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SYNTHESIZE AND STUDY THE EFFECTS OF SINTERING ON PHASE TRANSFORMATION AND MACROSTRUCTURE BEHAVIOR OF LANTHANUM ZIRCONATE TBC POWDERS

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ABSTRACT

Zirconate is the new advanced alternative material for thermal barrier coatings above 13500 C. In the present research work we focused on to develop a Lanthanum Zirconate and La2O3 have been used as the dopant or stabilizer to zirconia powder. Various characterization tests have been conducted such as structural phases using XRD, Microstructures by SEM, particle size analysis by sedigraph method, and finally it shall be evaluated for particle size, densification, porosity etc. to optimize and determine the dopant concentration for partial or full stabilization of Zirconia. To study the effect of stabilization of Zirconia, two methods have been followed: Powder preparation by Agate jar mixing and high-energy planetary wet ball mill. In Agate jar, stabilization of Zirconia is very less due to higher particle size and higher calcinations temperature of 16250C for four hours. In wet ball milling method, the particles are well grinded (5- microns) and calcined at 15500C for four hours. It is found that 98% of Zirconate formed which is most suitable for the TBC applications

Key words*: TBC, Zirconate materials, Powders Preparation, % Porosity, XRD, SEM and Sedigraph Method.*

1. Introduction

In Particular, transportation vehicles like truck engines, turbines and other prime movers that we use diesel as a basic fuel are major polluters.In our country the consumption of diesel for transportation purpose, captive, power generation account for 90% of the fuel consumed. The combustion characteristics of the engine can be improved by insulating the combustion chamber by providing them a Coating (Approximately about 250microns) of insulating ceramic which posses' very low thermal conductivity. These coatings are called THERMAL BARRIER COATINGS (TBC's) .*A* Thermal Barrier Coating (TBC) is typically a two-coat system that consists of a bond coat and a ceramic topcoat. One of the most widely used thermal barrier materials, 7-8% yttria stabilized zirconium oxide allows combustion chamber components in gas turbine and diesel engines to operate at higher Temperatures. TBCs are effective in protecting gas turbine components by insulating them from hot gas passing through. In addition, they provide prevention of thermal shock, oxidation resistance and improved engine efficiency.

1.1 Zirconates

Zirconates as a promising alternative to YSZ. These materials with a pyrochlore structure have a fair TEC (in the range of 9-10 x10-6 K-1) which is comparable with PSZ[14]. The main advantages of zirconates are their low sintering activity, low thermal conductivity (20% lower than PSZ), and good thermal cycling resistance.

In the present research work we focused on to develop new Lanthanum Zirconate powder and here La_2O_3 have been used as the dopant or stabilizer to zirconia powder and as a candidate for TBC. Various characterization tests have been conducted such as structural phases using XRD, Microstructures by SEM, Chemical analysis by EDAX, and finally it shall be evaluated densification, %porosity etc. to optimize and determine the dopant concentration for partial or full stabilization of Zirconia.

To study the effect of stabilization of Zirconia, two methods have been followed: Powder preparation by Agate jar mixing, and high energy planetary wet ball milling. In the agate jar method, stabilization of Zirconia is very less due to higher particle size and higher calcinations temperature of 1625^0C for four hours. In the high energy planetary wet ball milling method, the particles are well grinded (5- microns) and calcined at 1550^0C for four hours. It is found that 98% of stabilized Zirconate was formed.

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2. Experimental Work

2.1 Powder mixture preparation

The preparation of plasma sprayable grade powders consisted of the following steps as specified in the above Figure.1 and 2. The commercially available raw materials 99.5%La_2O_3 and 99.5% ZrO_2 Purity oxide doped with ZrO_2 [19], here in this work, three compositions of 50:50, 57:43, and 60:40 of both the oxides has been sellected. The raw material were weighed to an accuracy of 0.001 grams and mixed in an agate jar about 1 hour by human hand. The agate jar mixing is shown in above figure.1. The dry powder was mixed with 7.5% Polyvinyl alcohol (PVA) because ceramic material does not have any binding properties so adding PVA will not effect the composition, but it will automatically evaporated after sintering and it has compacted into 10mm diameter and 5mm thickness of circular pellets. By fly press at the application of force of 25N and we get a number of circular pellets.

