



HIGH TOUGHNESS ALUMINA - ZIRCONIA NANOCOMPOSITES FROM SOLGEL NANOPOWDERS

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ABSTRACT

Composite alumina – zirconia nanopowder using aluminium secondary butoxide and zirconium isopropoxide precursors was synthesized by the solgel process. These composite nanopowder of alumina - zirconia was synthesized under controlled conditions of butanol solvent with 1.52 M concentration of aluminium secondary butoxide. The hydrolysis water was diluted in butanol solvent having Solvent to water (S/H) ratio of 2. This reaction was at room temperature and at neutral pH. This led to 5.9 nm particle size powders. The nanopowder was compacted at 150 MPa and sintered at a temperature of 800°C for half an hour. Sintered compacts were also made by hot pressing at a pressure of 55 MPa using temperatures of 775° and 800°C. To improve the fracture toughness boron addition was done to the nanopowders and then hot pressed. at 800°C for 30 minutes and 2 hours. The pressureless sintered compacts and hot pressed compacts were evaluated for their hardness and fracture toughness by microindentation method. The pressureless sintered compacts showed high fracture toughness of 31 MPa√m and modest hardness of 54 VHN. The hot pressed compacts showed higher fracture toughness of 40 MPa√m and hardness of 288 VHN.

Keywords: Composite Nanopowder, Ceramic sub-nano composite, Indentation fracture toughness, Nano sintering, Hot pressing.

1. INTRODUCTION

Alumina-zirconia composites are used in ceramic toughening or catalytic studies¹ cutting tool inserts, high performance seals and wear parts in heat engines², corrosion and oxidation resistant structural materials, automobile engines³, paper making machines and wear parts⁴. Gleiter's work in the 1980s showed that drastic changes in mechanical, electrical, optical and chemical properties would be obtained if the materials are nanocrystalline. These changes in properties occur in two stages. First, at phase sizes of 100 nm and below, there is an increase in properties due to increase in number of atoms at the surface/grain boundary from 5% at 100 nm and even more as phase size is decreased⁵. There is a second set of property changes at 20 nm and below, due to effects of quantum confinement⁶. In both of these stages, there are rapid appreciation in properties as phase size is decreased. With these properties changes, nanocomposites of Al₂O₃ - ZrO₂ are used in high efficiency gas turbines, aerospace and automotive components⁷, corrosion and wear resistant coatings⁸, bone joint cup and head of the bone⁹, ceramic membranes in separation such as hyperfiltration, reverse osmosis and gas separation¹⁰ and catalytic and photocatalytic materials¹⁰. The mechanical properties of nanostructured ceramics and ceramic composites include considerable hardness, high elastic modulus, high fracture toughness, high strength and high ductility.

Nanopowders are produced by a number of methods¹¹. In combustion synthesis, the precursors are ignited to produce nanoparticles. There are possibilities for scaling up this process, but it usually has impurities. The high temperature (due to flame) means that only coarse nanosize greater than 10 nm can be produced.¹² Similarly chemical vapor condensation¹³ spray pyrolysis¹⁴ and inert gas condensation¹⁵ are all processes that can be scaled up. But the high temperatures used implies that fine nanosize less than 10 nm may not be produced. Plasma phase processes can provide fine nanosize as well as high purity, but scale-up is difficult and cost may be higher¹⁶. Laser based processes are high energy processes and have impurities¹⁷. The scale-up of laser process to high tonnage may be energy intensive. Nanopowders are also made from inorganic salts in molten salt processes¹⁸ but there are limitations on the purity of inorganic salts e.g. zirconium salts have about 2-3% hafnium. However, the solgel process with the organometallics as precursor is an effective alternative to all these processes. The organometallics are of very high purity. Solgel being a low temperature process it offers the greatest scope for the smallest nanosize material. In addition, organometallics are expected to produce narrow size distribution. Even though it may lead to effluents and drying shrinkage, it leads to best nanopowder. The actual reaction takes few hours and other steps such as calcination are split into separate operations of a few hours each. Realising the quality of the nanopowders produced by the solgel method, the present study embarks on making the Al_2O_3 - ZrO_2 nanopowders by solgel process and evaluates the fracture toughness of sintered compacts.

2. SYNTHESIS OF NANOPOWDER

The composite alumina - zirconia nanopowders were synthesized by solgel process using the organometallic precursors such as aluminium secondary butoxide and zirconium n-propoxide. Table 1 gives the source and other details of precursors and chemicals used.

