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Effect of calcination on the production of sintered $MgAl_2O_4$ by using different local waste Al_2O_3 powders

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Abstract Magnesium aluminate spinel is one of the important synthetic minerals which have lots of applications in ceramic, refractories and chemical industries. In this research, two different types of alumina and magnesia sources were used to produce sintered magnesium aluminate spinel. Different compositions were prepared and calcined at 1000, 1100, 1200, 1300 and 1400 °C for 2 h. Calcined spinel samples were characterized by using X-ray diffraction technique, and the amount of formed spinel after calcination was calculated. The physical properties such as bulk density, apparent porosity and the amount of formed spinel in the final sintered samples were also measured. It was shown that by increasing the calcination temperature, the amount of spinel is increased in all of the samples. The maximum amount of spinel was obtained by 1400 °C calcination of the composition that contained calcined magnesia and filter alumina powder 2. It is clarified that locally available waste filter powders can be used as alumina source to produce highly dense sintered spinel.

Introduction

Magnesium aluminate spinel is the only compound in the MgO–Al_2O_3 system, and it is an excellent refractory material because of its superior high temperature and mechanical, chemical, and thermal properties [1–6]. Spinel formation from constituent oxides is associated with 5% volume expansion which hinders the densification process [2–7]. Therefore, there is a need to calcine before sintering.

The effect of sintering temperature on the physical properties of the magnesia aluminate spinel was studied [2, 8–11], recently. Kashcheev et al. [8] produced spinel from caustic dust and alumina dust collected from electric filters and sintered at 1650 °C and achieved superior physicochemical properties with the compositions in which MgO/Al_2O_3 ratio was 0.75 [8]. Ghosh et al. [9] studied the effect of Indian magnesite on the properties of sintered spinel by utilization of calcined alumina. High bulk density was achieved at 1550 and 1600 °C for magnesia-rich spinel [9]. Sarkar et al. [2] worked on the effect of alumina reactivity of the sintered magnesia-rich magnesium aluminate spinel. They used calcined alumina at different temperatures and obtained that the reactivity of alumina has great influence on the spinelisation reaction but has no effect on sintered density [2]. Cunha et al. [10] used different bauxites and magnesia for synthesis of magnesium aluminate spinels.

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Table 1 Codes and batches of the compositions for the spinel production (wt.%)

Raw materials	Sintered magnesia (SM)	Calcined magnesia (KM)	Filter powder 1 (FT1)	Filter powder 2 (FT2)
SF1	30	–	70	–
SF2	30	–	–	70
KF1	–	30	70	–
KF2	–	30	–	70

Table 3 Specific surface area and particle size of the raw materials

Raw materials	Specific surface area (m^2/g)	d_{50} (μm)	Phase analysis	
			Major	Minor
Sintered magnesia (SM)	8.604E−01	28.38	Periclase	–
Calcined magnesia (KM)	8.672E+01	21.02	Periclase, brucite	Calcium silicate
Filter powder 1 (FT1)	6.572E+01	13.49	Corundum, gibbsite	Boehmite
Filter powder 2 (FT2)	8.644E+01	6.74	Corundum, gibbsite	Boehmite

The result of this study showed that the spinel reaction dynamics depend on the physical and chemical characteristics of both of the reactants [10]. Sarkar et al. [11] used different raw materials for producing magnesium aluminate spinel by sintering at the range of 1200–1600 °C and determined densification behaviour of spinels. They found that the spinel formation was completed at 1500 °C in all compositions and used pure materials to obtain high thermal expansion and lower density [11]. All of these studies were conducted by single firing process. Calcination process was not used and its effect of the amount of spinel formation and properties of sintered spinel properties were not obtained.

In this study, two different-grade magnesia and alumina, which are wastes of aluminium production, were used. The aim of this study was to show the usage of waste alumina sources for the sintered magnesium aluminate spinel and the effect of waste alumina sources on the properties. The effects of calcination temperature on the spinel formation and sintered spinel were also determined.

Experimental procedures

Raw materials used in spinel preparation (calcine and sinter magnesia) were provided by KUMAS Co.

(Turkey), and filter powder 1 and 2 were received from Eti Aluminyum Co. (Turkey). The raw materials were analysed by means of x-ray diffraction (XRD—Rigaku RINT-2000) to find out the existing phases. The XRD patterns were measured by using Cu K$_\alpha$ radiation in the 2θ range of 10–70° at a scan rate of 2°/min. The chemical analysis of the raw materials was determined by x-ray fluorescence (XRF—Rigaku ZSX Primus model). The specific surface area was analysed by the Brunauer–Emmett–Teller (BET) isotherm using a Quantochrome/Autosorb-1 model surface area analyser. The thermal analysis of raw materials were carried out with a thermal analyser (NETZSCH STA 409 PC/PG, Selb, Germany) from ambient temperature to 1400 °C at a heating rate of 10 °C/min. Raw materials of spinels were weighed and mixed according to Table 1. Sintered magnesia, calcined magnesia, filter powder 1, and filter powder 2 were named as S, K, F1, and F2, respectively.

