ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 5, May 2014

Synthesis and Processing of Zirconia-Spinel Refractory Ceramics

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ABSTRACT- MgO-Al_2O_3 Spinel possess low mechanical property at room and high temperature . This can be improved by partial attachment of ZrO_2 to the parent spinel phase. At the attachment of these ZrO_2, its mechanical properties are highly increased. It was confirmed that at high temperature monoclinic form of ZrO_2 was changed. The Monoclinic form of ZrO_2 was changed to tetragonal or cubic form at high temperature. The general structure of MgO-Al_2O_3 is similar to the spinel structure AB_2O_4 ($MgAl_2O_4$). The article reports the preparation of zirconia –spinel (composites) using sintering method and characterization of zirconia -spinel.

KEYWORDS: Pressing, Poly Vinyl alcohol, Densification, Spinel.

I. INTRODUCTION

Spinel ($MgAl_2O_4$) is any class of mineral having a general structure are AB_2O_4 where A and B occupy some or all of the octahedral and tetra- hedral side, respectively.MgO-Al_2O_3 having a similar characteristics to the spinel ($MgAl_2O_4$) [1]. $MgAl_2O_4$ Spinel ceramic is of significant technological interest for refractory and structural applications at elevated temperature because Spinel ($MgAl_2O_4$) is a refractory material, where no liquid formation takes place with any mixture of pure magnesia and alumina at temperature below 1900 °C. The addition of ZrO_2 ceramic has significantly improved the physical and mechanical properties of MgO-Al_2O_3.Spinel is very important material for steel ,cement and refractory industries but at high temperature its mechanical strength is very low the strength can be improved by incorporation of ZrO_2 atom in parent phase[2].

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II.EXPERIMENTAL PROCEDURE

Synthesis and fabrication of Spinel $MgAl_2O_4$ is known since long. A number of techniques such as, conventional solid-state-reaction (SSR), sol-gel, spray drying (atomization) and organic gel-assisted citrate complexation, have been extensively employed . The conventional SSR method is the most utilized one in spinel preparation.

Lightly Calcined (fine powder) magnesia and calcined Al_2O_3 (fine powder) were mixed and then ZrO_2 (fine powder) are mixed. The batches were comprised of MgO-Al_2O_3 with 1-5 contains x wt% ZrO_2 where the value of x are o%, 5%, 10%, 15% 20% respectively. The batches were attrition milled for 3 h and then dried at 110°C for 24 h. The powders were shaped in pellet (piece of small shot) form using hydraulic pressing machine (uniform pressing) in the presence of 4% PVA as binder .The applied pressure are 15 tonn respectively for each sample. The samples were fired at temperatures between 1300°C and 1500°C.The heating rate was maintained at 3°C/min and soaking period was 2 hour .The Experimental procedure diagram are shown in Figure 1. The sintered sample are characterised by XRD .The Bulk density , Apparent porosity and linear shrinkage are measured the physical analysis of the sample .The addition of ZrO_2 bulk density are highly increased due to the density of ZrO_2 are high comparing to both Al_2O_3 and MgO. The apparent porosity are highly decreased. we have measured here Apparent porosity, Bulk density , linear-shrinkage ,Cold crushing strength of each composition of ZrO_2 atom at temperature 1300°C,1400°C,1500°C respectively. Two ternary eutectics and one binary pseudo-eutectic (along the ZrO2–MgAl2O4 join) were identified, as shown on the Figure 1.2 [17-19].

IJIRSET ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

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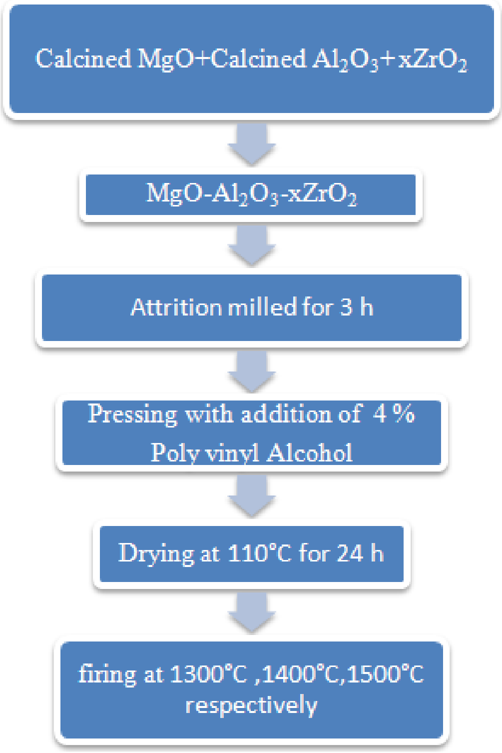

