Effect of Zirconia Addition on Pre Formed Magnesium Aluminate Spinel

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***Abstract* - Zirconia containing ceramics have exceptionally high fracture toughness compared with other structural ceramics. Application areas vary widely from traditional uses like refractory and glass to the more advanced fields like ball-bearing, automobile appliances, turbine blades, grinding media, cutting tools, space shuttles to bio-implantations. It has the potential to toughen and / or strengthen ceramic matrix utilizing the stress-induced tetragonal to monoclinic phase transformation of ZrO_2 .In the present work monoclinic zirconia (0.5-10wt %) doped preformed $MgAl_2O_4$ Spinel powder was synthesized and characterized. The mean particle size of the spinel powder was 8.54 µm and that of zirconia was 5.67 µm. The bulk density increased gradually from 2.34 gm/cm^3 of Spinel to 2.52, 2.66, 2.86 gm/cm^3 with 10% zirconia added sample at 1350ºC/1h ,1500ºC and 1650ºC for 1 hour respectively. The apparent porosity of spinel also decreased from 33.29% to 32.00, 29.78 & 23.28% at 1350, 1500 & 1650ºC/1h respectively with 10 wt.% zirconia addition. XRD of all the compositions fired at different temperature reveals that with increase in zirconia content and temperature, transformation of monoclinic to tetragonal phase increased up to 1500ºC, but slightly decreased thereafter at 1650ºC. The mechanical strength of the spinel increased gradually with increase in Zirconia content and temperature. The compressive strength increased three fold from 9.39MPa in spinel only to 24.7MPa with 10wt% zirconia at 1350ºC. With increase in temperature to 1650ºC the fracture toughness also exhibited an increase from 40.4MPa to 82.1MPa with 10wt% zirconia.**

Keywords - $MgAl_2O_4$ Spinel, Zirconia, X ray diffraction, compressive strength, phase transformation,

1.0 INTRODUCTION.

Magnesium aluminate spinel, which is the only stable compound in the $MgO-Al_2O_3$ system, has long been considered an important ceramic material. Many studies have reported its properties, applications and different processing methods [1,2,3]. Magnesium aluminate spinel ($MgAl_2O_4$) is an excellent refractory oxide of immense technological importance as a structural ceramic. It possesses useful physical, chemical and thermal properties, both at normal and elevated temperatures. It melts congruently at 2135ºC, shows high resistance to attack by most of the acids and alkalis and has low electrical losses. Due to these desirable properties, it has a wide range of application in structural, chemical, optical, and electrical industry. It is used as a refractory in lining of steel-making furnaces, transition and burning zones of cement rotary kilns, checker work of the glass furnace regenerators, sidewalls and bottom of the steel ladles, glass furnaces and melting tanks. Synthesis and fabrication of spinel $MgAl_2O_4$ is known since long[4,5].

Zirconia is a biomaterial that has a bright future because of its high mechanical strength and fracture toughness. Zirconia containing ceramics have exceptionally high fracture toughness compared with other structural ceramics[6,7,8,9]. Application areas vary from conventional/traditional like refractory and glass to the more advanced fields like ball-bearing, automobile appliances, turbine blades, grinding media, etc. Zirconia ceramics have several advantages over other ceramic materials due to the transformation toughening mechanisms operating in their microstructure that can be manifested in components made out of them[10}. The research on the use of zirconia ceramics as biomaterials commenced about twenty years ago and presently is in clinical use in total hip replacement (THR). But research efforts are in progress for application in other medical devices.

The field of application of Magnesium aluminate spinel ($MgAl_2O_4$) is limited due to its poor mechanical properties at room temperature. The dispersion of micrometric ZrO_2 particles as a discrete second phase is a well known method for the enhancement of mechanical properties of ceramics. It has the potential to toughen and / or strengthen ceramic matrix utilizing the stress-induced tetragonal to monoclinic phase transformation of Zirconia. Magnesium-Aluminum spinel ($MgAl_2O_4$) is one of those materials that are capable of stabilizing ZrO_2 because of its higher elastic modulus than ZrO_2, and it has been shown that the fracture toughness and flexural strength of spinel could be increased by the incorporation of the ZrO_2[11,12,13]. Spinel can also be strengthened by the precipitation of Al_2O_3 along the spinel grain boundaries, resulting from the aging of Al_2O_3–rich spinel. Those second–phase precipitates within grains are known to considerably increase the high-temperature strength of a material. This precipitation-strengthening gives us another important potential benefit of ZrO_2 toughened spinel (ZTS), since the effect of transformation toughening should decrease with increasing temperatures because of decreasing driving force for the phase transformation[14,15,16,17]. Thus the combination of precipitation–strenghthening of Al_2O_3-rich spinel and ZrO_2 toughening would allow us to get desirable mechanical properties at both room and high temperatures.