These batches were milled half an hour in alumina pot. Then, the slurries were dried at 100 °C in a laboratory oven for 24 h. Powdered samples of four batches were mixed with 5 wt.% MgCl$_2$ as binder (in the form of 40 vol.% aqueous solution) and uniaxially pressed at 30 bar pressure. After pressing, the samples were calcined at 1000, 1100, 1200, 1300 and 1400 °C for 2 h at the peak temperature. In the

Table 2 Chemical analysis of raw materials (wt.%)

Raw materials	SiO$_2$	CaO	Fe$_2$O$_3$	Al$_2$O$_3$	MgO	Na$_2$O	K$_2$O	Cr$_2$O$_3$	LOI
Sintered magnesia (SM)	0.90	1.89	0.57	0.31	95.66	0.51	0.02	0.14	0.25
Calcined magnesia (KM)	0.94	1.91	0.17	0.24	83.58	–	0.01	–	12.74
Filter powder 1 (FT1)	0.10	–	0.02	80.01	–	0.76	0.18	–	18.88
Filter powder 2 (FT2)	0.08	–	0.01	92.92	0.50	0.89	0.26	–	5.31

Table 4 TG/DTA analyses results of filter powder 1 and 2

Raw materials	LOI	DTA/°C			
		Endothermic peak temperature	Name of the reaction	Exothermic peak temperature	Name of the reaction
FT1	3.35	140.8	Removed moisture	–	–
	11.07	253.3	Boehmite decomposition	–	–
	3.36	329	Gibbsite decomposition	–	–
	0.96	539.7	γ-Al_2O_3 transformation	–	–
	0.30	–	–	1201	α-Al_2O_3 transformation
FT2	3.42	127.3	Removed moisture	–	–
	1.35	286	Boehmite decomposition	–	–
	1.02	525	γ-Al_2O_3 transformation	–	–
	0.30	–	–	1175	α-Al_2O_3 transformation

literature [12], magnesium aluminate spinel crystallization temperature was observed at 1000 °C. Because of that, in this study, the minimum calcination temperature was chosen as 1000 °C. Calcination was performed at 1000, 1100, 1200, 1300 and 1400 °C in order to determine the effect of calcination temperature. All of the calcined samples were milled and pressed again and were sintered at 1700 °C for 2 h at the peak temperature. Calcined and sintered samples were characterized by XRD, and amount of spinel was calculated by using MAUD program. Bulk density and apparent porosity were measured by water displacement method using Archimedes' principle. For microstructural investigations, the samples were