The Pellets which were sintered in a Lantern high temperature furnace at a temperature of 1000-1625^{0}C, and the soaking time of 1hrs to 4hrs with constant heating rate of 20^{0}C/min. the sintered pellets were crushed in to a powder and sieved the sieved powder has been taken in to XRD for phase analysis, from the XRD analysis we found that no formation of zirconate because stabilization of Zirconia is very less due to higher particle size and higher calcinations temperature of 1625^{0}C. This can be evident from the peak intensities of XRD results.

In the high-energy planetary wet ball mill method the commercially available raw materials 99.5%La_2O_3 and 99.5% ZrO_2 Purity oxide doped with ZrO_2 here we selected three compositions of 50:50, 57:43, and 60:40, both the oxides were weighed to an accuracy of 0.01gms and this mixture was wet milled (in 60ml deionized water) in planetary ball mill and as in Figure.2.

For the above process 25 zircona balls of 20mm diameter and 10mm diameter and 500ml zirconia jar were selected. The grinding speed and time changed in range of 100-500rpm, 12-24hr respectively. The ground slurry was spread on tray and dried at 150^{0}C in electric oven.6-12hrs.The agglomerates of particles were crushed with porcelain mortar and pestle to obtain fine powder[18,19]. The crushed fine dry powder was mixed with 7.5% polyvinyl alcohol (PVA) and it has compacted into 10mm diameter and 5mm thickness of circular pellets. By fly press at the application of force of 25N and we get a number of circular pellets.

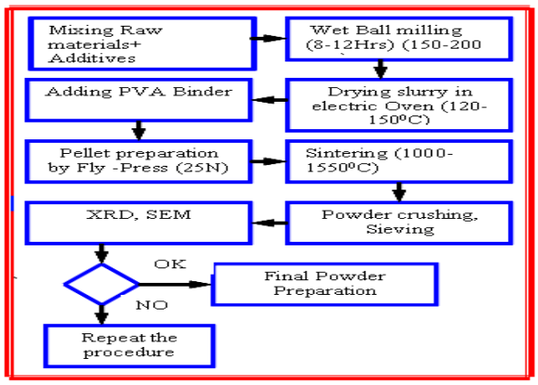

Fig. 1 Schematic Flow Chart Showing the Main Steps of Zirconate Powder Preparation by Agate Jar and Wet Ball Mill Method

3. Sintering

Sintering is a method for making objects from powder, by heating the material in a sintering furnace below its melting point (solid state sintering) until its particles to adhere each other. Sintering is traditionally used for manufacturing ceramic objects, and has also uses in the field of powder metallurgy.The sintering cycles for temperature of 15500C. The prepared 50:50%, 57:43%, 60:40% of un sintered pallets are kept in a Furness. once the sintering cycle start the furnace temperature are increase in a study state from room temperature to 10000C for about 50minutes in the first cycle, during second cycle the soaking at 10000C for 10minutes, during the third cycle the sintering temperature were increased from1000 to 12500c for about 25minutes, during fourth cycle the soaking at 12500C for 60minutes, during fifth cycle the sintering temperature were increased from 12500C to 15500C for about 150minutes., during sixth cycle the soaking period was 240minutes for the temperature of 15500C after 15500c it as brought 00 C by normal cooling. The calcinated products were crushed in an Agate jar to obtain very fine powder particles and for XRD and SEM analysis. The particles were sieved in 200 mesh sieve to obtain particle sizes of less than 53 microns.