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2.0 EXPERIMENTAL.

In this study, commercial grade preformed $MgAl_2O_4$ Spinel (AR78 grade, and ZrO_2 baddeleyite, were taken as starting material whose chemical compositions were analysed with XRF and is given in Table -1.

Table -1: Chemical composition and particle size of starting material

Material	ZrO_2 (%)	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	Mean particle Size (μm)
Spinel	-	-	74.46	24.79	0.31	0.005	8.54
Zirconia	97.84	0.16	-	0.69	0.16	0.14	5.67

The particle size of both Spinel and Zirconia were also measured with Galai CIS – I particle size analyzer and reported in Table 2. XRD of the starting sample was carried out using also done from Bruker D8 Advance equipment with Cu target to determine the phases present as well as the crystal size of the Spinel and Zirconia whose diffraction pattern are shown in Fig.1 & Fig.2.

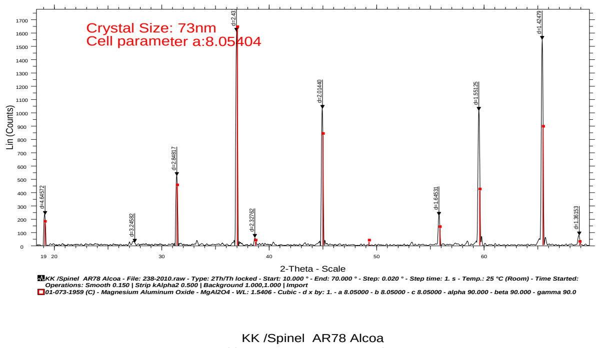

Figure 1: Diffraction pattern of Spinel AR 78

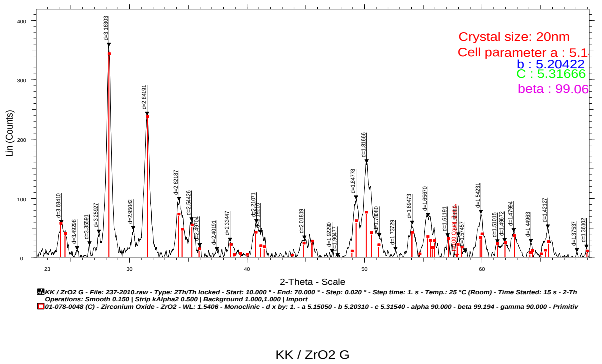

Figure 2: Diffraction pattern of Zircona green

Both the starting materials were dried in the oven at 110°C for 4 hours. Seven compositions were made by varying the Zirconia content from 0 to 10 weight percentage by keeping the spinel content fixed as shown in Table 2.

Sample Composition

Composition	Spinel (In gm)	Zirconia (In gm)
SZ-1	**100**	**0**
SZ-2	**100**	**0.5**
SZ-3	**100**	**1**
SZ-4	**100**	**2**
SZ-5	**100**	**3**
SZ-6	**100**	**5**
SZ-7	**100**	**10**

Table 2: Composition of Spinel with increasing wt % of Zirconia

All the mixed compositions were milled in Retsch make centrifugal ball mill for 8 hours in sintered alumina pot with highly sintered alumina balls of 9 moh hardness to minimize the contamination from grinding media at 100rpm by rotating alternately in clock wise and anti - clockwise direction. Dry mixing rather than wet milling was chosen to avoid the harmful effects as encountered in the experiment by Lagerlof and Dunlop(18). Development of agglomerates by the formation of hydroxides at the surface of powder was rationalized to be the cause of poor sinterability of powders milled in water. The different powder mixes were uniaxially pressed into pellets of 29 mm diameter and about 5.50 mm thick under a specific pressure of 1500kg/cm^2 in a 60T Carver lab press. The specimens were sintered in air at 1350°, 1500°, 1650°C for a period of 60 minutes after raising the temperature at the rate of 3°C per minute in 1800°C Naskar chamber furnace. The physical parameters like bulk density and apparent porosity were measured by using Archimedes' principle in water.