Fig. 1 XRD pattern of SF1 mixture calcined at **a** 1000, **b** 1100, **c** 1200, **d** 1300 and **e** 1400 °C (S spinel, P periclase, C corundum)
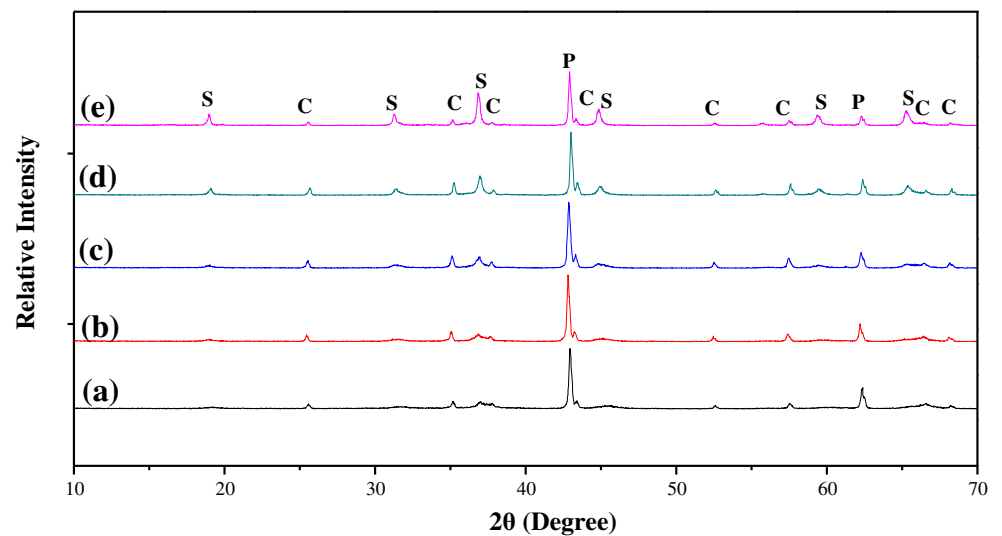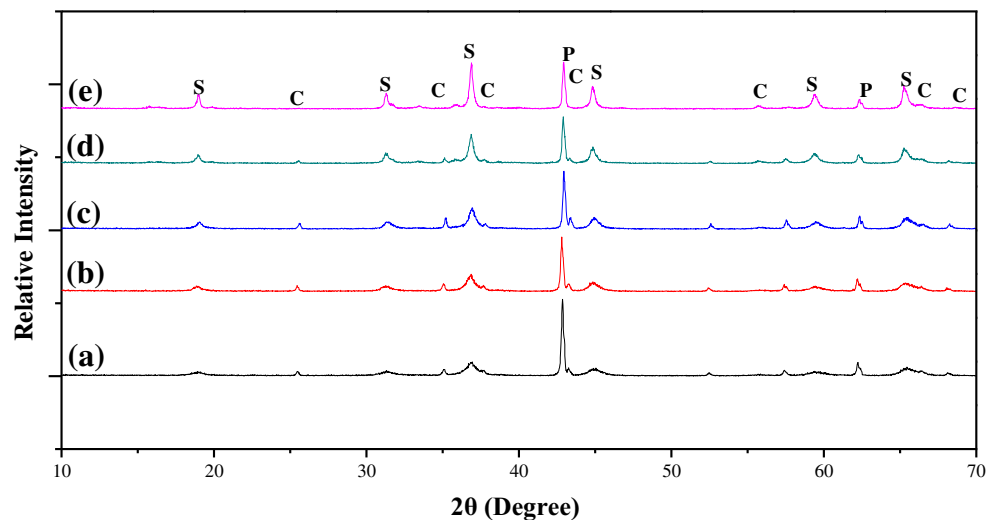
previously cut by means of diamond disc (Metacome, Germany) and then moulded by cold mounting method. Surfaces were polished by a coarse metal disc which was followed by abrasive discs (50 μm polymer disc (~1 min) and then 6 μm (~5 min), 3 μm (~5 min) and 1 μm (~3 min) abrasive papers) and finally diamond suspension for fine polishing. After surface finishing, the samples were processed via thermal etching by soaking in an electric furnace at 1500 °C for 1 h and then coated with a very thin Au–Pd coat to increase surface conductivity. The samples' surfaces were then examined by using scanning electron microscope (SEM, Zeiss Supra 50VP, Germany) equipped with energy-dispersive X-ray spectroscopy (EDS, Oxford Instruments

INCA 7430) detector. The analyses were performed at 20 kV accelerating voltage and 8–10 mm working distance.

