Synthesize the Praseodymium zirconate powder by agate and wet ball milling method and study the various surface properties for various calcinated temperatures for high temperature tbc applications

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***Abstract*: TBC is a layer, which resists the heat transfer or heat loss through it. The main aim of this TBC is to protect the metal components from thermal stresses, which are generated in them at high temperature and in dynamic conditions. The main objective of this present project is to study the effectiveness of Praseodymium Oxide (Pr_6O_{11}) as stabilizer to ZrO_2 to form praseodymium zirconate ($Pr_6Zr_2O_7$) and its suitability to function as TBC. Varying percentages of oxides of Praseodymium has been used to stabilize Zirconia. Plasma spray able powder was prepared by addition of suitable binders to attain flow ability and other favorable properties in the plasma conditions for spraying.TBC powder and powder made for plasma spray coating have been evaluated for structural phases using XRD, chemical composition (EDAX), microstructure (SEM). The data generated on this TBC system are being presented. To optimize and determine the dopant concentration for partial or full stabilization of Zirconia and to study the effects of stabilization of Zirconia two methods are followed 1.Powder preparation by agate jars mixing,2.Powder preparation by wet ball milling.**

Key Words: TBC, XRD, EDAX, SEM

1. INTRODUCTION:

The invention of internal combustion engine in the past is recorded as one of the greatest achievements of man. Since then the continuous application of this engine has revolutionized the world and has contributed significantly to industrialization, transport and various other fields. However, this revolution was followed by the destruction of the environment and because of that man has been forced to meet it face to face. This severe usage has already depleted the enormous natural resources of the earth like petroleum, coal, natural gas etc. and is the major source of environmental pollution. Especially the automobile sector[1-2] (e.g., all major vehicles, prime movers, turbines etc.) which uses diesel as the primary fuel is the foremost contributor for this pollution. In India, the consumption of diesel for transportation purposes and captive power generation accounts for 90% of the fuel consumed. Added to this, the diesel costs the national revenue on precious foreign exchange (an astonishing 10000 crores).Hence, it has become necessary to make use of the diesel at a sparing rate as well as to reduce the exhaust discharge level of the engines [3-4].

Thus, the primary concern now is to gain a total combustion of the fuel by increasing the operating temperature of the engine at its combustion zone. The combustion characteristics of the engine can be made better by giving some insulation to the combustion chamber by providing them with coatings (approximately 250 microns to 1mm) of insulating ceramic possessing very low thermal conductivity. These coatings are called thermal barrier coatings (TBC's)[5-6].

2. EXPERIMENTATION:

2.1. Preparation of Plasma Spray able Powder:

Table.1.0 powder compositions

Sl. No	Pr_6O_{11}	ZrO_2
1	20	80
2	24	76

2.2. AGATE JAR METHOD:

The preparation of plasma spray able grade powders consists of the following steps as specified in the below given chart

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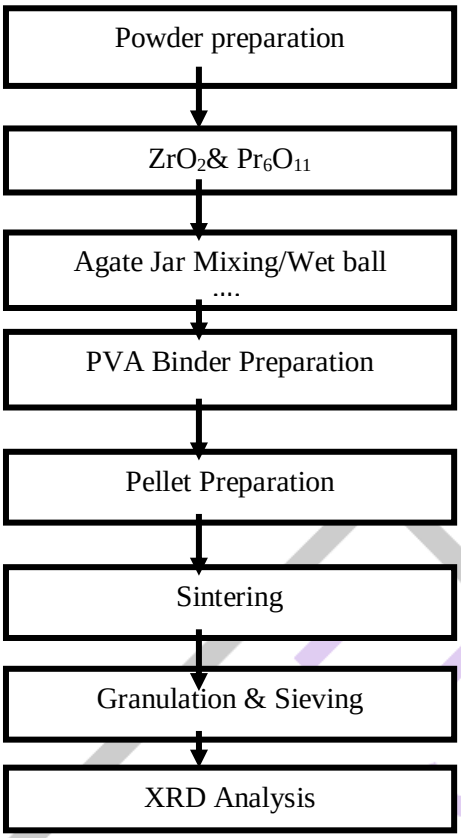

Fig.1.Agate jar method

The raw materials are weighed to an accuracy of 0.001 grams and mixed in an agate jar about 1 hour by human hand. For the solid powder we added 10% of PVA solution and compacted into a circular pellets of 10mm diameter and 5mm thickness are formed and then the circular pellets are dried in an open atmosphere, finally the dried pellets are taken for sintering in a high temperature furnace, the pellets are sintered at a temperature of 1630^0c, after sintering the pellets are crushed into a powder. Then sieved powder is taken for XRD analysis.