A sequence calcinations 1350, 1500 & 1650°C for 1h and systematic XRD analysis of $MgAl_2O_4$ spinel with zirconia ($MgAl_2O_4$-xZrO_2, where x = 0.5,1,2,3,5&10wt%) were carried out. A series of XRD phase investigation of the varied zirconia content spinel were carried out with BRUKER D8 Advance equipment. The phases present in each of the compositions and also the crystal parameters were identified with the help of Diffrac plus Eva software. TOPAS software which follow Rietveld refinement process, was used to know the crystal symmetry of all the fired samples. Mechanical behaviour of the fired samples were also measured using diametrical test method which is also known as Brazillian test with the help of 2 ton Murai Universal Testing Machine. The microstructure and morphology of the products were observed using a Scanning electron microscope (SEM, Zeiss) equipped with an energy dispersive spectroscopy (EDS, Oxford INCA). Samples were coated with gold to improve electrical conductivity prior to SEM observation.

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3.0 RESULTS & DISCUSSIONS.

3.1 Charecterization of powder

The starting material Natural Baddeleyite and Spinel were analyzed by XRF and presented in Table 1.The particle size of both the spinel and Zirconia were measured by Galai particle size analyzer. The mean particle size of spinel was 10.7µm and spinel was around 5.67µm. A lower particle size of zirconia facilitates its incorporation between the spinel particles and results in enhancing mechanical properties. The spinel is slightly alumina rich because it has around 75% alumina in the composition. Alumina rich spinel is comparatively more reactive compare to MgO rich spinel and helpful in zirconia phase transformation. The XRD pattern of starting material were also taken from BRUKER D8 Advance and evaluated by Diffrac plus eva software. The diffraction pattern of AR78 spinel confirms the total spinel phase of cubic form. The crystal size of the spinel was ~70nm. The XRD pattern of Zirconia confirms monoclinic phase whose crystal size was ~20nm which was calculated using TOPAS software following Rietveld refinement process.

3.2 Densification:

The bulk density of each of the composition fired at 1350, 1500 & 1650oC for 1 hour were measured and presented in Fig.3. It may be observed that as the zirconia addition increases the bulk density also increases steadily from 2.34 gm/cm^3(Spinel only) to a maximum 2.52 gm/cm^3 (with 10% zirconia) at 1350°C for 1 hour soaking. As the temperature increases the bulk density also increases which was from 2.48 gm/cm^3 to 2.64 gm/cm^3 at 1500°C for 1 hour and 2.66 gm/cm^3 to 2.86 gm/cm^3 at 1650°C for 1 hour.

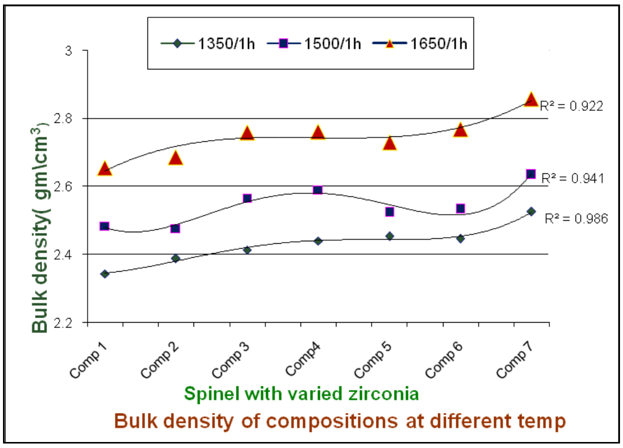

Figure 3: Bulk density of Spinel zirconia compositions fired at different temperatures

The apparent porosity also decreases with temperature as well as with increase in zirconia addition in Spinel and is presented in Fig 4. It may be seen that the apparent porosity of spinel decreases from 33.29 to 30.66 to 25.99% at 1350, 1500 & 1650°C for 1 hour respectively.

decreased.