Results and discussion

Chemical and physical properties of the raw materials are shown in Tables 2 and 3. MgO contents of sintered and calcined magnesia are 96 and 83 wt%. Al_2O_3 contents of filter powder 1 and 2 are 80 and 92 wt%, respectively. High loss of ignition (LOI) was observed in calcined magnesia due to the thermal decomposition of $Mg(OH)_2$. Specific surface areas of calcined magne-
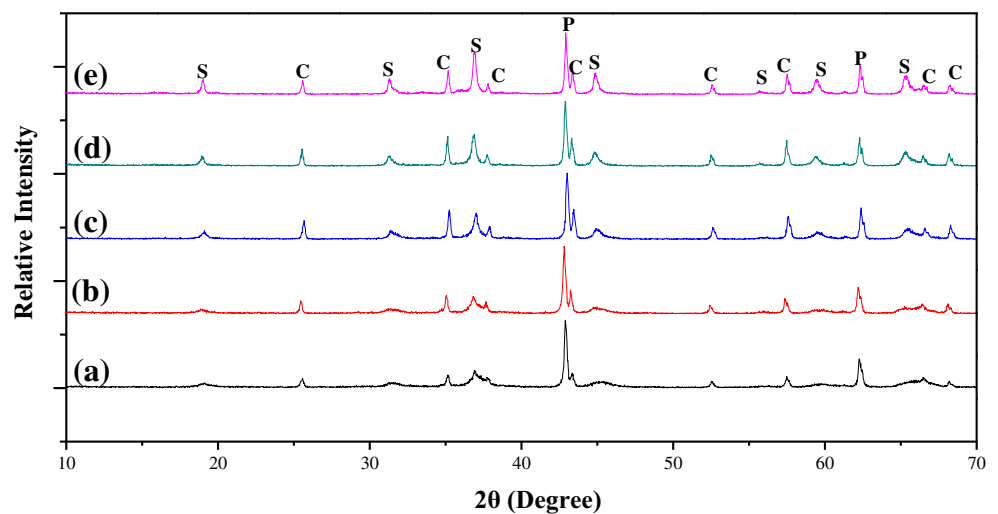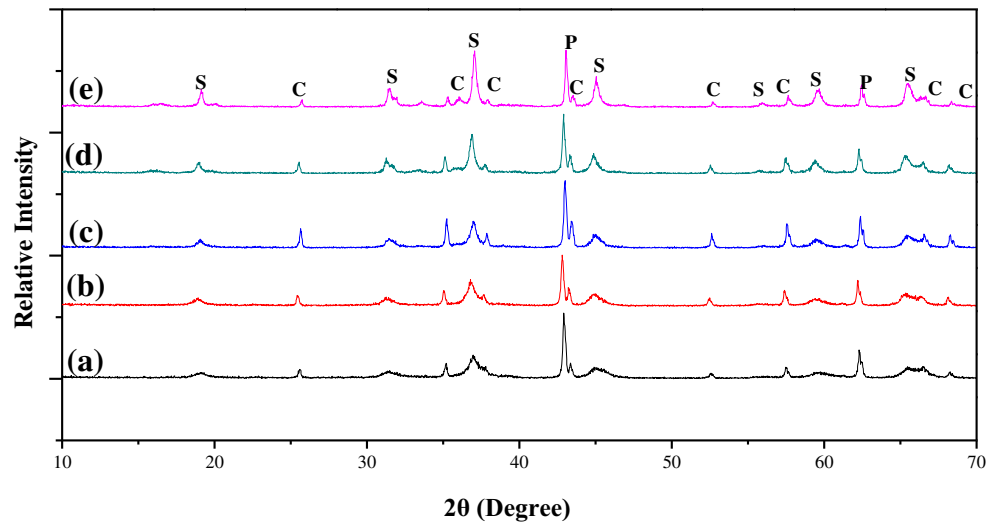
Fig. 4 XRD pattern of KF2 mixture calcined at **a** 1000, **b** 1100, **c** 1200, **d** 1300 and **e** 1400 °C (*S* spinel, *P* periclase, *C* corundum)

sia and filter powder 2 are bigger than the sintered magnesia and filter powder 1. Similarly, calcined MgO and filter powder 1 have larger particle size. All of these mean that the sinter magnesia and the filter powder 1 have less reactivity.

Table 3 also shows the existing phases in the raw materials. Periclase, brucite, and calcium silicate were present in the sintered and calcined magnesia. Filter powder 1 and 2 have gibbsite, boehmite, and corundum phases. TG/DTA analyses of filter powder 1 and 2 are also given in Table 4. FT1 shows high LOI because of boehmite decomposition.
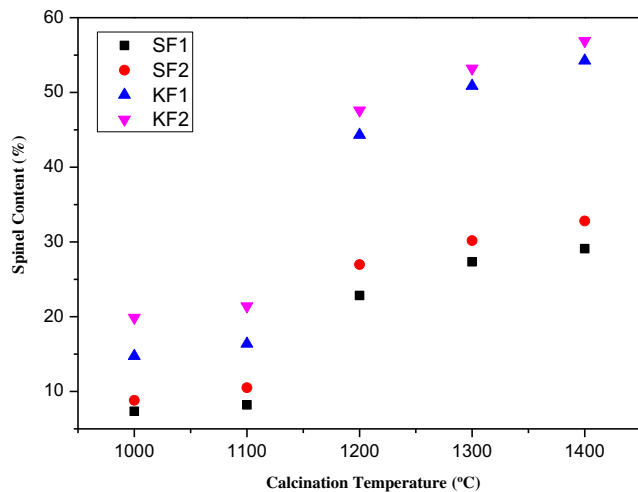

Fig. 5 Amount of spinel formation after calcination at different temperatures

The phase analyses of the different batches after calcination were determined by XRD and given in Figs. 1, 2, 3 and 4. Figure 1 represents the XRD pattern of SF1 spinel composition. Increasing the calcination temperature led to the reduction on the peak intensity at $2\theta = 25°$ which belongs to corundum.

The width of the $2\theta = 18°$ and $2\theta = 32°$ spinel peaks are not different at temperatures between 1000 and 1400 °C. On the other hand, a 32° spinel peak has larger width at 1000 °C. But, increasing calcination temperature led to sharper and more intense peaks because of increased spinel formation. The presence of unreacted corundum phase was determined in all of the calcination temperatures, but the amount of corundum decreases with increasing temperature. Figure 5 shows the effect of calcination temperature on the spinel content obtained from XRD results given in Figs. 1, 2, 3 and 4.

