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Synthesis and Characterization of Ceria Zinc Aluminate Nano-powder for Thermal Barrier Application

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Abstract. Presently zirconium based oxide materials are used for thermal barrier applications. The major difficulty associated with this compound is peak stabilization. Hence in the present work we have synthesized, ceriazincaluminate nano particle, a new ceramic oxide material which can offer better thermal barrier properties even at higher elevated temperatures, with extremely good phase stability. The newly synthesized ceriazincaluminate nanoparticle was characterized on the basic of its structural and surface properties, from which the stability of ceriazincaluminate for thermal barrier applications is assessed.

Key words: Nanoparticles, sol-gel, XRD, SEM.

1.INTRODUCTION: Powder metallurgy (P/M) is an efficient and versatile method for manufacturing ferrous and non-ferrous machine parts, electrical, and electronic components. It is the process of blending fine powdered materials, pressing them into a desired shape (compacting), and then heating the compressed material in a controlled atmosphere to bond the material (sintering). The powder metallurgy process generally consists of four basic steps: (1) powder manufacture, (2) powder blending, (3) compacting, (4) sintering. Several techniques have been developed which permit large production rates of powdered particles, often with considerable control over the size ranges of the final grain population.

The sol-gel process is undoubtly the simplest and cheapest one. According to Mackenzie(1982), sol-gel method have better homogeneity and better purity from raw materials, it minimizes the evaporation losses and air pollution. Cerium is a malleable, soft, ductile, iron-grey metal, slightly harder than lead. Cerium has a variable electronic structure, which means only small amounts of energy are required to change the relative occupancy of the electronic levels. This gives rise to dual valency states. It is used in the manufacture of: Pyrophoric alloys for cigarette lighters, making aluminium alloys and in some steels and irons, in cast iron it opposes graphitisation and produces a malleable iron, in stainless steel it is used as a precipitation-hardening agent.

Zinc is a lustrous bluish-white metal. It is brittle and crystalline at ordinary temperatures, but it becomes ductile and malleable when heated between 110°C and 150°C. It is a fairly reactive metal that will combine with oxygen and other non-metals, and will react with dilute acids to release hydrogen. The alloy brass contains copper and anywhere from 20-45% of zinc, depending upon the type of brass. Brass is easy to work and is a good electrical conductor. A large proportion of all zinc is used to galvanize metals such as iron so as to prevent corrosion. The oxide (ZnO) is used in the manufacture of paints, rubber products, cosmetics, pharmaceuticals, floor coverings, plastics, printing inks, soap, textiles, electrical

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equipment, and other products like ointments. It is used for the negative plates in some electric batteries and for roofing and gutters in building construction. Zinc is the primary metal used in making American pennies, is used in die casting in the automobile industry. Zinc metal is included in most single tablet, it is believed to possess anti-oxidant properties, which protect against premature aging of the skin and muscles of the body.

Aluminum is a soft and light weight metal. It has a dull silvery appearance, because of a thin layer of oxidation that forms quickly when it is exposed to air. Aluminum is nontoxic (as the metal) nonmagnetic and non-sparking in nature. Aluminum is used in manufacture of structural components made in aerospace industry and very important in other areas of transportation and building in which light weight, durability, and strength are needed. The most recent development in aluminum technology is the production of aluminum foam by adding to the molten metal a compound, which releases hydrogen gas. Different types of surface treatment such as anodising, painting or lacquering can further improve this property. It is particularly useful for applications where protection and conservation are required.

2.SOL-GEL PROCESS: The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. It is a wet-chemical technique widely used in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for an integrated network of either discrete particles or network polymers. Typical precursors are metal alkoxides and metal chlorides, which undergo hydrolysis and polycondensation reactions to form either a network "elastic solid" or a colloidal suspension -a system composed of discrete sub micrometer particles dispersed to various degrees in a host fluid. In the case of the colloid, the volume fraction of particles may be so low that a significant amount of fluid may need to be removed initially for the gel-like properties to be recognized. This can be accomplished in any number of ways. The simplest method is to allow time for sedimentation to occur, and then pour off the remaining liquid. Centrifugation can also be used to accelerate the process of phase separation.

Removal of the remaining liquid phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will clearly be strongly influenced by changes implemented during this phase of processing. Afterwards, a thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages of using this methodology as opposed to the more traditional processing techniques is that densification is often achieved at a much lower temperature.

The precursor sol can be either deposited on a substrate to form a film cast into a suitable container with the desired shape or used to synthesize powders. The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth metals, can be introduced in the sol and end up uniformly dispersed in the final product. Sol-gel derived materials have diverse applications

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in optics, electronics, energy, space,bio-sensors, medicine and separation technology.