4. Results and Discussions

4.1. X-ray analysis

The sintered pellets were powdered and placed in a X-ray Diffractometer to find out the various phases present in the powders, The XRD pattern of lanthanum

based zirconia prepared by agate jar mixing, lanthanum oxide based zirconia. Compared with the peak list obtained from XRD with the peaks Intensities of the standard ICDD values, majority of the XRD peak intensities are not exactly matched with standard ICDD values of peak intensities. From above results it has been observed that, there was no formation of zirconates because instead of zirconate, corundum was obtained due to higher calcinations temperature of 16250C and also higher particle size and hence powder prepared by agate jar mixing method stabilized zirconate will not be obtained. So there is no scope for future work in both lanthanum in agate method.

4. 2 Results Obtained from wet ball mill method

Figure.2(a),(b),(c). shows the XRD Patterns of 50:50,57:43,60:40 compositions, the strongest reflections in the majority of the XRD patterns indicate, the formation of Lanthanum oxide based Zirconia which could be matched with high intensity peak of the standard ICDD values, figure.2(a) shows the peaks with their respective intensities of.50:50 compositions are 6.67093(6.22900),3.11900(3.12830),2.70200 (2.70401),2.4780(2.48671),1.91000(1.91019), 1.62900(1.62806),

figure.2(b) shows the peaks with their respective intensities of 57:43 compositions are 6.21000(6.44935),3.11000(3.12506),2.69000(2.70033), 2.47000(2.48001), 1.62600(1.62825), 1.55700(1.55715) and lastly figure.2(c) shows the matched respective intensities of 60:40 are 2.28415 (2.28966), 2.06394 (2.08628),1.99173 (1.1217), 1.64141 (1.63121), 1.34931 (1.35112), 1.24587 (1.24106) to a first approximation. All the above three compositions phase has a cubic perovskite type structure in space. And it has been observed stable phase transformation and no phase change during heating and cooling cycle, so this confirms the formation of lanthanum Zirconate. Most of the peaks are cubic phases [20,21] and are homogeneous phases and mixed phases are not observed, because uniform distribution temperature due to steady state heating and the calcinations temperature have a strong influence on the crystal structure, homogeneity and the unit cell volume of the calcined powders of La2O3 and ZrO2. The resulting La2Zr2O7 powders presented more agglomerated as the calcinations temperature increased.

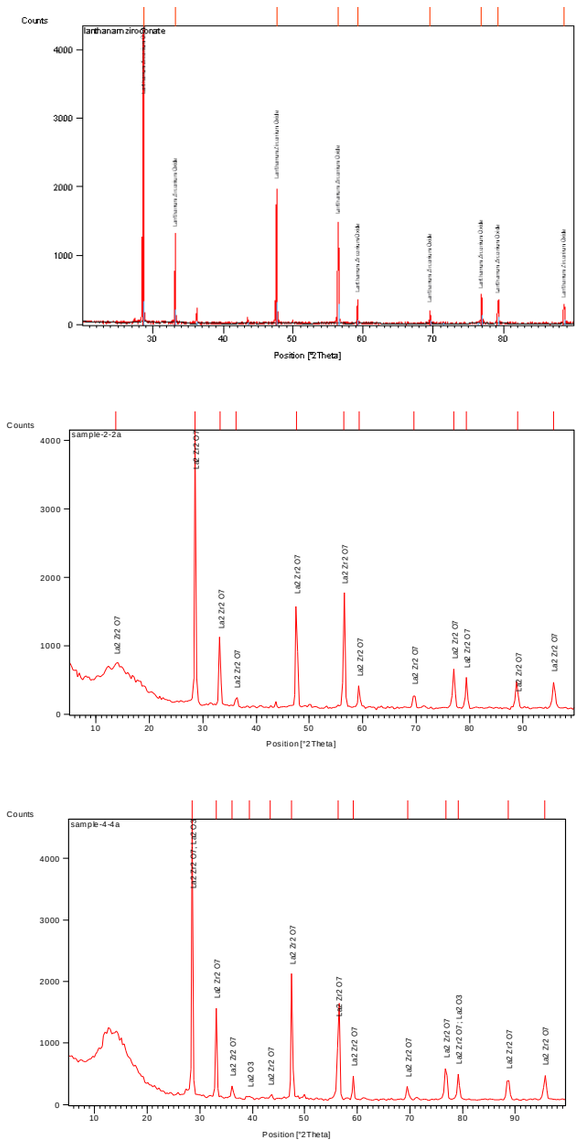

Fig. 2 (a), (b), (c) Shows XRD pattern of Lanthanum Zirconate of with Various Composition at the Calcinated Temperature of 1550^{o} C, (a) 50:50, (b) 57:43, (c) 60:40.