Spinel content of the samples was determined by using MAUD programme using the XRD patterns. Maximum spinel content was determined in KF2 composition containing calcined MgO and filter powder 2. Please remember that both of these powders have higher surface area and smaller grain sizes.

Therefore, the reactivity of these two starting powder led to increase in the spinel content. Tripathi et al. [13] also explained this situation with calcined magnesia which is more reactive than sintered magnesia according to its higher surface area.

Formation of $MgAl_2O_4$ by solid-state reaction of Al_2O_3 and MgO is explained by Wagner mechanism. The reaction proceeds by counter diffusion of the

Fig. 6 XRD pattern of sintered SF1 at 1700 °C after calcination at **a** 1000, **b** 1100, **c** 1200, **d** 1300 and **e** 1400 °C (*S* spinel, *P* periclase, *C* corundum)
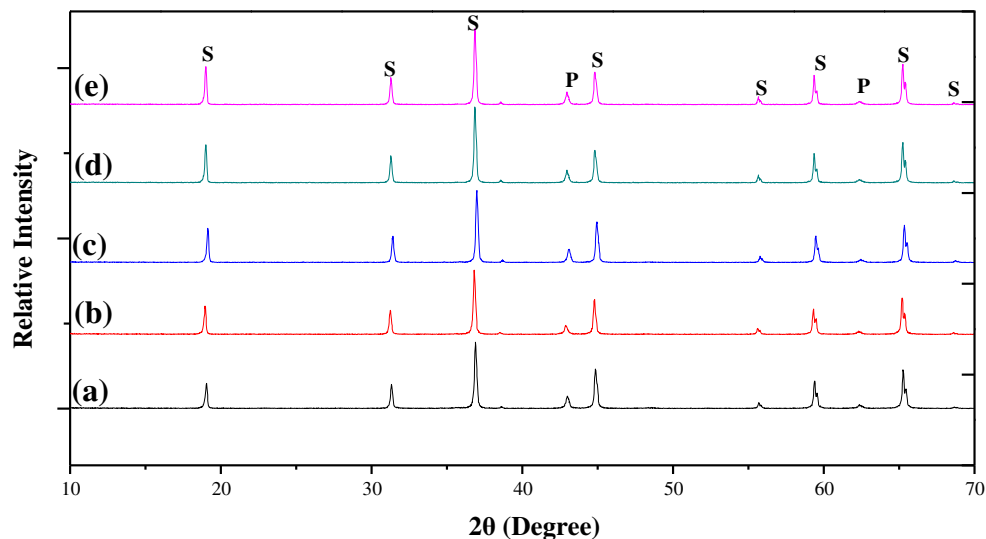
cations through the product layer, O^{2-} ions remaining at the initial sites. To retain the electroneutrality, 3 Mg^{2+} diffuse towards the alumina side and 2 Al^{3+} diffuse towards the MgO side to form 3 mol of $MgAl_2O_4$ [9]. Reduction of particle size can decrease the distance between vacancy sites (or that of grain boundaries) and enhance the vacancy diffusion to external surface and thus helped the formation of $MgAl_2O_4$. [14].

After the calcination, all the batches were subjected to grinding and pressing once more before sintering at 1700 °C. In Figs. 6, 7, 8 and 9, XRD patterns showed that two main phases were formed in all of the samples: $MgAl_2O_4$ and MgO. None of the XRD patterns showed corundum peak. Therefore, all of the corundum consumed to form spinel during sintering. On the other hand, periclase peak was observed after sintering for all of the calcination and sintering temperatures. This means that the Al_2O_3 content of the starting batches was not enough to consume all periclase. Mohapatra et al. [14] reported that residual periclase hinder the grain boundary motion and hence grain growth.

Bulk density and apparent porosity were measured by Archimedes' principle and results were presented