2. 3.Wet Ball Mill Method:

The combination of Pr_6O_{11} and ZrO_2 are used for preparing plasma sprayable powder. It consists of the following steps:

1. The raw materials are weighed to an accuracy of 0.01 grams and wet ball milled in distilled water for 24 hours at 130 rpm in ball milling machine.
2. Then, the obtained slurry is oven dried (150°C) to obtain a moisture free powder.
3. Powder is mixed with 10% PVA solution and then circular pellets of 10mm diameter and 5mm thickness are made with the aid of hydraulic press(2.0 kg/cm2) and then the circular pellets are dried in an open atmosphere, finally the dried pellets are taken for sintering in a high temperature furnace, the pellets are sintered at a temperature of 1550^0c, after sintering the pellets are crushed into a powder. Then sieved powder is taken for XRD analysis.

3.0.RESULTS AND DISCUSSION:

3.1.XRD Analysis:

3.1.1. By Agate mixing method:

The figure below represents the XRD plots for various dopant concentrations. The table gives the data relating to the peak values of the respective XRD plots**.**

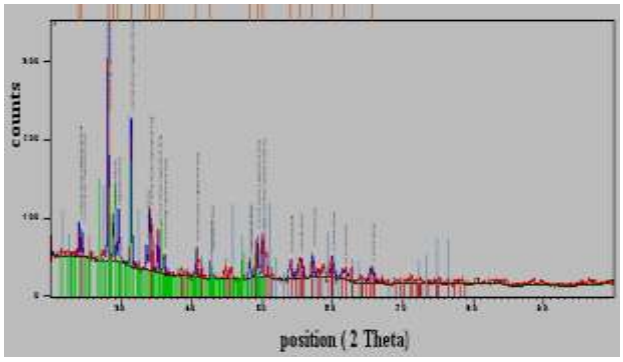

Fig.2a.XRD Peaks24% Pr_6O_{11} and 76% ZrO_2

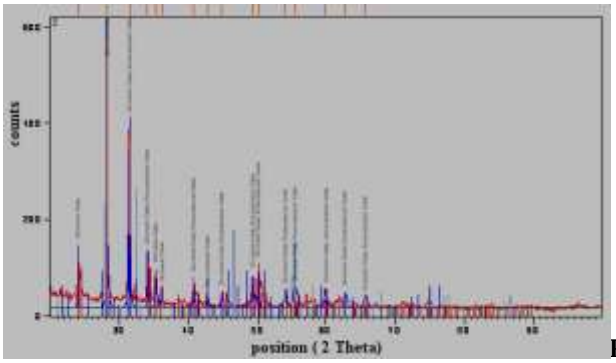

Fig 2b.XRD Peaks of 20% Pr_6O_{11} and 80% ZrO

3.1.2. By Wet Ball Milling Method:

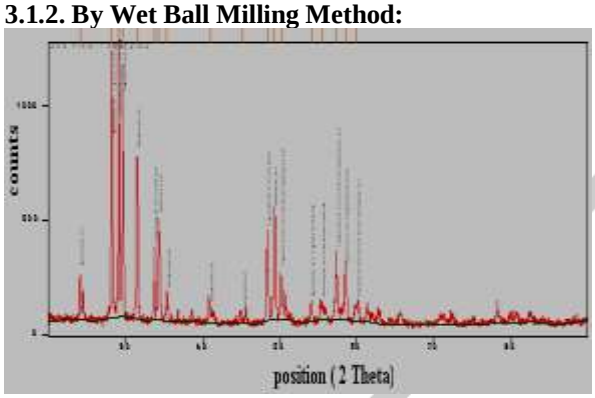

Fig 3a XRD peaks of 20% Pr_6O_{11} and 80% ZrO_2

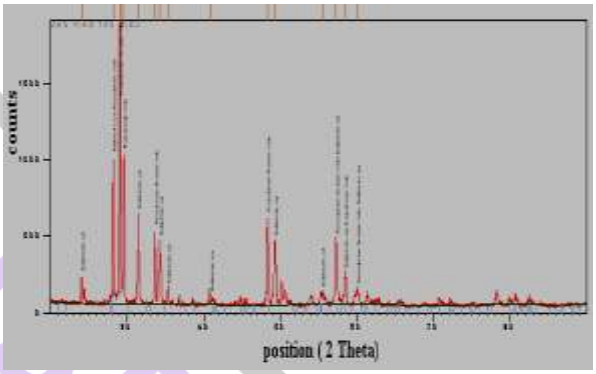

Fig 3b XRD peaks of 24% Pr_6O_{11} and 76% ZrO_2

From XRD analysis, we observed that the Pr_6O_{11}-ZrO_2 powders obtained from wet ball mill method are found to be more stabilized than the agate method.

3.3. Results obtained from the agate method:

