

Table 2: The results (XRD) of the product spinel ($MgAl_2O_4$) the addition oxide (TiO_2) in different proportions at a temperature (1400 °C).

TiO_2 %	2θ (Deg.)	FWHM (Deg.)	Intensity	d_{hkl} Exp.(Å)	C.S (nm)	d_{hkl} Std.(Å)	hkl	Phase
pure	31.7024	0.3382	1007	2.8202	24.4	2.824	(202)	$MgAl_2O_4$
	37.3168	0.2706	1489	2.4078	31.0	2.4083	(311)	$MgAl_2O_4$
	65.5242	0.3382	574	1.4234	27.9	1.412	(404)	$MgAl_2O_4$
	77.159	0.4735	449	1.2352	21.5	1.2181	(533)	$MgAl_2O_4$
2	31.7751	0.2646	1659	2.8139	31.2	2.8240	(202)	$MgAl_2O_4$
	37.3319	0.1985	2023	2.4068	42.3	2.4083	(311)	$MgAl_2O_4$
	65.6450	0.3308	669	1.4211	28.6	1.4120	(404)	$MgAl_2O_4$
	77.2216	0.4630	371	1.2344	22.0	1.2181	(533)	$MgAl_2O_4$
4	31.7089	0.1984	1230	2.8196	41.6	2.824	(202)	$MgAl_2O_4$
	37.2657	0.2646	1441	2.4109	31.7	2.4083	(311)	$MgAl_2O_4$
	65.5788	0.3969	538	1.4224	23.8	1.412	(404)	$MgAl_2O_4$
	77.2216	0.3969	262	1.2344	25.6	1.2181	(533)	$MgAl_2O_4$
6	31.7751	0.1990	1317	2.8139	41.5	2.824	(202)	$MgAl_2O_4$
	37.3319	0.1985	1579	2.4068	42.3	2.4083	(311)	$MgAl_2O_4$
	65.7111	0.3308	546	1.4198	28.6	1.412	(404)	$MgAl_2O_4$
	77.2216	0.5292	284	1.2344	19.2	1.2181	(533)	$MgAl_2O_4$
8	31.841	0.198	902	2.8082	41.6	2.824	(202)	$MgAl_2O_4$
	37.332	0.265	1070	2.4068	31.7	2.4083	(311)	$MgAl_2O_4$
	65.645	0.331	393	1.4211	28.6	1.412	(404)	$MgAl_2O_4$
	77.288	0.331	291	1.2335	30.8	1.2181	(533)	$MgAl_2O_4$

2-**Microstructure (SEM)**

In Figs. 3 and 4 image (SEM) at firing (1200 and 1400 °C) and the amount of pressure (14 MPa) the emergence of phase spinel. The addition of TiO_2 gives better homogeneity spinel conglomerate minutes and an increase in its growth and acquisition particleboard spherical shape which helps to achieve the crystallization of those at temperatures lower than those for models spinel without adding this oxide.

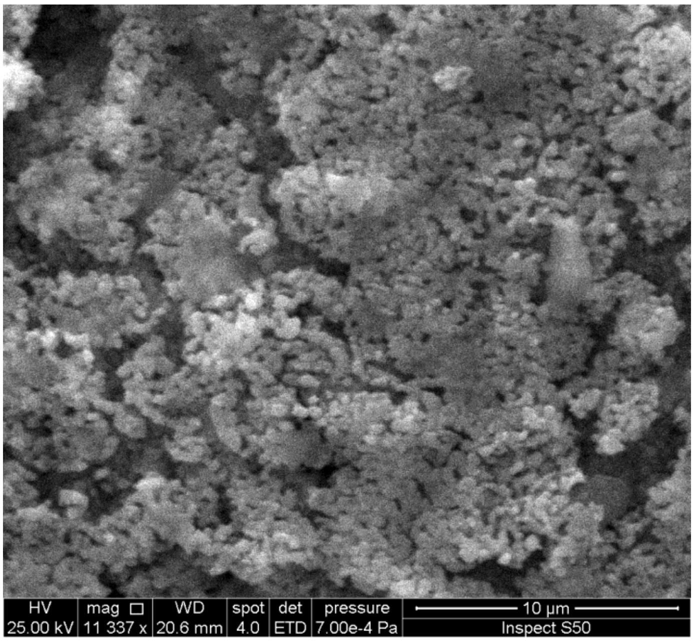

Fig.3: SEM image of spinel MA sample with additive of (8%wt TiO_2) at firing (1200 °C).