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FIGURE-1.1 EXPERIMENTAL PROCEDURE DIAGRAM OF MgO-Al_2O_3-ZrO_2

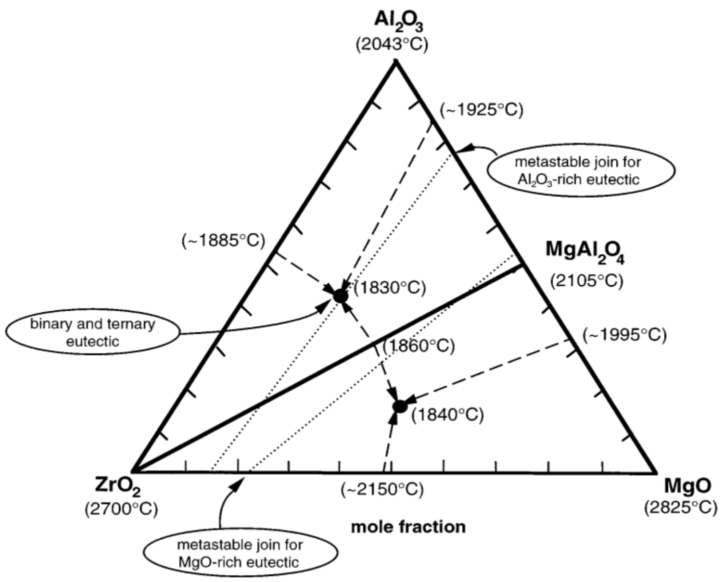

FIGURE - 1.2 PHASE DIAGRAM OF MGO-AL$_2$0$_3$-ZR0$_2$ SYSTEM

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III.RESULTS AND DISCUSSION

3.1 BULK DENSITY- The bulk density of refractory materials are measured, using the Archimedes buoyancy technique with dry weights, soaked weights and immersed weights in water (mercury, xylene or denatured alcohol if the refractory is water sensitive). The plotting figure and comparing them at temperature 1300°C,1400°C,1500°C respectively at soaking 2hour.

BD = Dry Weight / (Soaked Weight – Suspended Weight)

The bulk density are shown in Table 1 and Figure 2. It is clear from above result as the percentage of ZrO_2 are increased its bulk density are also increased .This is due to that because of increased densification in MgO-Al_20_3 at high temperature .

sample	Percent content	Temp 1300°C (BD-gm/cc)	Temp 1400°C (BD-gm/cc)	Temp 1500°C (BD-gm/cc)
1	50MgO-50Al_2O_3	3.5	3.51	3.66
2	47.5MgO-47.5 Al_2O_3-5ZrO_2	3.55	3.55	3.72
3	45MgO-45 Al_2O_3-10ZrO_2	3.6	3.61	3.78
4	42.5MgO-42.5 Al_2O_3-15ZrO_2	3.65	3.67	3.84
5	40MgO-40 Al_2O_3-20ZrO_2	3.7	3.72	3.90