Comparing the high intensity peak list obtained from XRD with the high intensity peaks obtained from the standard ICDD values, most of the XRD peak intensities are not exactly matching with ICDD values of peak intensities. From the above results it is observed that there is no formation of zirconates, so praseodymium zirconate was not found and it is observed that it will withstand up to 1630^0 C but due to higher particle size and calcination temperature the phases are not found. It is evident from XRD fig.2a and 2b. Therefore,there is no scope for future work in agate method of powder preparation.

Fig.3a Fig.3b shows the strongest reflections of high intensity of the XRD patterns, the formation of praseodymium oxide based Zirconiamajority of the highest intensity peakswhich are exactly matched with highest intensity peaks of the standard ICDD values. These phases have a tetragonal phase structure. In addition, we observed the stable phase transformation. There is no phase change during heating and cooling cycle, so this confirms the formation of praseodymium zirconate. Most of the peaks are tetragonal phases and are homogeneous phases [6-8]. Mixed phases are very less percentage because of uniform distribution temperature due to steady state heating and the calcinations temperature has a strong influence on the crystal structure, homogeneity and the unit cell volume of the calcinated powders of Pr_6O_{11} and ZrO_2.The resulting $Pr_6Zr_2O_7$ powders presented more agglomerated as the calcinations temperature increased. Fig .3b shows 24% and 76% praseodymium based Zirconia ,here we obtained more number of tetragonal phases and very less number of minor peaks compared to 20:80%.hence 24:76 composition is the suitable for TBC.

4.0. EDAX (ENERGY DISPERSIVE X-RAY ANALYSIS):

The following figures show various graphs of EDAX analysis on Pr_6O_{11} and ZrO_2.