5. Microstructures of La2Zr2O7

Microstructure of the sintered materials was dependent on material composition. In order to investigate the microstructure status of the synthesized crushed and sintered powder of different compositions of Lanthanum Zirconate. The secondary electron image of selected powder samples of different magnification is presented in Figure.3(a),(b),(c).Shows Microstructure of Lanthanum Zirconate, with different composition at the calcinations temperature of 1550oc,Figures.3(a),depicts the Effect of sintering temperature and soaking time on microstructure of lanthanum Zirconate was inspected by using SEM on backscatter electron images (BSE) of crushed sintered powder selected samples of 50:50, from this investigation it is observed the porosity is 38.87 % at the calcinated temperature of 15950C, These powders of 50:50 composition exhibit an almost spherical morphology and very good dense bond structure and there is no large gap between intermolecular grain boundary and also more number of grain size of cubic phase could be attributed to the absence of other mixed phases, and have a less % of porous agglomerated form.

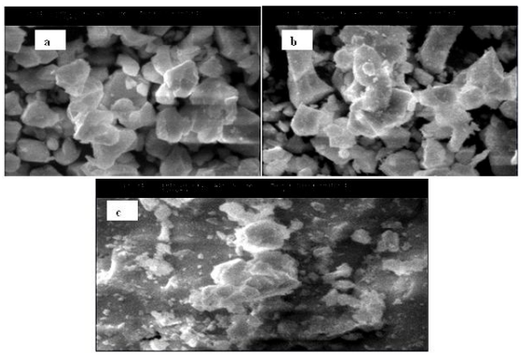

Fig. 3 (a), (b), (c) Shows Microstructure of Lanthanum Zirconate, with Different Composition at the Calcinations Temperature of 1550^{o}C. (a) 50:50, Mag.X7.00,5µm, (b) 57:43,Mag.X3.00,5µm, (c) 60:40, Mag.X7.00, 5µm.

Figure.3(b).shows10µm, Mag- 1.00kx, the % porosity decrease to 0.45% in the 57:43 compositions at the calcinated temperature of 15500C here there is significant improvement of microstructure and no large gap between internal molecular structure, so microstructure is very dense particle structure and it indicates the porous grain structure, the % porosity is decreased to 29.81% in the 60:40 compositions of 15950C and it can be evident from figure.3(c) (10µm, Mag-1.00kx, the %porosity again decrease to 2.7 % at the calcinations temperature, as the temperature increased, more agglomerate particles could be observed depending on their fineness and course size of particles, the porosity depends on various dopant concentration and temperature and also particles size. Hence it is conclude that the average particle sizes were D90=2.490µm, D50=0.982µm, D10=0.355µm with the calcinations temperature of 10000C, to 15950C respectively. Are desired to obtain very good bond structure by reducing porosity.

5.1 EDAX (Energy dispersive x-raya analysis)

Figure.4(a). shows the mixture containing 50% La_2O_3 and 50% ZrO_2. From the chemical analysis we found Zr element contain wt % is 38.19, La element contain a wt% of 41.28 and Oxide element wt % of 20.53 and the compound contain the wt% ZrO_2 is 51.59 and the La_2O_3. Compound contains the wt% 48.41 respectively. Figure.4.(b) shows the mixture containing 57 of %La_2O_3 and 43 of ZrO_2 .