Table 1 BULK DENSITY VS PERCENT CONTENT OF ZIRCONIA

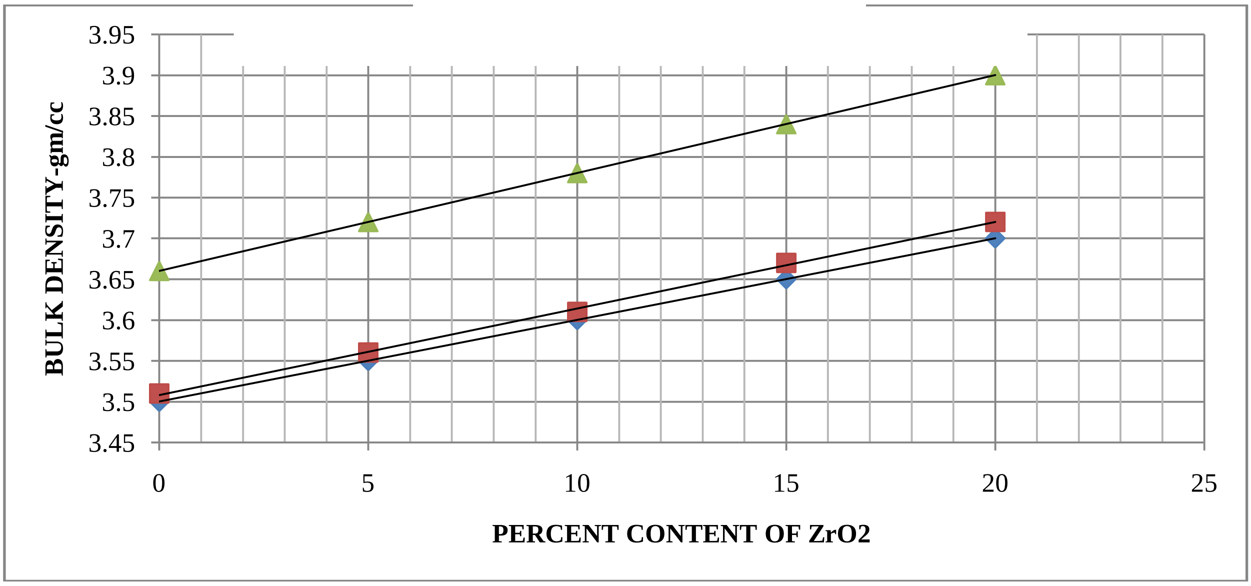

FIGURE-2 GRAPH OF BULK DENSITY VS PERCENT CONTENT OF ZIRCONIA

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3.2 APPARENT POROSITY- The apparent porosity of refractory material are inversely proportional of bulk density.The makeup of a porous body with solid, open pores and closed pores, and how water absorbed into the open porosity (by vacuum or boiling) presents when weighed either suspended or soaked. The Apparent Porosity, are calculated from the Dry, Soaked and Suspended weights as follows-
objects, connected component labelling is applied to the resultant image.(c) represents text detection by applying second set of criteria which eliminates all the objects whose area is less than 300 and filled area is less than 500.

III. CONCLUSION

% AP = (Soaked Weight - Dry Weight) x 100 / (Soaked Weight – Suspended Weight)

If percentage content of ZrO_2 are increase therefore apparent porosity are decrease in MgO-Al_20_3 -ZrO2 as shown in Table 2 and Figure 3.

sample	Percent content	Temp 1300°C(%)	Temp 1400°C(%)	Temp 1500°C (%)
1	50MgO-50Al_2O_3	17.8	15	14.8
2	47.5MgO-47.5 Al_2O_3-5ZrO_2	15.8	13.2	13
3	45MgO-45 Al_2O_3-10ZrO_2	12.8	11.9	11.7
4	42.5MgO-42.5 Al_2O_3-15ZrO_2	11	9.2	9
5	40MgO-40 Al_2O_3-20ZrO_2	9.8	8.9	8.7

Table 2 APPARENT POROSITY VS PERCENT CONTENT OF ZIRCONIA

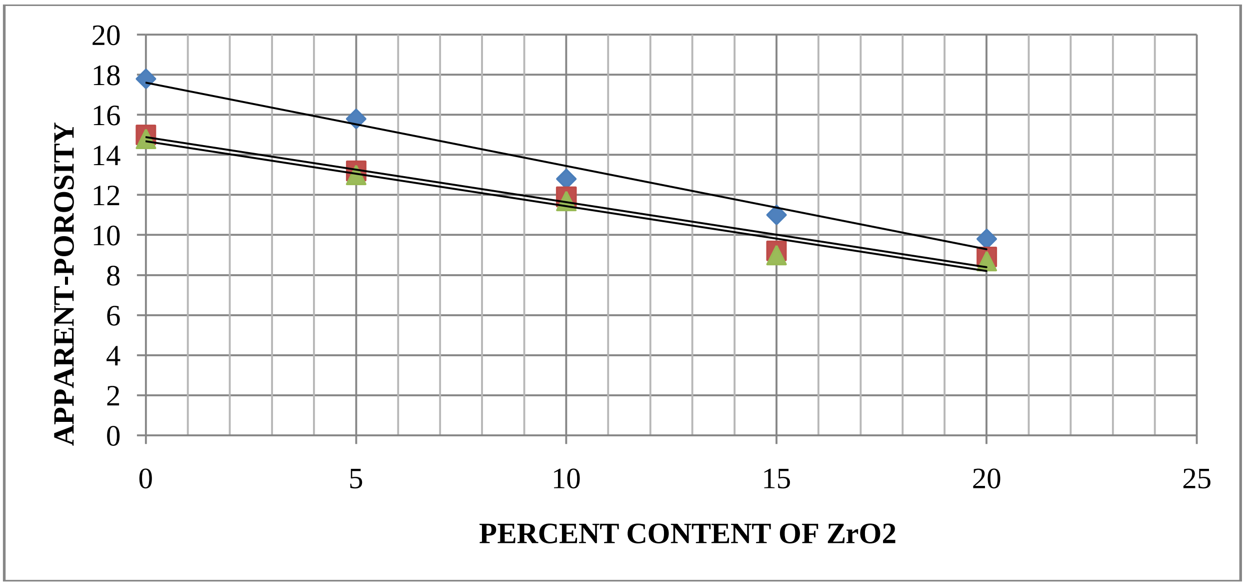

FIGURE-3 GRAPH OF APPARENT POROSITY VS PERCENT CONTENT OF ZIRCONIA

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3.3 MEASUREMENT OF COLD CRUSHING STRENGTH-