Fig. 7 XRD pattern of sintered SF2 at 1700 °C after calcination at **a** 1000, **b** 1100, **c** 1200, **d** 1300 and **e** 1400 °C (*S* spinel, *P* periclase, *C* corundum)
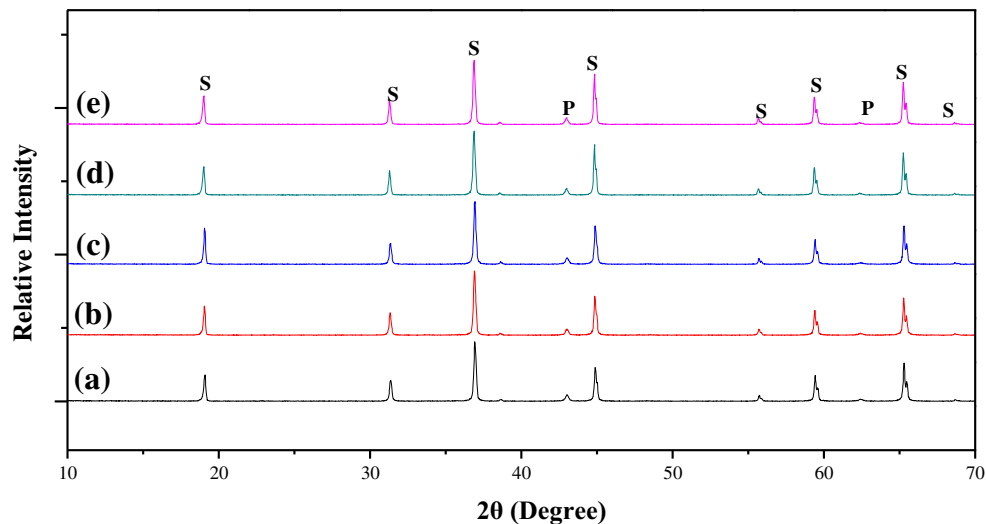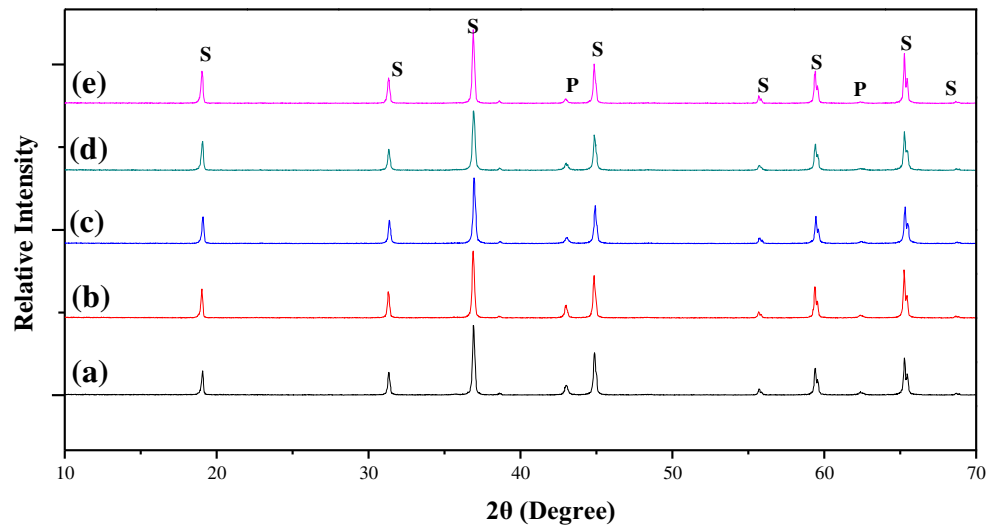
Fig. 8 XRD pattern of sintered KF1 at 1700 °C after calcination at **a** 1000, **b** 1100, **c** 1200, **d** 1300 and **e** 1400 °C (*S* spinel, *P* periclase, *C* corundum)


in Fig. 10. According to the Ghosh et al. [15], the theoretical density of magnesium aluminate spinel is equal to 3.58 g/cm^3. Obtaining very dense MgAl$_2$O$_4$ is very important for refractory applications [14]. Because of this reason, sintering stage is important like the other ceramic applications. In this study, it is found that bulk density generally increase with the increasing calcination temperature (Fig. 10). Samples having the highest bulk densities were obtained by calcination at 1400 °C and with the composition of SF2.

It can be concluded that densification was affected by the calcination temperature and the high surface area of filter powder 2. When the two different types of magnesia were used in the samples compared, it could be seen that the bulk densities were increased with the use of calcined magnesia thanks to its high specific surface area which affects the spinel formation more than densification [13]. Figure 10c shows the effect of calcination temperature on the quantity of spinel formation after sintering. KF2 coded spinel calcined at 1300 °C has the maximum amount of spinel which is 96%. When the filter powder 2 was used as an alumina source, the spinel amount was increased in all of the batch since filter powder 2 has higher surface area than filter powder 1.