Aluminium secondary butoxide is dissolved in butanol containing acetyl acetone. This is partially hydrolyzed by addition of distilled water and anhydrous butanol and then stirred for one hour in ambient environment. Subsequently, zirconium n-propoxide is added and stirred for two hours. Finally water and butanol mixture is added in a continuous stream under vigorous stirring. This leads to the formation of a clear yellowish sol.

The sol obtained was dried in an oven at 110°C for four or more hours to cause gellation and drying of the gel. The dried gel was calcined at 500°C for two hours to produce powder.

The calcined powder was then milled in a planetary mill to break the lumps of powder. The milling was carried out for 5 hours at 100 rpm.

The surface area of the powder was measured by BET method using sorptomatic, carlo erba instrumentazione and the particle size was calculated by the following relation:²⁰

| | | | | |
|-------|--------|---|--|-----|
| | d | = | K_s / S_p | (1) |
| where | d | = | particle size, Microns | |
| | K_s | = | shape factor = 6 | |
| | S | = | Surface area (in m^2/g) | |
| | ρ | = | Density, g/cc | |

3. DENSIFICATION OF THE COMPOSITE NANOPOWDER

Pressureless sintering

Green compacts of 11.7 mm diameter were made. The powder was compacted at a pressure of 150 MPa²¹ in a cylindrical die of bore diameter 11.7 mm with aspect ratio of less than 1. The green compacts were sintered at 800°C in air atmosphere for time varying from 30 minutes to 120 minutes.

Hot pressing

Hot pressing of nanocomposites with boron addition varying from 0.06 to 6.1% was done at a pressure of 55 MPa at 800°C for 30 minutes to 120 minutes.

4. CHARACTERIZATION

Since the sintered compacts were a regular circular disk, the dimensions were measured to obtain its volume. Then, from the mass of the piece, the apparent density was calculated. This in relation to the reference density gave the porosity.

Phase analysis

The phase analysis of the sintered samples was also done by XRD using CuK_{α1} line. The phase size was determined from peak broadening using the following relation²²:

$$d = \frac{0.9 \lambda}{B \cos \theta} \quad (2)$$

d = phase size, Å
 λ = wavelength of X-ray = 1.542 Å
 B = full width at half maximum, radians
 θ = position of X-ray peak

5. THE INDENTATION METHOD FOR HARDNESS AND FRACTURE TOUGHNESS

The sintered samples were studied to obtain the hardness and fracture toughness. The Vickers hardness was calculated²³ using the formula:

$$\text{VHN} = \frac{1.8544P}{d^2} \quad (3)$$

P = load, kg
d = diagonal length of the indentation, mm.

The fracture toughness K_{Ic} was calculated from the lengths of the two diagonals of the indentation²⁴:

$$K_{Ic} = 0.59 \left[\frac{E}{H_V} \right]^{1/8} (\sigma_0 P^{1/3})^{3/4} \quad (4)$$

where E = Elastic Modulus, GPa
H_V = Hardness, GPa,
σ₀ = Strength, MPa
P = Load, N

The quantities in the relation are from the diamond Vickers Indentation.²³

6. RESULTS AND DISCUSSION

The BET surface area was found to be 243.41 m²/g which corresponds to a particle size of about 5.9 nm.

The density measurement of pressureless sintered samples showed 60% porosity. The green compact showed 100% density but at the high temperature of sintering, the solgel nano powders loose molecular water so much that it leads to 60% porosity. The solgel nanoparticles have aluminium (Al) and zirconium (Zr) atoms on the surface of the nanoparticle forming Al(OH)₃ and Zr(OH)₄. Since the nanopowders have high surface area per unit weight, the powder has a large mole fraction of hydroxide molecules instead of oxide molecules. On sintering at 800°C, the hydroxyl groups are volatilized and the hydroxides of Al and Zr convert to the respective oxides losing mass and creating porosity. This leads to 60% porosity i.e., 40% of reference density.

The hot pressed samples had about 65% porosity. The hot pressed samples have no loss of hydroxyl groups or loss of mass. But they are of high friction²¹, this impedes densification and leads to high porosity.

Table 3 gives the phase/grain size analysis of pressureless sintered compacts Figures 1,2,and 3 are the XRD and grain/phase size analysis of hot pressed compacts. From the line broadening, the phase/grain sizes were calculated.