The cold strength of a refractory material is an indication of its suitability for use in refractory construction. (It is not a measure of performance at elevated temperatures) These test methods ASTM C 133 are for determining the room temperature flexural strength in 3-point bending (cold modulus of rupture) or compressive strength (cold crushing strength), or both, for all refractory products. Considerable care must be used to compare the results of different determinations of the cold crushing strength or modulus of rupture. The specimen size and shape, the nature of the specimen faces (that is, as-formed, sawed, or ground), the orientation of those faces during testing, the loading geometry, and the rate of load application, may all significantly affect the numerical results obtained. Comparisons of the results between different determinations should not be made if one or more of these parameters differ between the two determinations. The relative ratio of the largest grain size to the smallest specimen dimension may significantly affect the numerical results. For example, smaller, cut specimens containing large grains may present different results than the bricks from which they were cut. Under no circumstances should 6- by 1- by 1-in. (152- by 25- by 25-mm) specimens be prepared and tested for materials containing grains with a maximum grain dimension exceeding 0.25 in. (6.4 mm).

Cold crushing strength is the load at which cracks appear in the specimen. The test piece was prepared to standard size of 76.2 mm cube on a flat surface. The test piece was fired in a furnace at 1500°C, The temperature maintained for 2hours, 4hour respectively. It was cooled to room temperature and then placed on a compressive strength tester. Loads were applied axially by turning the hand wheel at a uniform rate until failure occurred. The load that caused cracks was then recorded.

Cold crushing strength (CCS) was calculated using the formula-

CCS - LOAD APPLIED / AREA

The Table 3.1 , and Figure 4.1, shows the indication of improvement of cold crushing strength by the partial attachment of zirconia.

sample	Percent content	Temp 1300°C	Temp 1400°C	Temp 1500°C
1	$50MgO\text{-}50Al_2O_3$	250 n/cm2	253 n/cm2	264 n/cm2
2	$47.5MgO\text{-}47.5\ Al_2O_3\text{-}5ZrO_2$	255 n/cm2	256 n/cm2	267 n/cm2
3	$45MgO\text{-}45\ Al_2O_3\text{-}10ZrO_2$	256 n/cm2	258 n/cm2	269 n/cm2
4	$42.5MgO\text{-}42.5\ Al_2O_3\text{-}15ZrO_2$	258 n/cm2	264 n/cm2	275 n/cm2
5	$40MgO\text{-}40\ Al_2O_3\text{-}20ZrO_2$	260 n/cm2	268 n/cm2	280 n/cm2

Table 3 .1 COLD CRUSHING VS PERCENT CONTENT OF ZIRCONIA AT SOAKING PERIOD 2h

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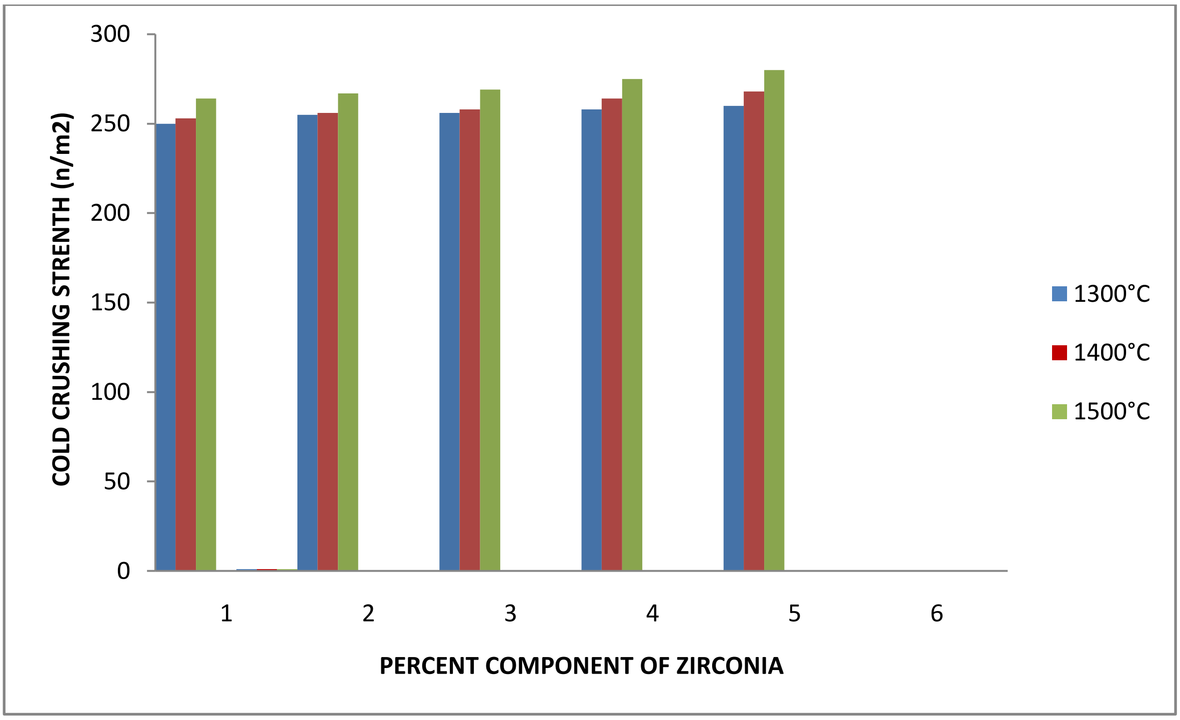

