CHEMICAL SYNTHESIS AND CHARACTERIZATION OF THORIA INCORPORATED YTTRIA CERIA-STABILIZED ZIRCONIA NANO PARTICLES FOR HIGH TEMPERATURE APPLICATIONS

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There are exceptionally extreme prerequisites anticipated from materials that are to be utilized as a part of aero plane engines. These materials ought to survive extreme working conditions with high operating temperature and pressure. Turbine section is the one where the impact of advancements in materials and material procedures can be best prized. The basic mechanical properties anticipated from all materials must be temperature dependent. Fabricating super alloys to meet the higher working temperature and requirements such as higher creep strength and better resistance to corrosion or oxidation is highly cumbersome. Cubic stabilized zirconia is a promising material in Thermal Barrier Coatings (TBCs) for high temperature applications, which can be utilized to climb the surface temperatures up-to 1200°C. Our present work is focused on preparation of 8 mol% yttria-stabilized zirconia with 10 mol% ceria (10Ce–8YSZ) incorporated with Thoria. A wet chemical route powder synthesis method was applied to make homogeneous Yttria and Ceria-Stabilized Zirconia (YCSZ) ceramics from its core and Thoria was synthesized from its Nitrate independently and blended with YCSZ to upgrade its properties for high temperature coating application. The crystalline structure and morphological properties of the YCSZ nano particles were studied by using Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray emission Spectrometry (EDXS), X-ray Diffraction (XRD) and UV diffuse reflectance spectrum.

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1. Introduction

Zirconium dioxide is one in every of the foremost studied ceramic materials. ZrO_2 adopts a monoclinic crystal structure at normal temperature and transitions to polygon and isometric at higher temperatures. The amount growth caused by isometric to polygon to monoclinic transformation induces giant stresses and these stressed cause ZrO_2 to crack upon cooling from high temperature [1]. The cube-shaped section zirconia (ZrO_2) is a polymorphic oxide which might be dried-up to its temperature of 2677 °C are often stabilized by Mg^{2+}, Ca^{2+} or Y^{3+}[2].

When the zirconia is mixed with some different oxides, the tetragonal or potentially cubic stages are balanced out. Effective dopants incorporate Magnesium Oxide (MgO), Yttrium Oxide (Y_2O_3, yttria), Calcium Oxide (CaO), and Cerium Oxide (Ce_2O_3, Ceria)[3].

Yttria-balanced out zirconia (YSZ) is generally utilized as electrolyte material in warm covering boundary coatings. This high temperature unmanageable oxide is alluring in light of the fact that it introduces a high radiation steadiness, a high softening point and a capacity to frame strong arrangements in an extensive variety of solvency with some actinide components

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(Pu,U,Th). Due to its extensive variety of high temperature applications and outstanding properties such as high mechanical strength, good chemical stability, corrosion resistance and low thermal conductivity, yttria ceria stabilized zirconia (YCSZ) plays a vital role among the doped combinations of zirconia.

The partial goal of this work was intended to deliver 8 mol % yttria-settled zirconia with 10 mol % ceria (10Ce–8YSZ). The blend of a homogeneous and single-staged 10 mol % ceria-doped 8 mol % yttria-balanced out zirconia was performed by methods for a negligible exertion and direct process in light of a wet course and a solid state reaction. Unfortunately, most sintering aids for stabilized zirconia result in the formulation of a multiphase zirconia body which compromises such properties as refractroriness, high temperature creep resistance and optical properties. Because of the low cation diffusion rate of zirconia, sintering temperatures in the neighborhood of 2000°C or more are needed to consolidate a single phase stabilized zirconia to 95% or greater of theoretical density. It has been found that the addition of thoria or thorium oxide to a batch of zirconia prior to sintering results in the formation of a relatively pure, single phase zirconia body at sintering temperatures considerably lower than employed here to fore. The resultant zirconia body is a stable solid solution of cubic crystal structure upto its melting point [4].

Accordingly, the primary aim of this work is to prepare yttria ceria stabilized zirconia (YCSZ). Still another object of this work is to provide a method that employs thoria as a sintering aid for yttria ceria stabilized zirconia, which can be used as coating material for high temperature applications.