From chemical analysis we found Zr element % is 29.56, La element % is 51.22, and oxide element % of 19.22 and here the Zr elements contains 8.81ions and ZrO_2 compound39.93% and La_2O_3 compound of 60.07, Figure.4(c). Shows the mixture containing 60 of %La_2O_3 and 40% of ZrO_2 . From chemical analysis we found Zr element % is 27.02, La element % is 54.15, and oxide element % of 18.83 and here the Zr elements contains 8.05ions and La elements contain 10.60 and ZrO_2 compound36.49% and La_2O_3 compound of 63.51 respectively.

Based on the above three results we observed From the chemical composition $La_2Zr_2O_7$ using EDAX analysis pure lanthanum zirconate has been found and no other chemical impurities and chemical composition changes found from the calcinated powder in 50:50 and 60:40 and there is slightly small amount of Al impurity found in 57:43 composition calcinated at 1550^{0}C. Here there is a more number of La_2O_3 , ZrO_2 peaks contains higher atomic numbered elements and elements with lesser atomic numbers have a very few intensities, because the mixture contains 50:50,57:43,and 60:40 and also no stability losses atoms are observed at the calcinations temperature of 1550^{0}C.

6. Percentage Density and Porosity of Unsintered and Sintered Pellets

From the experimental investigation we found for the 50:50 an d 57:43, 60:40, compositions of un sintered pallets, the measured pallet weight of 1.132grams and the measured diameter (D) is 1.586cm and thickness (T) of 0.202cm and the theoretically calculated volume (V) is.40cm3, theoretical density(ρ)is

6.255gm/cm and the green density is of 2.83gm/cm, and the corresponding, % density and %porosity of unsintered pellets are 45.24and 54.76.The some of calculated volume, %density, and % porosity of circular lanthanum zirconate pellets were more before sintering for the various composition of 50:50, 57:43,60:40, after sintering, the above properties were changed at a temperature of 15500C, for all the above three compositions, mainly the %porosity of will be reduced to 38.87 from 54.76 for the composition of 50:50 and %porosity will again reduced to 38.42 from 59.15 for the composition of 57:43 and finally the % porosity will be again drop down to 30.14 from 57.51 for the composition of 60:40 at the calcinations temperature of 15500C the % porosity is inversely proportional to temperature and it can be evident from figure.5.,

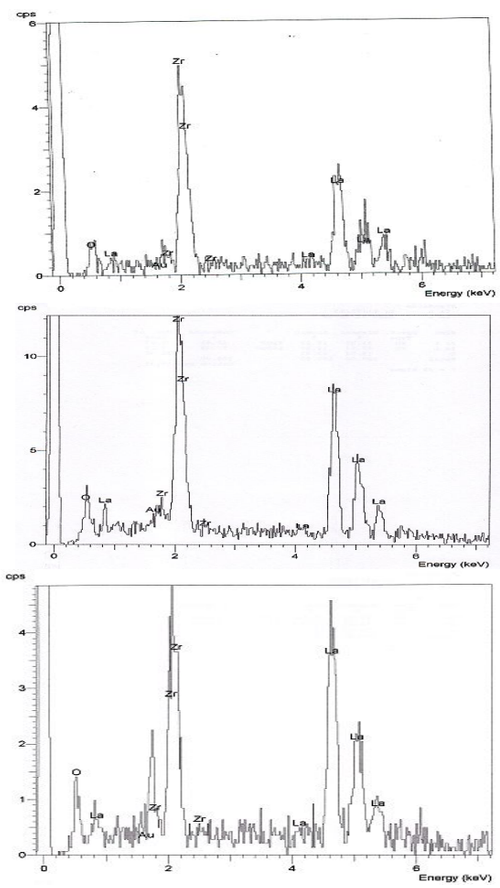

Fig. 4(a), (b), (c) Shows EDAX Result of $La_2Zr_2O_7$ with Various Compositions at the Calcinations Temperature of 1550^0 C.
(a) 50:50, (b) 57:43, (c) 60:40.