FIGURE-4 .1 COLD CRUSHING VS PERCENT CONTENT OF ZIRCONIA AT SOAKING PERIOD 2h

The Table 3.2 , and Figure 4.2, shows the indication of improvement of cold crushing strength by the partial attachment of zirconia

sample	Percent content	Temp 1300°C	Temp 1400°C	Temp 1500°C
1	50MgO-50Al2o3	287 n/cm2	355 n/cm2	456 n/cm2
2	47.5MgO-47.5Al2o3-5zro2	293 n/cm2	365 n/cm2	477 n/cm2
3	45MgO-45Al2o3-10zro2	305 n/cm2	408 n/cm2	489 n/cm2
4	42.5MgO-42.5Al2o3-15zro2	356 n/cm2	445 n/cm2	533 n/cm2
5	40MgO-40Al2o3-20zro2	404 n/cm2	467 n/cm2	567 n/cm2

Table 3.2 COLD CRUSHING VS PERCENT CONTENT OF ZIRCONIA AT SOAKING PERIOD 4h

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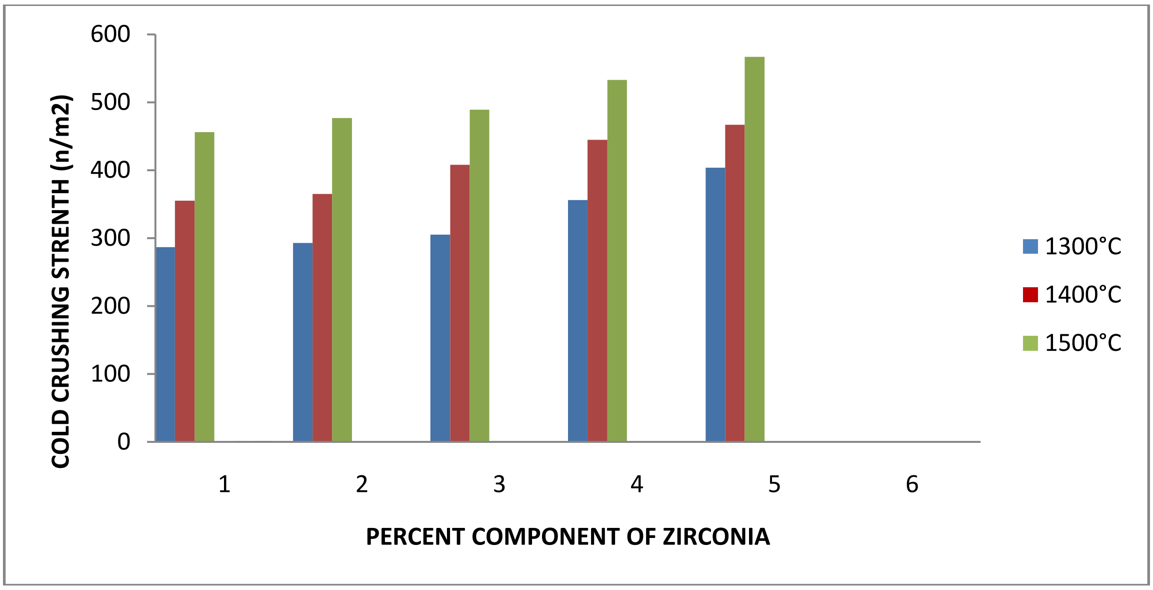

FIGURE-4 .2 COLD CRUSHING VS PERCENT CONTENT OF ZIRCONIA AT SOAKING PERIOD 4h

3.4 SHRINKAGE CHARACTERISTICS-- The PLC and the reversible thermal expansion are followed in the design of refractory linings for provision of expansion joints. Linear Change (PLC) on reheating and cooling of the bricks give an indication on the volume stability of the product as well as the adequacy of the processing parameters during manufacture.As the percentage of ZrO_2 are increased its shrinkage are decreased . This is due to that because of increased densification in $MgO-Al_20_3$ at high temperature by attachment of zirconia. The plotting graph and comparing them at temperature 1300°C,1400°C,1500°C respectively .Initially we take a soaking time 2 hour as shown in Table 4 and Figure 5. Any material when heated expands, and contracts on cooling. The reversible thermal expansion is a reflection on the phase transformations that occur during heating and cooling.