As the Zirconia increases in the spinel from Comp1 to Comp7, the apparent porosity also decreases from 32.00 to 29.78 to 23.28% at 1350, 1500 & 1650°C for 1 hour respectively with 10 wt.% zirconia addition. Thus it can be concluded that as the density increases, the apparent porosity decreases with increase in temperature and Zirconia addition.

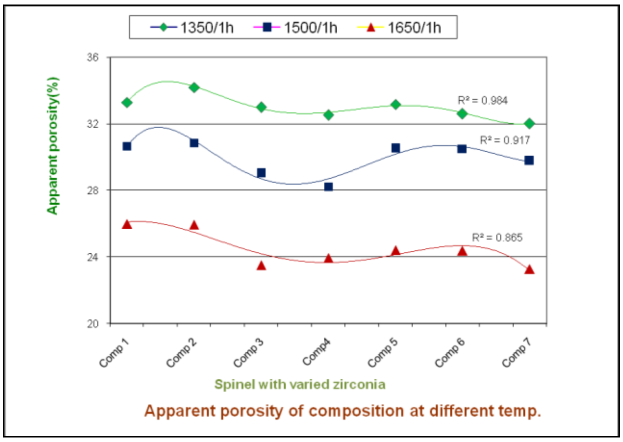

Figure 4: Apparent porosity of Spinel zirconia compositions fired at different temp.

3.3 XRD analysis

In all the systems where chemical reactions or crystallization operate through the solid phase, mass transport takes place through apparently regular crystal lattices. The particular mineral phases and degree of crystallinity of the solid phases are important controlling parameters in most solid state mechanisms[19]. X-ray diffraction analysis was carried out in order to ascertain the crystalline nature of synthesized spinel with zirconia powders. A detailed XRD analysis of higher zirconia content composition with respect to different temperatures is outlined.

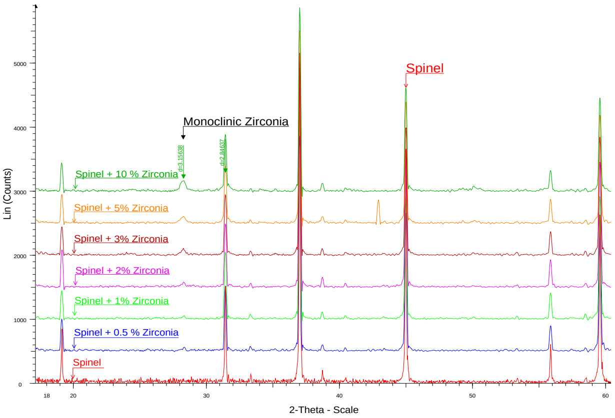

Figure 5: XRD pattern of green compact composition with varied zirconia

The XRD of the green and pressed composition were carried out which is presented in Fig 5. It may be observed that as the Zirconia content increases the Spinel decreases. Presence of monoclinic phase of Zirconia in the compositions was also observed.

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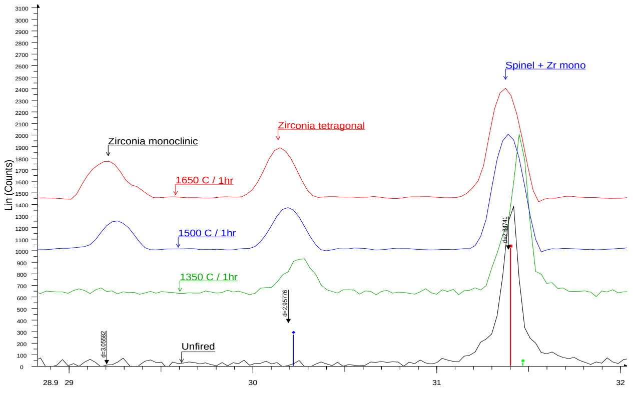

Figure 6: XRD pattern of Spinel with 5% Zirconia fired at different temp.