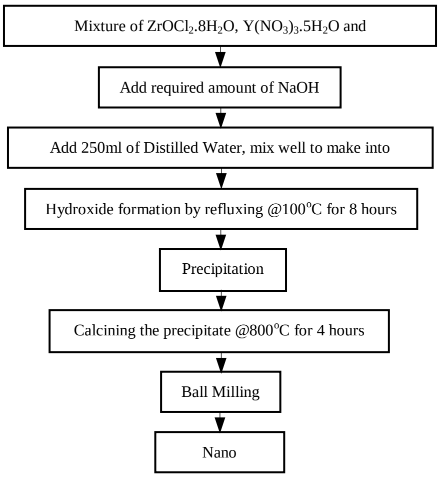
2. Experimental Procedure

2.1. Chemical Synthesis

The ceramic powder preparation was based on the co-precipitation method by wet chemical synthesis. For the preparation of Yttria Cerium stabilized zirconia (YCSZ) powder by co-precipitation method, zirconium oxychloride ($ZrOCl_2.8H_2O$), Yttrium nitrate ($Y(NO_3)_3.5H_2O$) and Cerium nitrate ($Ce(NO_3)_3.6H_2O$) were used as base material for synthesis. As per our requirement, 8 mol % Yttria and 10 mol % Ceria was used to stabilize Zirconia. The details are listed in below Table1.

Table 1. Material content

Material	Mol. Wt.	Grams/mole	Mole %	Wt. (Grams)
Yttrium Nitrate.6H_2O	383.01	0.766 gm/2mole	8 * 2	0.0621
Cerium Nitrate.6H_2O	434.20	0.434 gm/mole	10	0.1042
Zirconium oxychloride.8H_2O	322.25	0.322 gm/mole	Balance	0.2189



Scheme 1 Flow chart of the synthesis procedure that was used to prepare stock solutions.

2.2. Reactions

The required amount of NaOH is added to base material. Then 250ml of distilled water is added and mixed well to get the solution after which hydroxides of zirconia, yttria and ceria were formed.

$$ZrOCl_2.8H_2O \xrightarrow{NaOH} Zr(OH)_4 \underset{-2H_2O}{\overset{\Delta}{\rightarrow}} ZrO_2$$

$$2Y(NO)_3.6H_2O \xrightarrow{NaOH} 2Y(OH)_3 \underset{-3H_2O}{\overset{\Delta}{\rightarrow}} Y_2O_3$$

$$Ce(NO)_3.6H_2O \xrightarrow{NaOH} Ce(OH)_3 \underset{-H_2O}{\overset{\Delta}{\rightarrow}} CeO_2$$

The reaction mixture is refluxed for 8 hours to complete the hydroxide formation. As a result of reaction process, a colloidal solution was formed in form of precipitate. The precipitate is filtered and then calcined at 800^{O}C for 4 hours in muffle furnace to get oxides.

Fig.1. Experimental setup and Formation of Precipitate

Then the calcined powder is placed in a ball mill in order to grind and blend the material to get its fine powder. Thus the Nano composite is formed and then further allowed to get characterized according to the applications.

Thorium dioxide, also known as thoria is obtained through chemical synthesis by adding Oxalic Acid Dihydrates along with Thorium Nitrate. This involves ionic addition to thorium molecules.

$$Th(NO_3)_4.5H_2O + 2\begin{bmatrix}COOH\\COOH\end{bmatrix}.2\,H_2O \xrightarrow{yields} Th^{+4}\begin{bmatrix}COO^-\\COO^-\end{bmatrix}2.7H_2O + 4HNO_3 \overset{\Delta}{\rightarrow}$$

$$ThO_2 - H_2O$$

Thoria is added to the zirconia in a concentration which is within the solid solution field. The thorium ions segregate to the grain boundaries limiting grain growth, thus allowing more time for pore removal prior to pore entrapping grain growth. Thus, higher relative densities are achieved during sintering without the formation of a discrete second phase. The zirconia products with thoria are preferable combination, which maintain their intrinsic properties such as refractoriness, creep strength and optical properties [4].

After decay, the 10Ce–8YSZ powder was ground and 5 weight % of Thoria is added with YCSZ powder. The dried mixture is then placed inside a ball mill in order to grind and blend the material to get its fine nano powder.

In order to obtain a density close to that of the dense material, the sintering process is carried out. The sintering was performed in a muffle furnace, in static air with a heating rate of 1 to5 K/min upto 1400°C, for holding time of 10 hours at 1400°C. Thus the Nano composite is formed and then further allowed to get characterized according to the applications.

3. Results and discussion

3.1. Morphological Characterization:

At all steps of the synthesis, the chemical composition and the homogeneity of samples were determined, first by EDAX associated to SEM, and afterwards by XRD. The EDAX analyses were carried out on various selected areas with incidence energy of 30keV. Yttrium, zirconium, cerium and few elements in very less wt % are detected such as Cu, Ag being an impurity in the ceramic powder. First the chemical composition and zirconia presence in the ceramic powder was verified. SEM morphology of the ceramic sample reveals some little zones enriched in cerium, thorium and pore distributions. In areas containing little dispersed pores, the composition is homogeneous, but in areas where large pores are gathered enrichment in cerium is noticeable.