3.Experimental Methodology

The objective of this project is to prepare the nanopowders of cerium-zinc-aluminate. The main processes are sol-gel process, converting powders in micron levels into nano-powders, and heat treating the powders.

Mixing of the chemicals. The mixture of water with the chemicals in the beaker is placed on a magnetic stirrer and it made to mixed. The temperature is set in the hot plate of the magnetic stirrer for 80 ^{0}C and it is maintained in an optimum speed. The liquid in the beaker changes to a gel form after some time by continous running of the stirrer.

Gel Formation. When touching the level of 100ml, the nature of the mixture changes from liquid state to gel form. From that onwards it should be carefully watched because it should not be over heated and so, the powder may changes into brown colour. After it touches to hard gel form the speed of the stirrer should be reduced. Then a foam is produced it is nothing but the formation of powders. When the formation of powders occurs, the magnet in the beaker is removed.

Powder Formation. Now the temperature is reduced to get the powders. The powder formed was taken out immediately. Because it should not overheated. The powders should be completely dehydrated, the moisture are completely removed in the stirrer itself. The powder we got is made to grind in a hand mortar and the powder we grinded are in microns.

Grinding. The powder formed is then taken out from the beaker and placed in a hand mortar. It is then grinded manually by hand for some time until the particle size is reduced. The powder after grinding for a sometime is dispayed below. The grinded powder is kept in a furnace for 450 ^{0}C for 5h. Due to heat treatment the particle size is gets reduced.

Heat treatment. The powder we got is kept in a alumina crucible and is kept in furnace. The furnace is maintained in 550 ^{0}C for 5 h. During heat treatment, the grains are arranged and the grain size is still reduced to nano form. The powders are allowed to anneal by allowing the powder to cool in the furnace itself. By annealing, the hardness of the powders are made to increased and the properties of the powders are also increased.

4. Result and Discussion

The sol-gel process is a wet-chemical technique widely used recently in the fields of materials science and ceramic engineering. Such methods are used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for an integrated network of either discrete particles or network polymers.

The XRD pattern for ceria-zinc-aluminate powder annealed at 450 ^{0}C and 750 ^{0}C is shown in fig (1). The XRD plot indicates the magneto plumbite structure with preffered orientational peak at 2φ = (30^o).The other characteristics peak observed corresponds to 2φ = (25^o) and 2φ = (34^o) for the powder anneled at 450 ^{0}C and corresponds to 2φ (29^o) for the powder annealed at 750 ^{0}C. Broadening of the peak conforms the average particle size of the synthesized powder lies in the nano scale. The sharpness and maximum intensity of the characteristic peak is formed to be high for the ceriazincaluminate powder synthesized at 750 ^{0}C. The average particle size is evaluated from the XRD data using the debye scherrer's formula and is found to be nanometer. Grain size of the cerizincaluminate compound annealed at different temperature has been estimated using Debye sherre's formula given below:

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Element	App. Conc	Intensity corn.	Weight %	Weight % sigma	Atomic %
O k	83.57	1.4246	50.64	0.66	75.10
Al k	15.74	0.6279	21.63	0.42	19.02
Zn k	5.98	0.8425	6.12	0.55	2.22
Ce k	21.32	0.8518	21.61	0.60	3.66
Totals			100.00		

$$\text{Mean grain size} = \frac{0.91\lambda}{\beta\cos\omega}$$

wher λ=1.540A^0, β = B-b; β is the observed width of the peak at an angle 2ω, a half the maximum intensity,(half width full maximum), and b is the effect of the instrument as determined from the nano crystalline diffraction line.

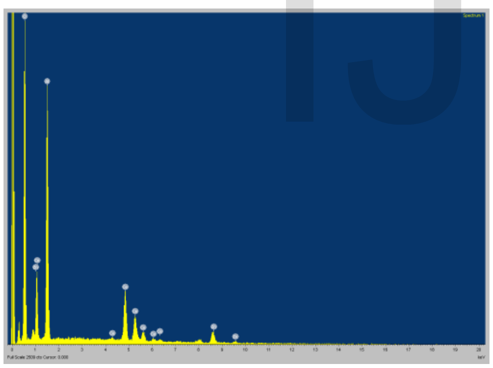

Figure.1: Result of XRD calcinated at 450 ^{0}C .

The report which gives the information about composition present in the powder. The peak rises at the particular temperature is also determined.