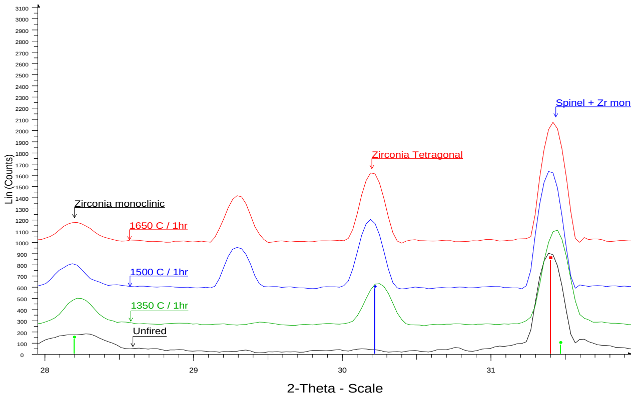

Figure 7: XRD pattern of Spinel with 10% Zirconia fired at different temp.

Phases	1350/1h	500/1h	1650/1h	1600/3h
Spinel	91.72%	91.26%	91.99%	92.34%
Baddeleyite ZrO_2 monoclinic	5.44%	4.67%	4.33%	3.36%
ZrO_2 tetragonal	2.84%	4.07%	3.69%	4.30%

Table 3: Phases present in composition with 3% Zirconia sintered at different temp. and their quantification by XRD

The phases evaluated by the software of Spinel with 3% zirconia composition are presented in Table 3.It may be noted that as the temperature increases from 1350ºC to 1650ºC the transformation of monoclinic to tetragonal phases increased from 1.18% to 1.72%. However when the sample is heated at 1600ºC for 3 hours, the volume fraction of tetragonal phase increased to 2.41%.

As increase the content of zirconia increases to 5% in the composition, more transformation of monoclinic to tetragonal phases may be observed from 1.84% to 2.68% with the temperature increased from 1350ºC to 1650ºC which are presented in Table 4. Retention of tetragonal phases also increased for higher soaking time at 1600ºC for 3 hours to 3.44%.

Phases	1350/1h	1500/1h	1650/1h	1600/3h
Spinel	95.55%	95.42%	95.55%	95.48%
Baddeleyite ZrO_2 monoclinic	2.62%	2.29%	1.77%	1.08%
ZrO_2 tetragonal	1.84%	2.29%	2.68%	3.44%

Table 4: Phases present in composition with 5% Zirconia sintered at different temp. and their quantification by XRD

Phases	1350/1h	1500/1h	1650/1h	1600/3h
Spinel	97.70%	97.38%	97.95%	96.41%
Baddeleyite ZrO_2 monoclinic	1.12%	0.85%	0.33%	1.18%
ZrO_2 tetragonal	1.18%	1.77%	1.72%	2.41%

Table 5: Phases present in composition with 10% Zirconia sintered at different temp. & their quantification by XRD

The phases evaluated by the software of Spinel with 10% zirconia composition are presented in Table 5.It may be observed that as the temperature increases from 1350 to 1500 ºC the transformation of monoclinic to tetragonal phases increased from 2.84% to 4.07%. Further increase in temperature to 1650ºC resulted in a reduction in tetragonal phase to 3.69%. The retention of tetragonal phases may be increased to 4.30% at 1600ºC due to higher soaking time.

3.4 Mechanical Behavior:

The compressive strength of each sintered compositions (set of three) fired at 1350, 1500 & 1650ºC for 1 hour were measured by universal testing machine and reported in Fig 8(20). The compressive strength of compositions fired at 1350ºC /1h increased with an increase in zirconia percentage in spinel, from 9.39MPa without zirconia to 24.7 MPa with 10% zirconia content.

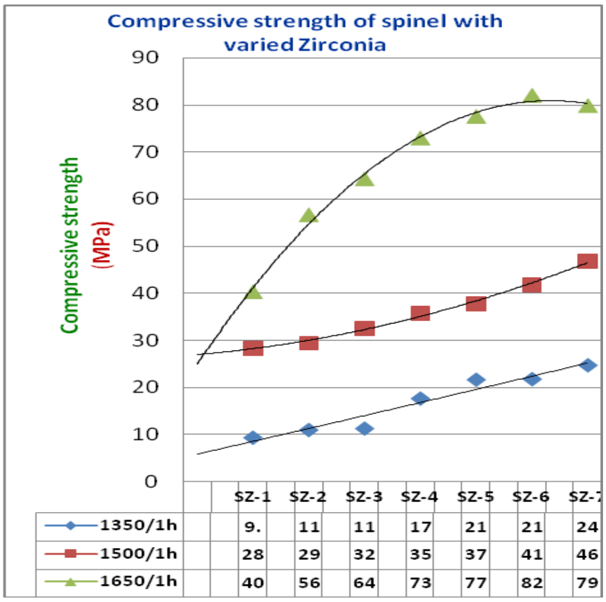

Figure 8: Compressive strength of *ZrO_2–$MgAl_2O_4$* composite at room temperature fired at 1350, 1500 & 1650ºC for 1hr.