F E I Quanta FEG 200 - High Resolution Scanning Electron Microscope (SEM) was utilized to portray the morphology and the microstructure of powder.

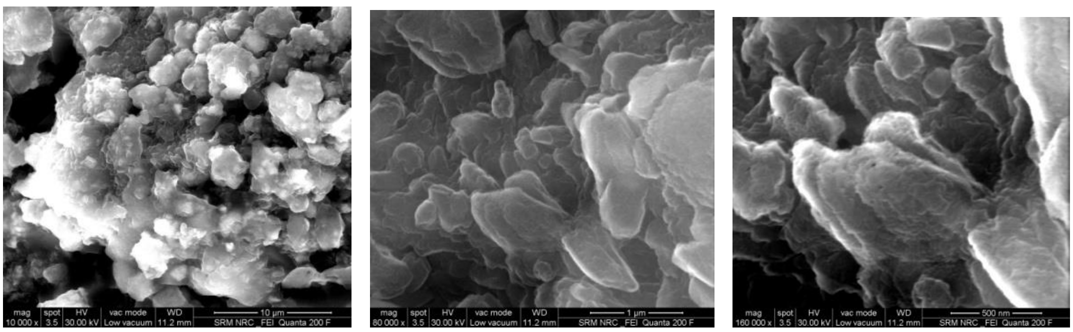


Fig.2 SEM images of synthesized ceramic powder

Fig.2 shows SEM micrographs of the Thoria incorporated YCSZ ceramic powder, which demonstrates agglomerates made up of different shapes of platelets, whose normal size is around 100 nm. Additionally, the porosity is not homogeneously conveyed. The particles are in petal like shape, narrow size distribution and course particles. It is seen that equi axial particles, non-uniform in shape and size, with a relative tendency of agglomeration are observed. The white specimen gets to be distinctly dim because of contamination. The outcome of these reviews is that, by the procedure held for the synthesis of ceramic material, thick earthenware is acquired with little grains.

The FEG 200 is also furnished with a dispersive X-beam spectrometer. Fig. 3 demonstrates the X-beam diffraction designs for Thoria incorporated 10Ce–8YSZ nano ceramic powder after thermal decomposition. It ensures the presence of ceramic compounds.

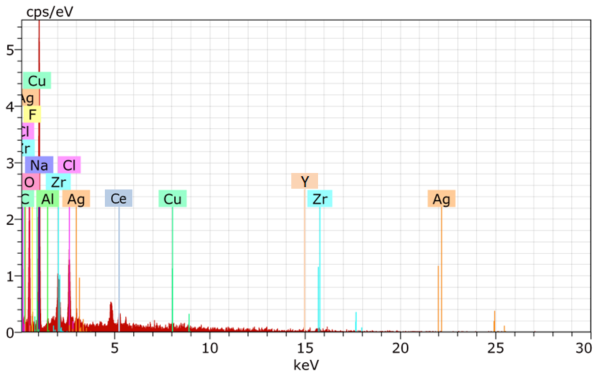


Fig.3. EDAX image

The spectrum confirms the purity and content of the synthesized sample clearly. The yttrium, cerium rate given by EDAX is littler, however it was likewise confirmed that the yttrium and cerium are approximately homogeneously distributed in the ceramic. The high ratio of oxygen shows the formation of oxides. The presence of thorium was not witnessed in this analysis. However, other characterization methods have shown the presence of Thoria.

3.2. Structural Characterization

The structure of the powder was explored by X-beam diffraction (XRD). The XRD hardware comprises of a PANalyticalX'Pert Pro MRD diffractometer Cu– Kα radiation (λ = 1.5406 nm). Information was gathered with a stage size of 0.02°(2θ) and a period for each progression of 1.5s. They permit one to check that yttrium and cerium are in a strong arrangement.

X-ray diffraction pattern using Cu-Kα radiation for chemical synthesized ceramic sample is given in figure 4 The lattice parameter of Thoria incorporated Yttria Ceria-Stabilized Zirconia nano particle is higher than that of the reference ceramic.