sample	Percent content	Temp 1300°C	Temp 1400°C	Temp 1500°C
1	50MgO-50Al2o3	19.3	19.3	19.3
2	47.5MgO-47.5Al2o3-5zro2	19.2	19.2	19.2
3	45MgO-45Al2o3-10zro2	18.4	18.4	18.4
4	42.5MgO-42.5Al2o3-15zro2	18.3	18.3	18.3
5	40MgO-40Al2o3-20zro2	18.3	18.3	18.3

Table 4 SHRINKAGE VS PERCENT CONTENT OF ZIRCONIA

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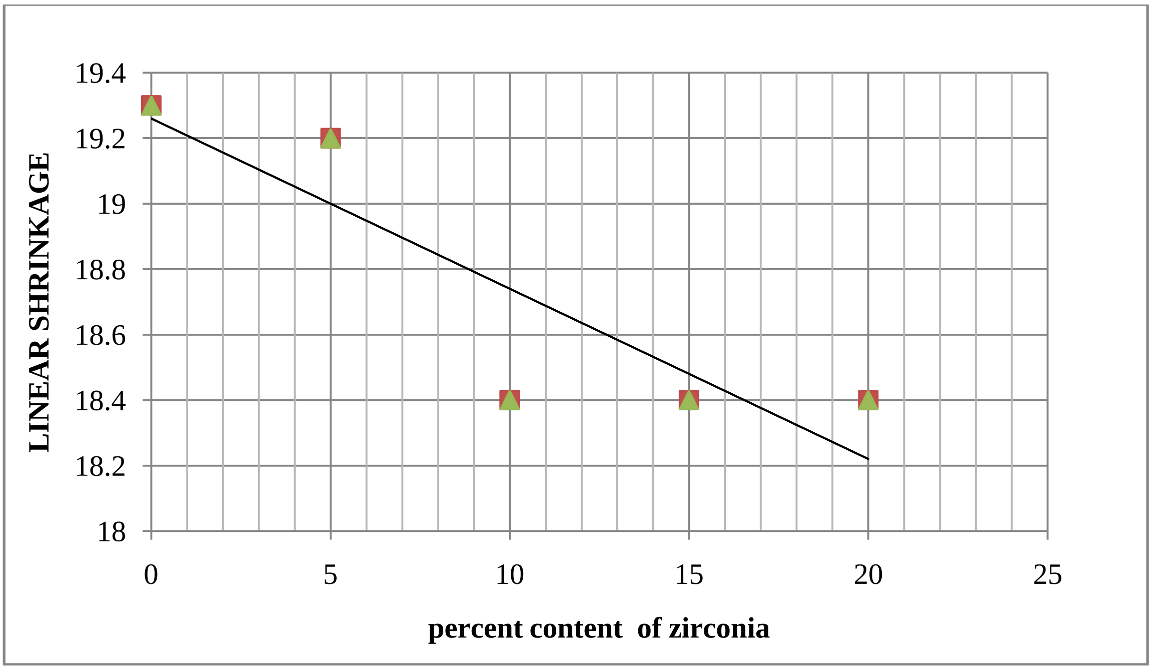

FIGURE-5 GRAPH OF SHRINKAGE VS PERCENT CONTENT OF ZIRCONIA

3.5 XRD ANALYSIS- The XRD signatures of the three compositions (Al_2O_3, $MgAl_2O_4$, MgO) calcined at 1400°C/2 h are displayed in Figure 6. Figure 6 shows the XRD patterns of the Spinel and the support (Al_2O_3, $MgAl_2O_4$, MgO). The peaks at 2h = 19.1, 31.3 ,36.8, 43.0 were detected on the MgO–Al_2O_3 . These peaks comprise of several groups of peaks arising from different crystal phases. The peaks at 2h = 43.0 matched well to the characteristic peaks specific to MgO (PDF code: 01-079- 0612). The peaks at 2h = 19.1, 31.3, 37.0, appearing in $MgAl_2O_4$ spinel (PDF code: 01-073-1959) and the peaks at 2h = 37.4, appearing in Al_2O_3 (PDF code: 00004-0880) occurred on the MgO–Al_2O_3 as well. Obviously, the overlapped peaks on the support broadened. This suggests that the binary MgO– Al_2O_3 is composed of mixed oxides of MgO, Al_2O_3. Theoretically, the formation of MgAl2O4 requires an equal molar ratio of MgO to Al_2O_3. In this study, the co-existence of Al_2O_3 and $MgAl_2O_4$ shows that only a part of magnesia transforms to $MgAl_2O_4$ The phase stability of the $MgAl_2O_4$ spinel has been studied by means of high-pressure X-ray diffraction for pressures up to 30 GPa. The XRD analysis of MgO-Al_2O_3-xZrO_2 shows a different peak are obtained at different percent content of zirconia atom.. (x=10%) Comparison with the standard cards showed that all major diffraction peaks belonged to $MgAl_2O_4$.The Figure 7 shows the highest peaks are from spinel remaining peak are from tetragonal and monoclincal form of zirconia .