Figure 11 shows the microstructures obtained by using back-scattered SEM imaging technique from polished surfaces of SF2 and KF2 spinels calcined at

Fig. 9 XRD pattern of sintered KF2 at 1700 °C after calcination at **a** 1000, **b** 1100, **c** 1200, **d** 1300 and **e** 1400 °C (*S* spinel, *P* periclase, *C* corundum)
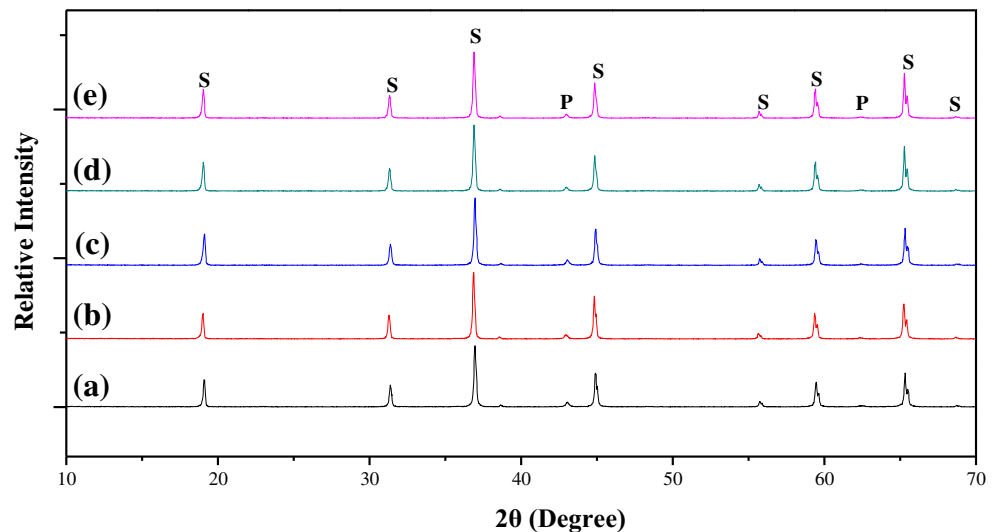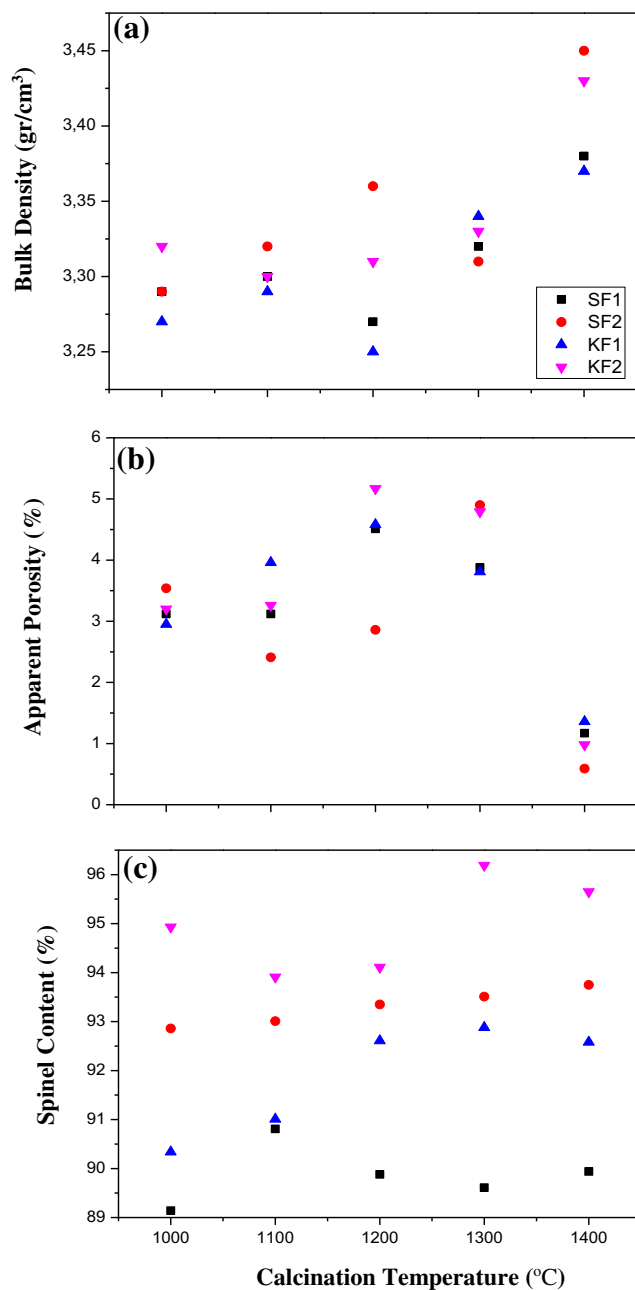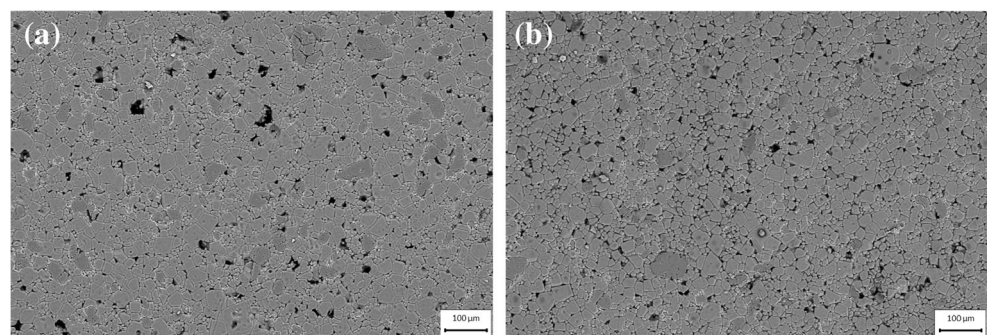
Fig. 10 **a** Bulk density, **b** apparent porosity and **c** amount of spinel sintered at 1700 °C after calcination at different temperatures