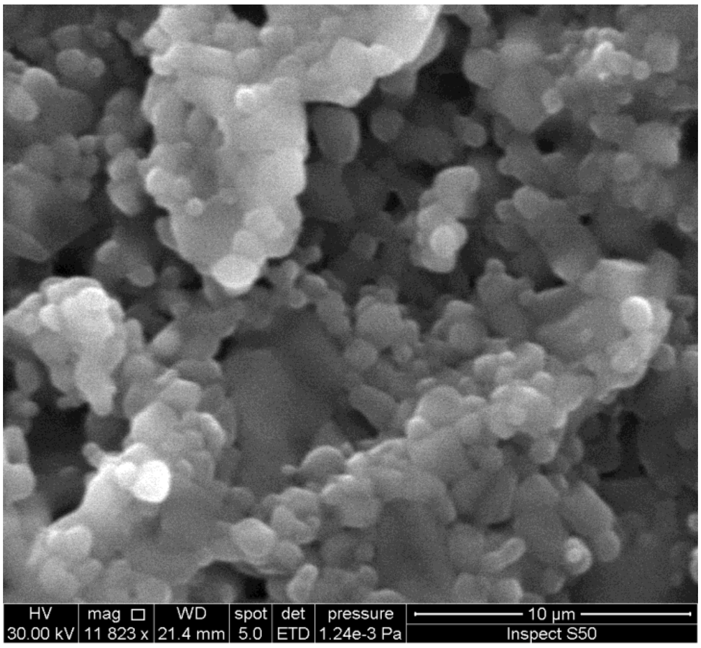

Fig. 4: SEM image of spinel MA sample with additive of (8%wt TiO_2) at firing (1400 °C).

3-Physical properties

Noting a significant increase in density at high additive ratios of TiO_2 and high temperatures burning. We find that the highest density is (1.91g / cm^3) at firing (1400 °C) as shown Fig. 5. There is a marked increase in product density increase ripening time as a result of the grain growth of spinel completeness down to complete (spinellisation process). From the equation it was calculated Density [16]:

$$\text{Density} = \frac{M}{V}\ (\text{g/cm}^3) \qquad (2)$$

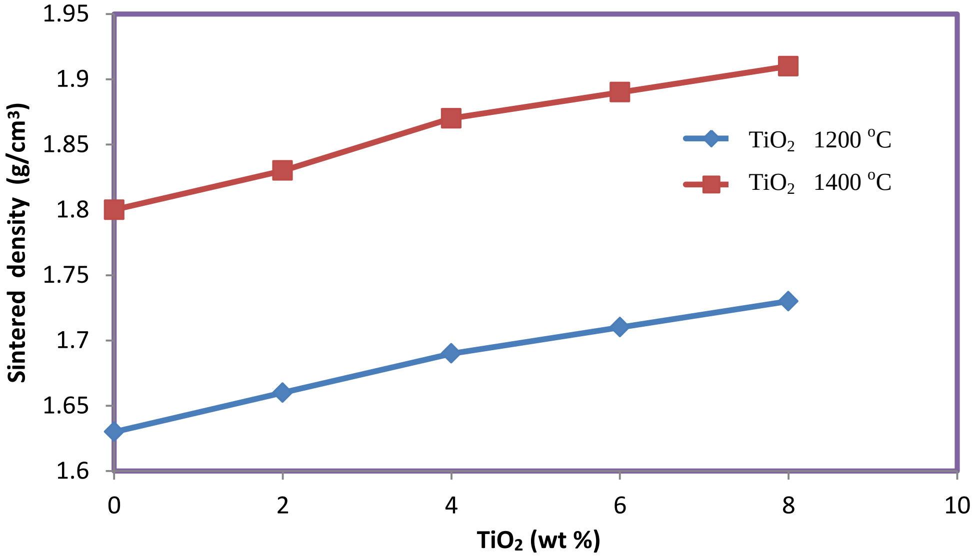

Fig. 5: Sintered density of spinel MA sample with additives (TiO_2) at firing (1200 and 1400 °C).

4- Porosity

The porosity is considered one of the important properties of the materials, ceramic and when the increase index to increase the absorbance of the product and a decrease in durability of mechanical stimuli, as porosity factors: the first important affected by the impact of the burning process and the second will be channels and voids inside the body as a result of liberated gases, that the impact of these two factors will be contrasted, as it shows the influence one of the workers superiority over the other. As reduced porosity spinel after the addition of titania oxide, which confirms its positive role as an adjunct in the sintering process, which complies with many of the previous research, we also note the advantage of titania in low porosity spinel models treated thermally burn at temperatures (1400 °C). As shown Fig. 6 at firing (1200 and 1400 °C).

From the equation it was calculated apparent porosity:

$$AP = \frac{Ws-Wd}{Ws-Wi} \times 100\% \qquad (3)$$

where W_d= the weight of the dry sample (in air). W_s = the weight of sample after saturation with kerosene (in air). W_i = the weight of the sample suspended in kerosene [5].