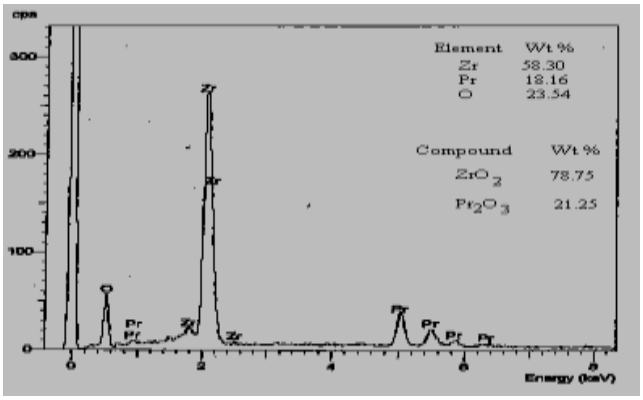

Fig4a. Results of EDAX 20% Pr_6O_{11} and 80% ZrO_2

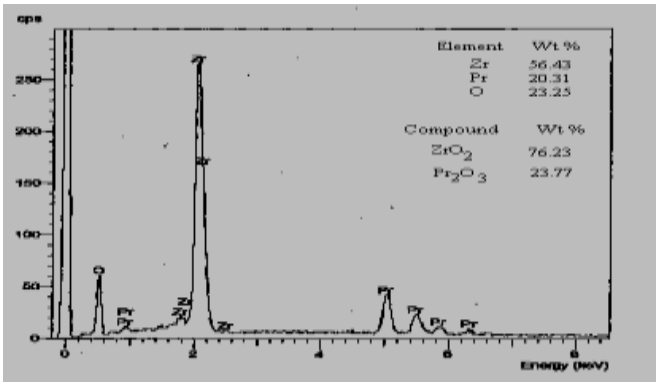

Fig4b. Results of EDAX24% Pr_6O_{11} and 76% ZrO_2

Fig.4a shows the chemical composition of 20% Pr_6O_{11} and 80% ZrO_2. After sintering we observed praseodymium oxide contains 21.25weight % and zirconate dioxide contains 78.75wt % and the element of Zirconia is 58.0wt %, the element of praseodymium is 18.16wt % and element of oxygen is 23.54wt%, during the calcination cycle no other impurities found, it is evident from the intensity peaks of EDAX results.

Fig.4b shows the chemical composition of 24% Pr_6O_{11} and 76% ZrO_2.After sintering we observed praseodymium oxide contains 23.77weight% and zirconate dioxide contains 76.23wt % and the element of Zirconia is56.43wt %, the element of praseodymium is 20.31wt % and element of oxygen is 23.25wt % here also no other impurities found, hence we found pure praseodymium zirconate, it is evident from the intensity peaks of EDAX results.

Based on the above EDAX analysis we observed there is no other chemical impurity found and there is a slight variation of chemical compounds after sintering for various dopant concentration of zirconium dioxide and praseodymium oxide. These chemical composition changes will occur during the sintering cycles[8-10]. Here we observed pure praseodymium zirconate and hence these pure praseodymium zirconate is suitable for TBC applications.

5.0. PR_6O_{11}-ZRO_2 SEM RESULTS:

The Scanning Electron Microscopy of Pr_6O_{11}-ZrO_2 plasma sprayable powder is shown in figures below at different magnifications.

The above Fig .5a,5b shows the microstructures of a sintered samples of 20:80and 24:76 wt% at a calcinated temperature of 1550^0c. The Fig 5a shows the 20:80 weight percentage the porosity is 29.35, the corresponding densification factor is 78.46% and theoretical density is 6.092gm/cm^3. We observed the uniform particle distribution due to steady state heat during sintering. Hence, the percentage of porosity goes on decreases as the temperature increases. Fig.5b shows the microstructure for the same composition at same temperature but at higher magnifiction.Fig.5c shows the microstructure of 24:76 compositions