Project: Project 1
Spectrum Label: Spectrum 1
Owner: INCA
Livetime 50.0 s
Site: Site of Interest 1
Acquisition geometry (degrees): Tilt = 0.0
Azimuth = 0.0 Elevation = 35.0
Accelerating voltage = 20.00 kV
Total spectrum counts = 65117

Sample data :	Energy (eV)	Resn. (eV)	Area
Strobe :	7.5	49.38	504203

Optimization data : Cobalt ...

	Energy (eV)	Resn. (eV)	Area
Strobe	.0	50.32	500127
Optimization element:	6923.5	135.74	18296

Sample is unpolished X-ray corrections may be approximate. Sample is uncoated
Detector efficiency : Calculation
Spectrum processing :
Peaks possibly omitted : 0.270, 8.029 keV
Processing option : All elements analyzed (Normalised)
Number of iterations = 4
Standard :
O SiO2 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Zn Zn 1-Jun-1999 12:00 AM
Ce CeO2 1-Jun-1999 12:00 AM

The SEM micrograph of the ceria- zinc -aluminate powder annealed at 450 ^{0}C and 750 ^{0}C shown in the fig (2,3,and 4). The SEM micrograph shows smooth an uniform pattern associated with fine grains in the range 66 and 75nm, for ceria-zinc-aluminate powder annealed at 450 ^{0}C and 750 ^{0}C . The SEM image is shown below:

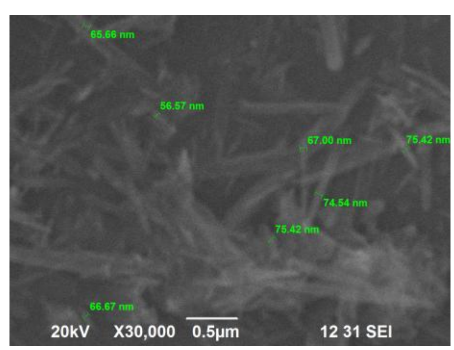

Figure.2: Image viewed at a magnification of 30000x shows nanosize of the powder

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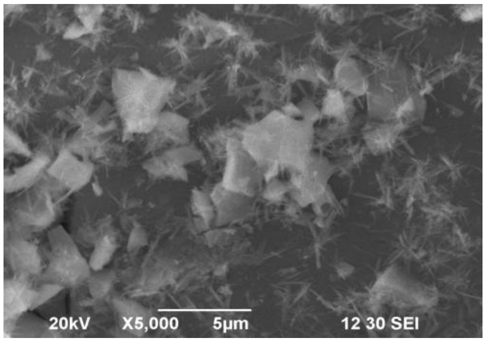

Figure.3. SEM Image viewed at a magnigication of 5000x

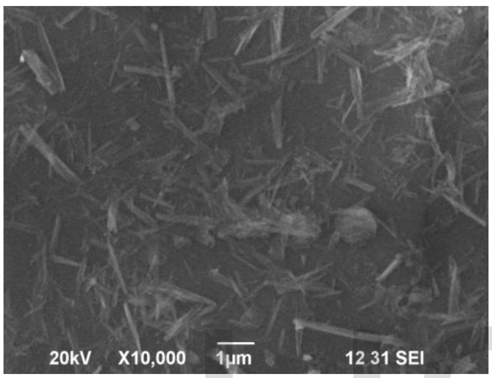

Figure.4. SEM image viewed at amagnification of 10000x.

5.Conclusion

The Formation of an oxide network through poly condensation reactions of a molecular precursor in a liquid is termed as sol-gel process. The idea behind sol-gel synthesis is to "dissolve" the compound in a liquid in order to bring it back as a solid in a controlled manner. The sol-gel method prevents the problems with co-precipitation, which may be Inhomogeneous, be a gelation reaction. In this work, we tried to combine Cerium nitrate ($Ce_2(NO_3)_3.6H_2O$), Zinc nitrate ($Zn(NO_3)_2$), Aluminium nitrate ($Al(NO_3)_3.9H_2O$) and Citric acid ($C_6H_8O_7$). By studying the properties of above materials reveals that, all these materials have high melting and boiling points. The SEM micrograph of the ceria zincaluminate powder annealed at 450 ^{0}C and 750 ^{0}C shown shows smooth and uniform pattern associated with fine grains in the range 56.75nm and 75.42.nm for ceriazincaluminate powder annealed at 450 ^{0}C. Cerium Zinc Aluminate is a new material which is formed by combining of three different sols. The unique feature of these materials is to withstand high temperature. Here the combination of these materials leads to the increase in their thermal property.

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