Nanosintering involved the separation of the alumina and zirconia phases from the molecular mixture of the solgel nanopowder²⁵ and simultaneous crystallisation of alumina and zirconia phases. High temperature with long sintering time is inadequate. Diffusion should be enabled with high temperature, but too much time is deleterious since the phases will would coarsen. When phase separation and crystallisation of composite nanopowders takes place in the close packed plane along the close packed directions, the growth is rapid as it is a low energy process. The third direction perpendicular to the close packed plane has a

high energy requirement for growth. The third direction is hence, of very fine nanosize. The similarity in the size of both alumina and zirconia shows that the original nanopowders were composite with alumina and zirconia mixed at the molecular level.

The two samples were sintered for different time 30minutes and 2hrs. The result was that the sample crystallized as well as sintered. Both these processes require diffusion of atoms. There may be multiple mechanisms but they all lead to diffusion²⁶. The different mechanisms require an activation energy for lattice jumps that are the basis of diffusion. As the time of sintering is increased, coarse phases are formed. The fraction of atoms having required activation energy is constant. But on increasing time, each atom having required activation energy makes more lattice jumps and hence, diffuses to longer distances. In addition, as time at the same temperature is increased, the possibility of atoms having activation energy to transfer it to another molecule during a collision of atoms also increases. This sets up a sort of diffusion chain and multiple atoms are involved in diffusion through lattice jumps over longer distances and leads to more diffusion over longer spatial lengths. This also means that as time is increased, more number of atoms participate in the diffusion process. Due to these reasons, longer time increases length of diffusion and causes coarsening of nanophases/nanograins.

Thus, increase in time increases phase/grain size. In turn, this means too less a time leads to inadequate amount of diffusion. But enough diffusion is required to transform the amorphous powder by making phase separation as well as crystallization. The pressureless sintered sample No.2 (Table 2) sintered at 800°C for two hours showed fine nanosize in one lattice direction and coarse sizes in other two lattice directions. When time is decreased to thirty minutes, two directions showed fine nano structure.

The Comparison of Table 2 and table 3 shows that the hot pressed samples has phase/grain sizes much finer than the pressureless sintered samples. The minimum effective phase size is 2.19Å and the maximum effective phase size is 3.21Å. Thus, they are of subnanometric structure. The maximum size (though it was not an effective size) is 17.29Å ie. 1.7 nm. The sub-nanometer structure could be due to applied pressure (55 MPa) or the vacuum atmosphere or their combination.

Table 4 and Table 5 give the hardness and fracture toughness of the pressureless sintered and hot pressed samples.

The pressureless sintered samples had hardness lower than the hot pressed samples. The pressureless sintered samples have much higher fracture toughness compared to conventional microscopic materials. However, the hot pressed samples had fracture toughness even higher than the pressureless sintered nanocomposites. The hot pressed samples have the best properties at 0.06% Boron, beyond that properties decrease. This could be due to softening from excess boron.

7. CONCLUSIONS

Composite nanopowders of very fine nanosize 5.9 nm were synthesized by the solgel process. They were sintered to nano/nano as well as sub-nano composites. The pressureless sintering upto 120 minutes produced nano/nano composites whereas hot vacuum pressing produced sub nano composites. The nano composites has high fracture toughness of 31.2 MPa√m and the sub-nano composites exceeded even this high fracture toughness at 40MPa√m .

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TABLES

Table 1. Source and properties of precursors and chemicals

| Sl. No. | Chemicals | Purity in Wt% | Manufacturer |
|---------|---|-----------------|---|
| 1. | Aluminium Secondary Butoxide $C_{12}H_{27}AlO_3$ | 95 | Fluka, Steinheim, Switzerland |
| 2. | Zirconium (IV) propoxide $C_{12}H_{28}O_4Zr$ | 70% in propanol | Fischer Inorganics and Aromatics, Madras, India. |
| 3. | N-Butyl alcohol | 98 | |
| 4. | Acetone | 99 | |
| 5. | Ethyl alcohol | 99.9 | Hayman, Essex, England. |
| 6. | Acetyl acetone | 98 | Ottokemi, Mumbai, India. |
| 7. | Methanol | 99.98 | Ranbaxy Laboratories, SAS Nagar, Punjab, India. |

Table 2:Phase/grain size of pressureless sintered samples

| Sample No. | Temperature (°C) | Time (minutes) | α -Al ₂ O ₃ dimension, nm | | | m--ZrO ₂ dimension, nm | | |
|------------|------------------|----------------|--|-------|-------|-----------------------------------|--------|-------|
| | | | (024) | (104) | (211) | (102) | (111) | (022) |
| 1. | 800 | 30 | 3.5 | 20 | 27 | 3.5 | 3 & 20 | 27 |
| 2. | 800 | 120 | 5.5 | 23 | 29 | 5.5 | 23 | 29 |