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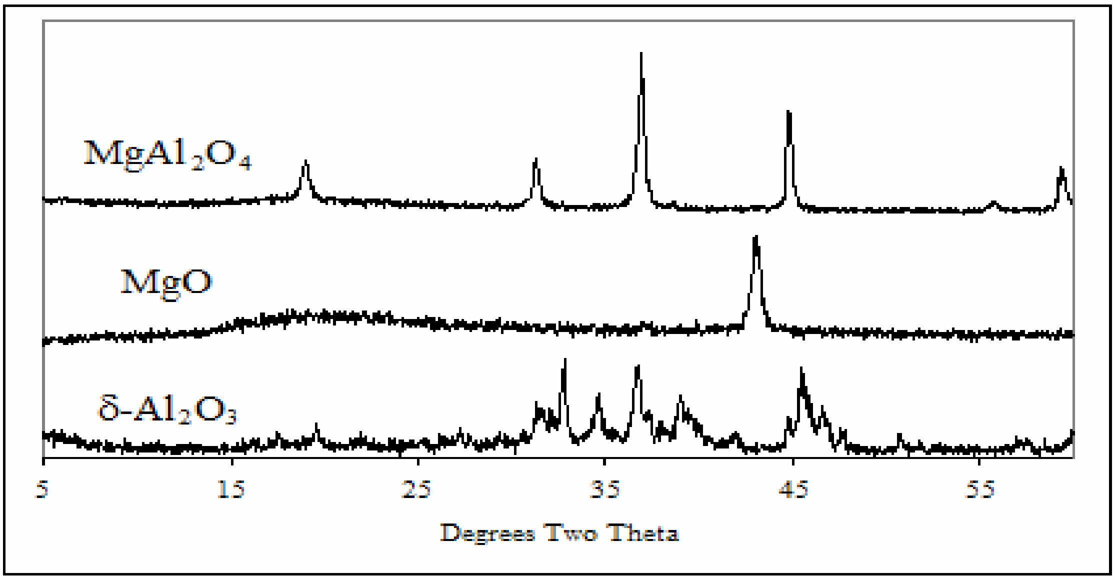

FIGURE-6 XRD of $MgAl_2O_4$

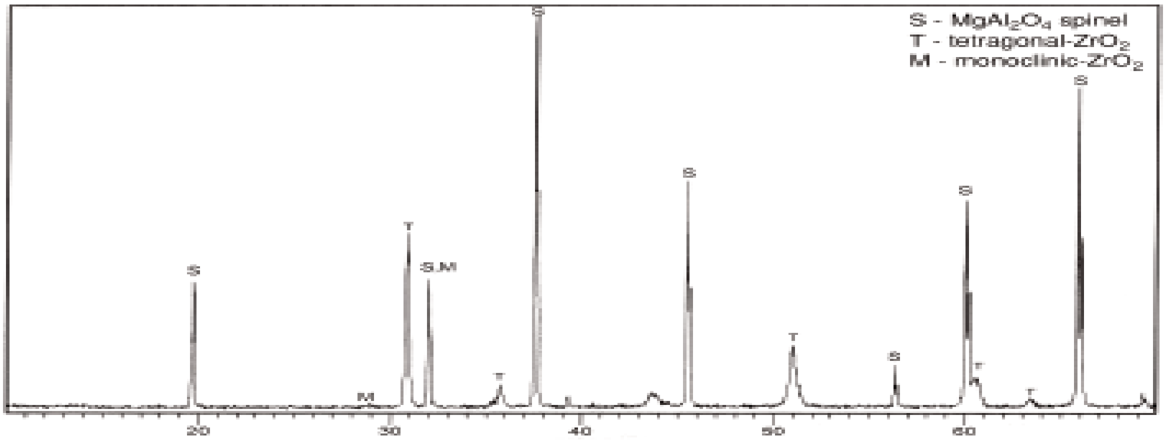

FIGURE-7 XRD of $45MgO-45Al_2O_3-10 ZrO_2$

3.6 SEM ANALYSIS- SEM micrographs of $45MgO-45Al_2O_3-10 ZrO_2$composite fired at 1400 and 1500°C were studied (Fig.8 and 9). The ZrO2 grains were small in size and occurred as intergranular grains between the MgAl2O4 grains.Grain growth of both phases was observed with increased firing temperature. Pores were eliminated at higher sintering temperature.