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The compressive strength of compositions fired at 1500/1h was higher than fired composition at 1350/1h. It was observed that the fracture toughness increased from 28.3MPa without zirconia to 46.7MPa with 10% zirconia.

The compressive strength of compositions fired at 1650/1h was more than fired composition at 1350/1h. It was observed that the strength increased initially from 40.4MPa without zirconia to 82.1MPa with 5% zirconia but it again decreased slightly with higher zirconia to 79.9 MPa. This may be due to some diffusion and little less transformation of zirconia from monoclinic to tetragonal. Compared to the unreinforced spinel, a twofold increase in compressive strength was observed for materials with the highest zirconia content (10 wt%).

4.0 MICROSTRUCTURE

SEM micrographs of $MgAl_2O_4$ spinel with varied percentage of Zirconia compositions fired at 1350°C/1h, 1500°C/1h and 1650 °C /1h are shown in Figure 9, 10 and 11 respectively. The microstructures of spinel only show the grain growth with increase in temperature. In spinel with 5% of zirconia sample the zirconia can be seen dispersed in slightly white colour. The grain size can also be observed to increase with temperature. Zirconia grain are clearly visible to exist separately upto 1500°C, but at 1650°C slightly fusion of grains are seen (Fig.10C). In spinel with 10% of zirconia, more grains of zirconia are seen at lower temperature (1350°C) but at 1500°C the spinel grains are clearly visible whereas at 1650°C the grains are mostly fused (Fig.11C).

The grain growth of spinel confirm with the increase in grain size as the temperature increased. The ZrO_2 grains were small in size and occurred as intergranular grains between the $MgAl_2O_4$ grains. Grain growth of both phases was observed with increased firing temperature. Pores were eliminated at higher sintering temperature.

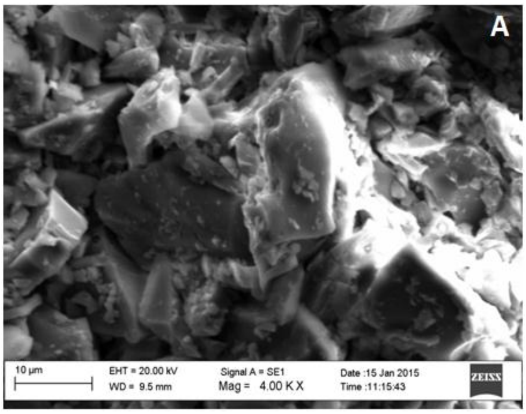

Figure 9A: SEM micrograph of Spinel fired at 1350°C / 1hr

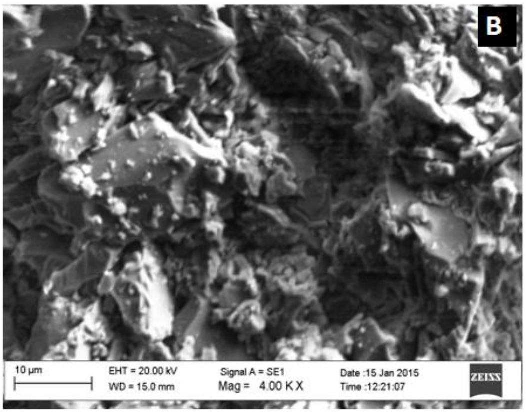

Figure 9B: SEM micrograph of Spinel with 5% zirconia fired at 1350°C / 1hr 1350°C / 1hr