Similarly the densification is directly proportional the temperature and it as shown in Figure.5.1. Based on the above two results we observed as the % porosity decrees gradually correspondingly the densification will be increase drastically for various dopent compositions in the similar way it gives very good dense bond structure. From this investigation the % porosity will be very less for the composition of 57:43 for the sintering temperature of 1550^0C; theoretically calculated properties were shown in the following equations.

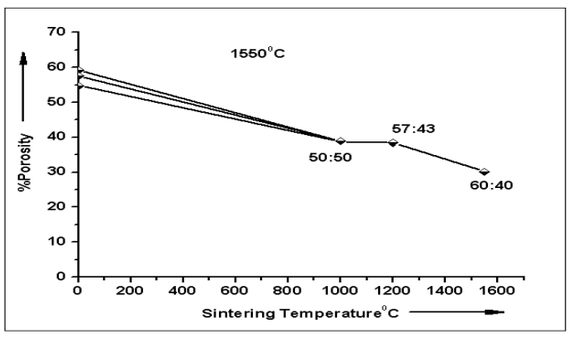

Fig. 5 % Porosity of Various Lanthanum Based Zirconia Compositions with 1550^0 C.

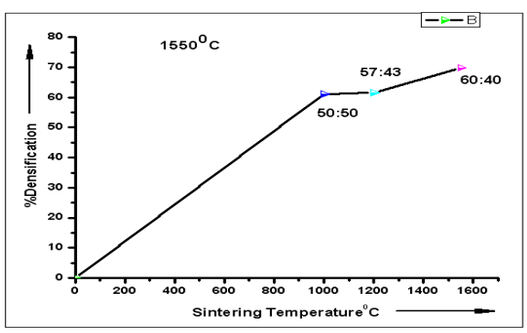

Fig. 5. 1 Densification of various Lanthanum based Zirconia compositions with 1550^0 C.

Let the theoretical density of A = x gms/cc and B = y gms/cc respectively. Let the mixture be composed of a and b weight % of A and B respectively. The theoretical density of the mixture is,

$$\rho th = Aa + Bb \quad (1)$$

The green densities of the pressed samples of each composition were calculated from the following relation, $\rho g = M/V$, where M and V are the mass and the volume of the as pressed samples respectively.

7. Conclusions

Some of the structural properties of La2Zr2O7, of 50:50, 57:43 and 60:40 compositions were studied and the powder was synthesized by Agate jar mixing and high energy planetary wet ball milling. Based on the experimental investigation, the following conclusions are drawn.

In the agate jar method there is no formation of Lanthanum Zirconate because stabilization of Zirconia is very less due to large particle size and high calcinations temperature of 16250C.

In the planetary high-energy wet ball mill method Lanthanum Zirconate was formed for because the particles are very fine due to well grinded by ball mill (i.e. 1 to 5 microns) and it has been shown that pure 98%,La2Zr2o7 powders can be formed by the reaction of Lanthanum oxide and Zirconia dioxide, at a calcined temperature at 15500 C. Hence planetary high-energy wet ball mill method is most suitable to get 98% of stabilized Zirconate, where smaller powder particles sizes are essential.

From the SEM analysis it obtained improved dense bond structure for different composition because porosity is inversely proportional temperature but densification directly proportional temperature, from this investigation the percentage of porosity for composition 60:40 at the temperature 15500C was very less compared to remaining two compositions.

From EDAX analysis no chemical impurity observed in 50:50 and 60:40 at 15500 C and there is a negligible amount of Al impurity was found in 57:43 compositions at the same temperature.

Bond formation is more densed due to less % of porosity in60:40 compositions at 15500 C compared to remaining two compositions

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Nomenclature

Symbol	Meaning	Units
F	Force	N
d	diameter	mm
t	thickness	mm
V	Voltage	KV
I	Current	mA
TBC	Thermal Barrier Coating	
XRD	X-ray diffraction data	
ICDD	International crystallographic diffraction data	
SEM	Scanning Electronic Microscope	

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