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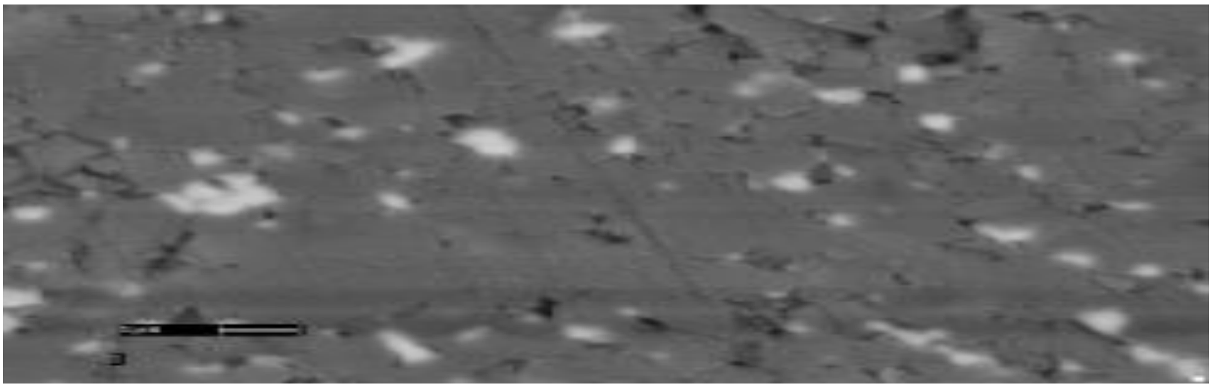

FIGURE -8 SEM micrographs of 45MgO-45Al_2O_3-10 ZrO_2 composite fired at 1500 *ºC*

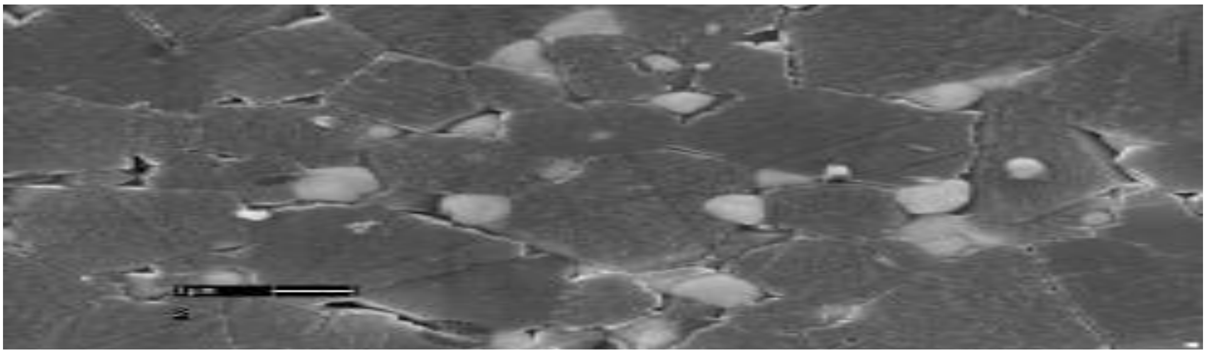

FIGURE -9 SEM micrographs of 45MgO-45Al_2O_3-10 ZrO_2 composite fired at 1500 *ºC*

1V. CONCLUSIONS

A high densification are classified by the partial attachment of zirconia atom at parent spinel phase It also was confirmed that densification was further improved by increased firing temperature. Increased densification with increased ZrO_2 may have been caused by the presence of a discrete secondary ZrO_2 phase, which retarded grain growth of the primary spinel phase. Retarded grain growth did not allow pores to become trapped within the grains. As a result, the pores did not grow in size but were eliminated from the surface of the grains. This phenomenon led to decreased porosity and improved densification of the ZrO_2–$MgAl_2O_4$ composite. From the above graph –

At different temperature, it is clear that-

- Where a percentage content of zirconia are increases, Bulk density are also increases.
- Where a percentage content of zirconia are increases Apparent porosity are decreases
- The percent content of zirconia are increases the Cold crushing strength of a material are increases. Improvement of Cold crushing strength due to high densification are achieved by addition of zirconia atom in parent phase spinel .
- The temperature are increases in zirconia- spinel ,its has a good Cold crushing strength response as comparison to normal spinel.
- Percent linear shrinkage are decrease as percent content of zirconia are increases.

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LIST OF FIGURE