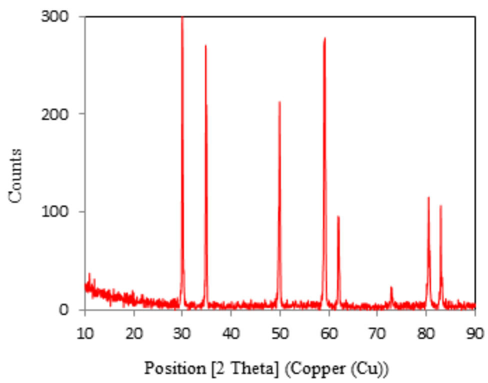


Fig. 4. XRD patterns of as synthesized ceramic

The XRD pattern shows main reflections characteristic of Yttrium Zirconium Oxide, Cerium Zirconium Oxide and Thoria (JCPDS-ref code no. 01-077-0743, 00-026-0359, 03-065-0290) in cubic phase.

In the case of ZrO_2, both monoclinic and tetragonal ZrO_2 phases are evidenced in the sample. On the other hand, X-ray analysis of mixed oxide products shows the formation of yttrium and cerium stabilized solid solutions. The XRD lines of the solid solutions are similar to those of CeO2 indicating the stabilisation of the fluorite structure by zirconia substitution.

The average grain size (D) was calculated using the classical Scherrer formula

$$D = \frac{k\lambda}{\beta cos\theta}$$

Where, k is a shape factor = 0.9, λ is the X-ray wavelength = 0.154 nm for Cu-Kα, β is the peak width and θ is the peak angle. The average grain size was calculated from X-ray line broadening using Scherrer equation and it was found to be about 16 nm.

3.3. UV-Vis diffuse absorbance spectroscopy

The YCSZ powder mixed with thoria contained was expected with much absorption property, which can be used for coating purpose. This aspect was studied UV-vis diffuse reflectance techniques.The DRS spectra of two samples of YCSZ and Thoria incorporated YCSZ ceramic powder are given in figure 5. Two absorption bands are observed in the UV region between 200 and 420 nm for both the samples. The DRS spectra corresponding to YCSZ sample shows two absorption peaks at 206 and 321 nm with an absorption edge at 234nm and Thoria incorporated YCSZ sample shows two absorption peaks at 200 and 307 nm with an absorption edge at 245nm. Both YCSZ and 5 wt% mechanical mixture of ThO_2 and YCSZ exhibits spectral features composed of one main absorption thresholdsZrO_2 (240 nm) components. However, the DRS spectra for two samples are slightly different and resolve bands at 321 and 307nm. For solid solutions, the intensities of the two strong bands at 250 and 297 nm seen in the CeO_2spectrum are reduced without any change in the band positions. The weak band between 200 and 206nm seems to be related to transition from Ce ions embedded in the zirconia matrix. The broad shoulder-type bands at 300-350 nm on the higher wavelength side in the DR spectra may consist of inter band and $Zr^{4+}\rightarrow O^{2-}$transitions. When 5 wt % of ThO_2 is mechanically mixed with YCSZ the high intense DRS features slightly about 14nm, but notably shifted to left and are maintained with a very broad band, which intern declares the advantageous of thoria presence with YCSZ for high temperature applications.

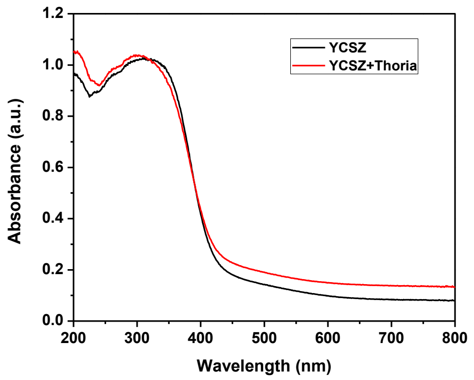


Fig. 5. Typical UV-vis diffuse absorbance spectrum for YCSZ and YCSZ+ThO_2

4. Conclusions

This work on the synthesis of 10Ce–8YSZ ceramic was performed with the objective to simulate the incorporation of a zirconia stabilized by yttria and ceria. By chemical synthesis, our thoria incorporated yttria ceria stabilized zirconia nano ceramic particles were prepared successfully. It can be reasoned that the goal of this work is achieved as ayttria-ceria stabilized zirconia with ceria in strong arrangement. The earthenware is homogeneous and the porosity sum is generally adequate for atomic utilize. The synthesized samples were ascertained by SEM and EDAX analyses and the sizes calculated were in nanometers. Our synthesized earthenware product is superior than other compared, however the element of these specimen is not appeared in EDAX image. The structure was confirmed from the XRD pattern. The optical properties were studied by using the UV spectrum. It can be concluded as, the thoria incorporated yttria ceria stabilized zirconia nano ceramic is most appropriate for high temperature coating applications for acting as a healthier barrier.

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