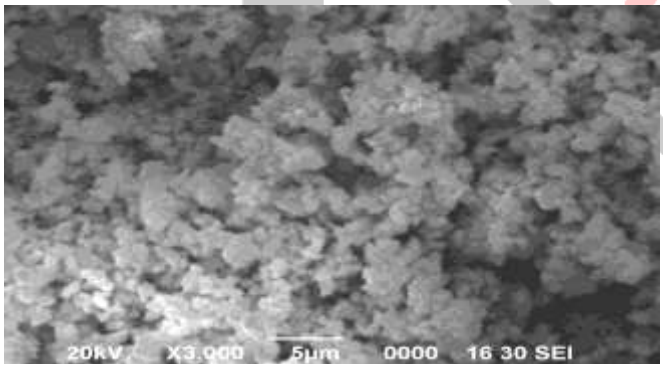

Fig.5a 20:80 composition of praseodymium zirconate at temperature 1550°C

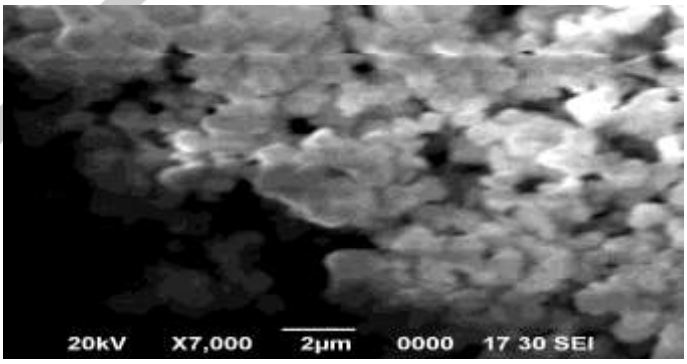

Fig.5b 20:80 compositionof praseodymium zirconate at temperature 1550°C

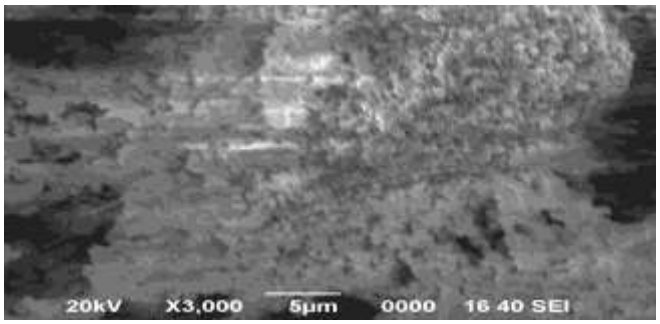

Fig. 5c 24:76 composition of praseodymium zirconate at temperature 1595°C

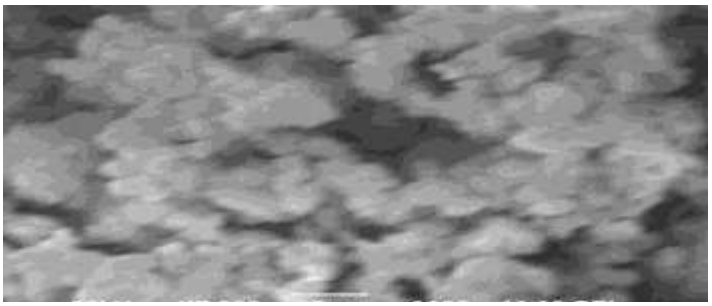

Fig.5d 24:76 composition of praseodymium zirconate at temperature 1595°C

at a temperature of 1595^0c.The percentage of porosity decreases to 0.07 due to more densification factor.Fig.5d shows the microstructure of 24:76 composition at a temperature of 1595^0c but at higher magnification. From this result, we observed that there is a proper distribution of the particles due to moredense and hence the percentage of 24:76 composition of Praseodymium Zirconate powder is best suited for TBC[11-12].

6.0. CONCLUSION:

From the experimental results the following conclusions are drawn

1. The phase transformation temperature is inversely proportional to the particle size. From the experiments, it has been concluded that phase transformation temperature decreased from 1595^o C to 1450^0 C when particle size was reduced by ball milling.

2. By agate mixing the maximum particle size was 53 microns. This is reduced to around 10 microns by wet ball milling which resulted in the decrease of the phase transformation temperature. There is no formation of zirconate phase due to higher particle size and for a higher calcination temperature.

3. The peaks obtained from the XRD did not match with standard ICDD (International Crystalline Diffraction Data) values. This incurs that phase transformation in Zirconia is achieved marginally. Hence, heating cycle has to be optimal.

4. The heating method is the optimum possible cycle for TBC powder preparation. Adequate diffusion at the molecular level has taken place by wet ball milling method. In the wet ball milling method, the particles are very fine (i.e. 1 to 5microns) and it has very fine grain size. Therefore, it has very good affinity to undergo phase transformation when sintered at temperature of 1550 ºC and 1595 ºC.

5. From the Wet milling method the peaks obtained from XRD analysis were in union with ICDD values. XRD of the samples confirmed the formation of Tetragonal phased Praseodymium Zirconate which is best suited for TBC applications.

6. Chemical composition is analyzed by using EDAX analysis. Here we obtained very good chemical composition of Praseodymium Zirconate. During the sintering cycle no other impurities found. The SEM depicts the very good particle size and porosity of various compositions of Praseodymium zirconate.Hence it is very good chemical composition for TBC application.

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