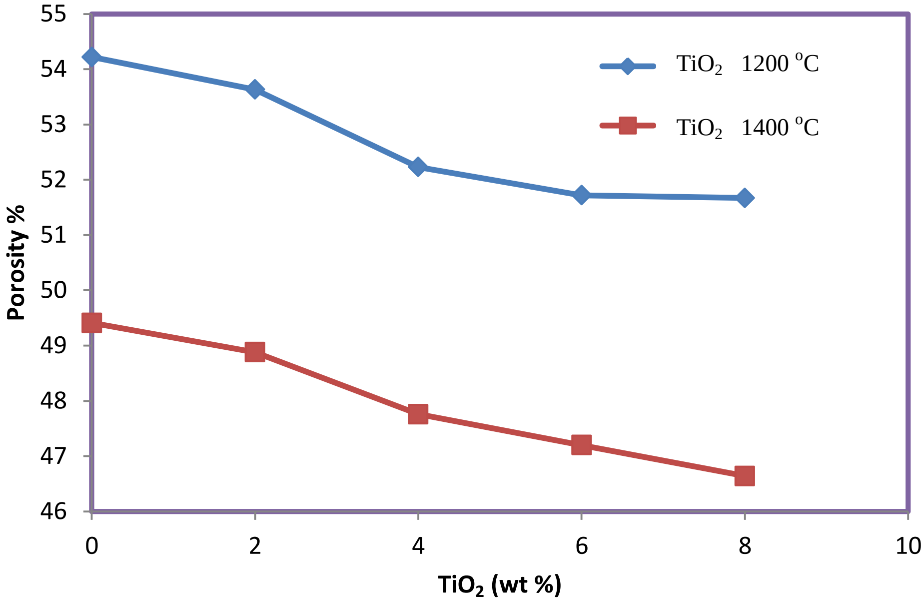

Fig. 6: The porosity of spinel MA sample with additives (TiO_2) at firing (1200 and 1400 °C)

5-Thermal conductivity

The decrease in thermal conductivity models spinel ($MgAl_2O_4$) high temperature sintering and the proportion of added and of which lead to low porosity and complete (Spinallization Process) which helps the emergence of developed spinel. The best value for thermal conductivity (5.754×10^{-3} W/cm.°C) for firing (1400 °C) from Fig.7. Lee's method was used to calculate the thermal conductivity of the $MgAl_2O_4$. From the equation it was calculated thermal conductivity:

$$Q = - KA (T_B - T_A / x) \qquad (4)$$

if; K= (W/m.°C), $A = \pi r^2$ (mm), Q: energy, x: thin, T_B- T_A: different temperatures disks.

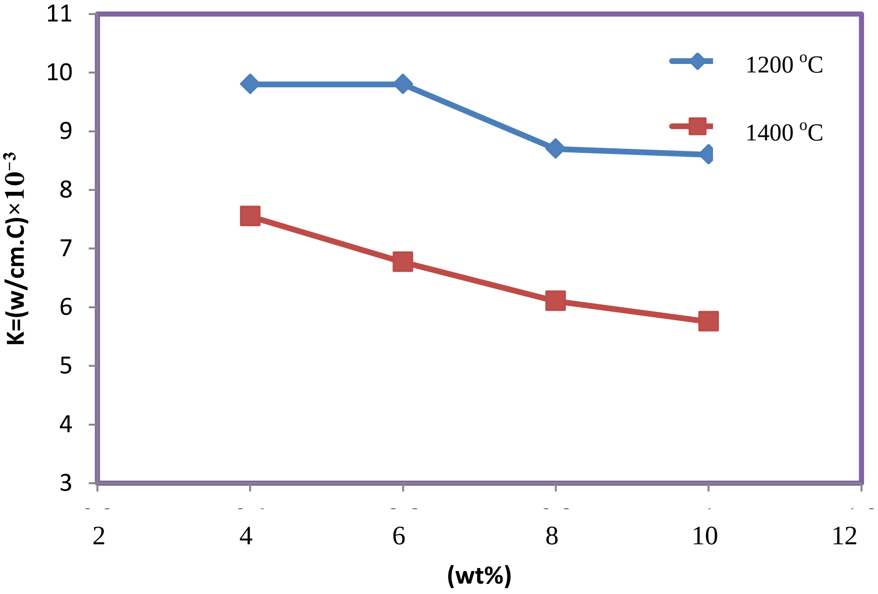

Fig. 7: Thermal conductivity of spinel MA with additives (TiO_2) at firing (1200 and 1400 °C).

Conclusions

The results showed that increasing the degree of sintering increases the crystallization and grain growth spinel result of sintering which will reflect positively on its physical properties, as well as properties Insulating. Micrographs (SEM) show that the high temperature sintering temperatures increase the regularity of the grain growth and homogeneity in the bloc minutes as well as the acquisition of spherical shape for a few minutes with spinel advantage when adding (TiO_2) by adding (8 wt%) and the degree of sintering (1400 °C). (XRD) were pattern show the existence of crystallization phase spinel. These properties can be used as a thermally and electrically insulating material

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