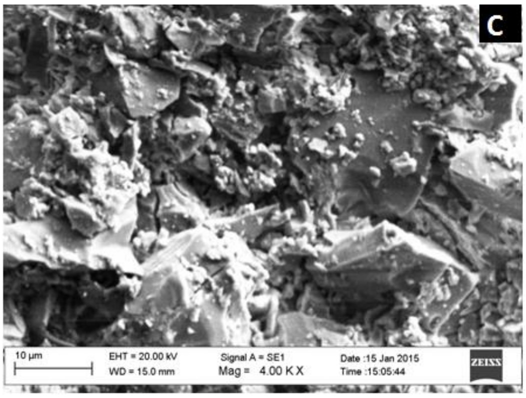

Figure 9C: SEM micrograph of Spinel with 10% zirconia fired at 1350°C / 1hr

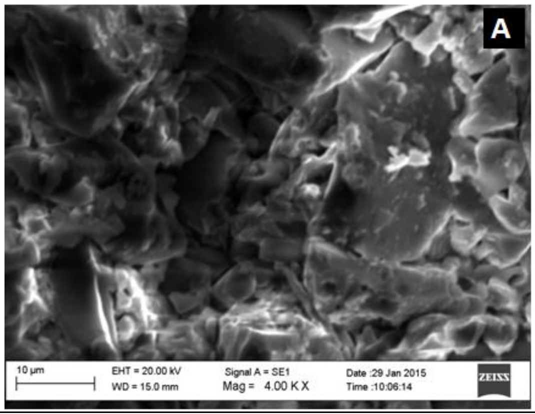

Figure 10A: SEM micrograph of Spinel fired at 1500°C / 1hr

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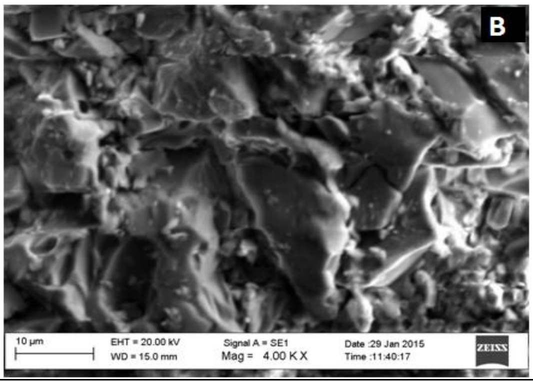