Table 3:Phase/grain sizes of hot pressed samples

| Sample No. | Boron % | Time (Minutes) | α -Al ₂ O ₃ dimension, Å | | m-ZrO ₂ dimension, Å | | |
|------------|---------|----------------|---|-------|---------------------------------|-----------------|-------|
| | | | (024) | (104) | ($\bar{1}$ 02) | ($\bar{1}$ 11) | (022) |
| 1. | 0 | 30 | 11.54 | 15.6 | 15.71 | 2.38 | 13.4 |
| 2. | 0.06 | 30 | 15.85 | 14.3 | 14.4 | 2.19 | 15.64 |
| 3. | 0.31 | 30 | 11.5 | 14.3 | 14.4 | 2.6 | 13.4 |
| 4. | 0.62 | 120 | 17.29 | 14.3 | 14.39 | 2.38 | 17.06 |
| 5. | 3.1 | 120 | 13.58 | 14.27 | 14.39 | 3.21 | 13.39 |
| 6. | 6.2 | 120 | 15.85 | 12.23 | 12.33 | 2.98 | 15.64 |

Table 4: Hardness and fracture toughness of pressureless sintered samples

| Sample No. | Sintering Time, min | Hardness (VHN) | Fracture toughness (K_{IC}) MPa \sqrt{m} |
|------------|---------------------|----------------|--|
| 1. | 30 | 54 | 31.52 |
| 2. | 120 | 43.18 | 22.94 |

Table 5: Hardness and fracture toughness of hot pressed samples

| Sample No. | Boron (%) | Time of Hot press, min | Hardness (VHN) | Fracture toughness (K_{IC}) MPa \sqrt{m} |
|------------|-----------|------------------------|----------------|--|
| 1. | 0 | 30 | 211.3 | 34.29 |
| 2. | 0.06 | 30 | 283 | 40.11 |
| 3. | 0.31 | 30 | 266.1 | 37.61 |
| 4. | 0.62 | 120 | 209.6 | 36.69 |
| 5. | 3.1 | 120 | 182.5 | 31.02 |
| 6. | 6.2 | 120 | 205.6 | 38.59 |

FIGURES

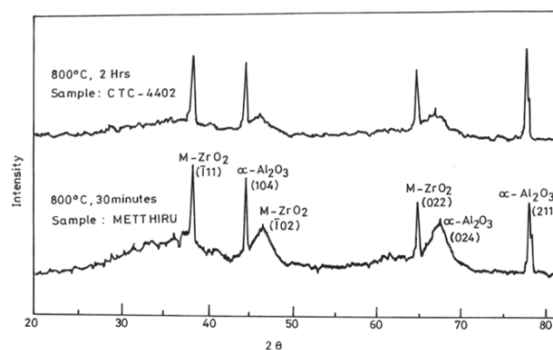


Fig.1 XRD of pressureless sintered nano/nao composite

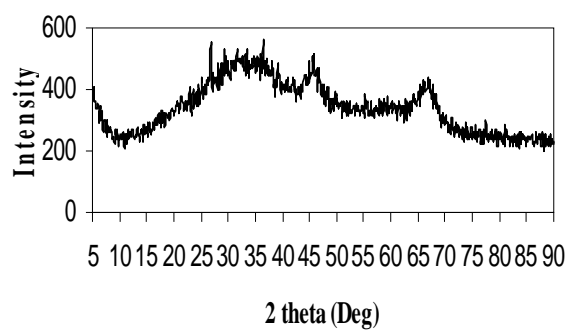
0%B-XRD/30 Minutes

Fig.2 XRD of hot pressed sample 1 with no boron

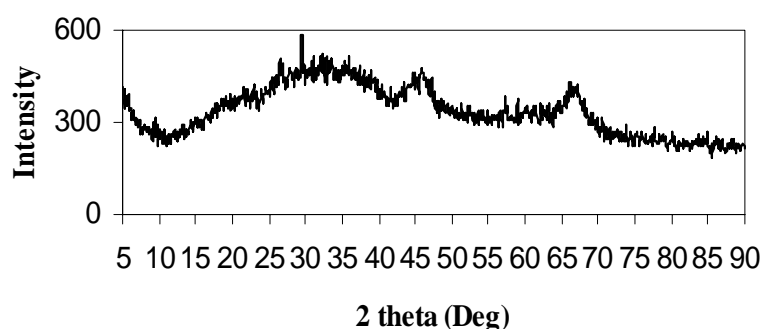
0.06%B-XRD/30 Minutes

Fig.3 XRD of hot pressed sample 2 with 0.06% boron (optimal)