1400 °C and sintered at 1700 °C. Dark grey particles containing less heavy elements are residual periclase phases in SF2 and KF2 batches. SF2 composition has spinel grains with similar size and a homogen microstructure. The black parts in these figures may related to the holes which were generated during the surface finishing of the samples. Figure 12 shows the typical EDS analysis of the main grain phases (bright and dark grey matrix grains in Fig. 11a) of sample KF2 which had the highest amount of synthesized MA spinel phase. According to the XRD results, it revealed that the main constitution phases of the samples are MA spinel (as major) and periclase (as minor) phases after sintering at 1700 °C (Figs. 6, 7, 8 and 9). However, there was not any trace of impurity phases which could be attributed to the impurities such as Ca, Fe, Cr or other metallic elements in the final samples. EDS spectra from matrix grains of KF2 sample also show the presence of Al, Mg and O elements in spinel (Fig. 12a) and Mg and O in periclase (Fig. 12b) grain phases with no any other detectable impurities. It can be concluded that metallic impurities migrated to the boundaries or evaporated due to the high sintering temperature at 1700 °C.

Conclusions

X-ray diffraction results showed that all of the samples contained corundum and periclase phases after calcination. When filter powder 2 was used with calcined magnesia (KF2), the highest amount of spinel was obtained because of high surface area. Formation of spinel was promoted by increasing the calcination temperature. In the sintered samples, there was no corundum phase meaning that all of this phase was consumed during spinel formation, whereas MgO phase was presented in all of the compositions. KF2 sample has the highest spinel content after calcination and sintering at 1300 and 1700 °C, respectively. Maximum bulk density value
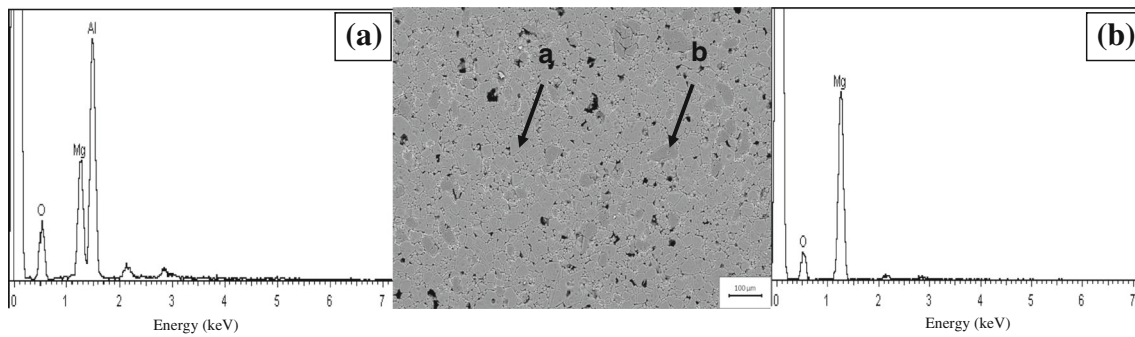

Fig. 11 Backscattered SEM images of **a** KF2 and **b** SF2 samples calcined at 1400 °C and sintered at 1700 °C

Fig. 12 EDS analysis of bright and dark grey grain phases of KF2 sample sintered at 1700 °C: **a** EDS from spinel and **b** periclase grain phases

was obtained for SF2 sample. Calcined magnesia has higher surface area than sintered one. Therefore, this increases the spinel formation in comparison to densification. It can be concluded that the calcination process before sintering is important to obtain high spinel content and also higher values of density. It is also shown that locally available waste filter powders can be used as alumina source to produce highly dense sintered spinel.

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