Figure 10B: SEM micrograph of Spinel with 5% zirconia fired at 1500^{o}C / 1hr

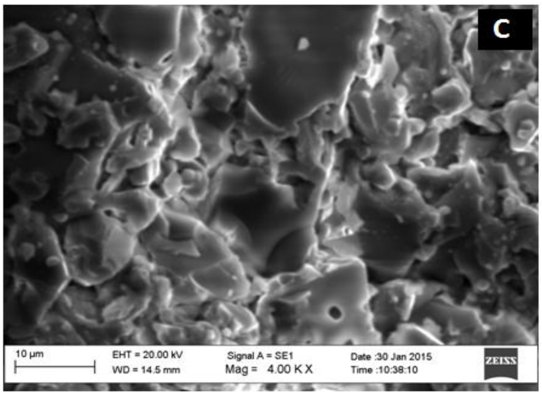

Figure 10C: SEM micrograph of Spinel with 10% zirconia fired at 1500^{o}C / 1hr

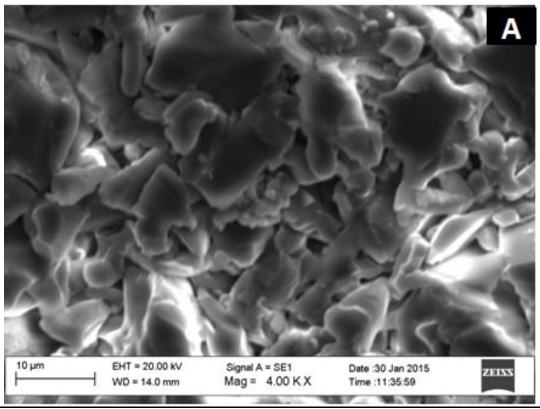

Figure 11A: SEM micrograph of Spinel fired at 1650oC / 1hr

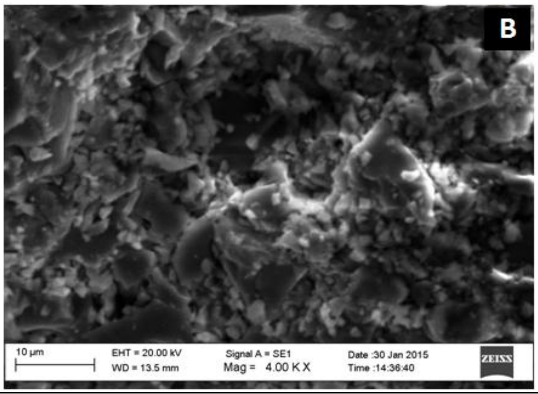

Figure 11B: SEM micrograph of Spinel with 5% zirconia fired at 1650oC / 1hr

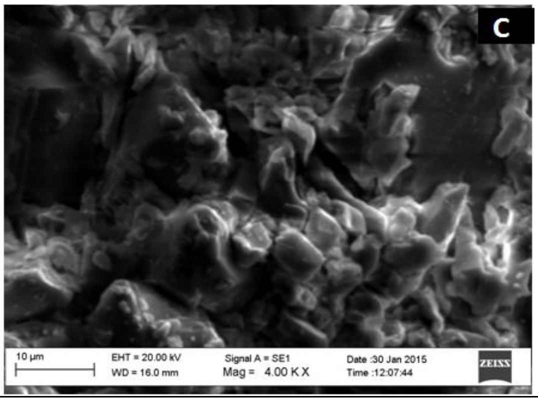

Figure 11C: SEM micrograph of Spinel with 10% zirconia fired at 1650oC / 1hr

4. CONCLUSIONS

- The zirconia (0.5-10wt %) doped MgAl$_2$O$_4$ Spinel powder was synthesized.. The phases of spinel and zirconia were also identified by XRD which confirmed the Spinel and monoclinic zirconia phases were only present in respective powders. The mean particle size of spinel and zirconia was 8.54 µm and 5.67 µm respectively.
- The densification study was carried out of the corresponding compositions. The bulk density increased gradually from 2.34, 2.48 and 2.66 gm/cm^3 of 0% zirconia Spinel to 2.52,2.64 and 2.86 gm/cm^3 with 10% zirconia added sample at 1350^{o}C,1500^{o}C and 1650^{o}C for 1 hour respectively.
- Apparent porosity also decreases with temperature as well as with increase in zirconia addition in Spinel. The apparent porosity of spinel decreases from 33.29, 30.66 and 25.99% to 32.00, 29.78 and 23.28% at 1350, 1500 & 1650^{o}C for 1 hour respectively.
- The shrinkage was 2.63% with 1% Zirconia addition in Spinel, which gradually increased to 2.98% with 10% Zirconia addition.
- XRD of all the compositions fired at different temperatures reveals that with increase in zirconia content and temperature transformation of monoclinic to tetragonal phases increased upto 1500^{o}C but slightly decreased at 1650^{o}C.
- The crystal size of spinel was also increased with increase in temperature and zirconia content. It was increased from 155nm with 3wt% zirconia composition to 262.5nm with 10wt% zirconia composition beyond at 1650^{o}C.
- The crystal symmetry of the composition also changed with increase in zirconia content with temperature. Transformation of monoclinic to tetragonal phases of zirconia increased with increase in zirconia content upto 1500^{o}C but slightly decreased at 1650^{o}C. Maximum transformation was with 10wt% zirconia composition which was around 4%.The cell mass and volume also varied with increase in temperature along with its lattice parameters.

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- The compressive strength of the compositions was also increased with increase in zirconia content and temperature. It was increased from 9.39MPa in spinel only to 24.7MPa with 10wt% zirconia at 1350ºC.As the temperature increased, the compressive strength also increased from 40.4MPa to 82.1MPa with 10wt% zirconia.
- From the microstructure it was also revealed that as the temperature increased the grain growth also increased. The ZrO_2 grains were small in size and occurred as intergranular grains between the $MgAl_2O_4$ grains.
- The microstructure at lower temperature upto1500C shown grain growth whereas with higher temperature (1650C) with 10% ZrO_2 fusion tendency of grain were visible.
- With fusion of grains at higher temperature (1650C) with higher zirconia content (10% ZrO_2) the compressive strength had tendency to decrease whereas below this temperature the zirconia grains were clearly visible and the compressive strength were increasing with zirconia content and increase in temperature .

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