Ph. D synopsis report

On

Development of zirconia toughened alumina ceramic nano-composites with addition of MgO and CNTs

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JUNE 2019

ABSTRACT

Composites are a class of materials developed by reinforcing one or more materials to the matrix. The properties of a composite mainly depend on the factors like reinforcement material and processing method. The main objectives of the present work were to investigate the effect on properties such as density, surface roughness, microhardness, fracture toughness and microstructure varying with reinforcement of MgO, MWCNTs and ZrO_2 in the alumina matrix were conducted using microwave and spark plasma sintering through powder metallurgy route.

Investigations with reinforcement of MgO and ZrO_2 in the alumina matrix were conducted using microwave sintering process in which the powders were compacted at a pressure 100 MPa and sintered at 1300°C, 1450°C, 1500°C, and 1550°C and held for 20 minutes under pressure-less condition. Similarly, the reinforcement of MgO and ZrO_2 in the alumina matrix was investigated using spark plasma sintering process in which heat and pressure were applied simultaneously at a pressure 60 MPa and sintered at 1250°C, 1300°C, and 1350°C, and held for 5 minutes. In the MW and SPS sintering process, the composition varying with reinforcement of MgO (0.5 vol. %, 1 vol. % and 2 vol. %) and 3 mol % yttria stabilized zirconia (5 vol. %, 10 vol. % and 15 vol. %) in the alumina matrix and developed of MgO-ZTA ceramic composites. The optimum properties were found with reinforcement of 1 vol. % of MgO and 10 vol. % of ZrO_2 in the alumina matrix using microwave sintering. The highest density (97.79 %), minimum surface roughness (1.511 µm), highest micro-hardness (18.09 GPa), and minimum average grain size (0.466 µm) were obtained. The highest fracture toughness (6.6 $MPa.m^{1/2}$) was found with reinforcement of 1 vol. % of MgO and 15 vol. % of ZrO_2 in the alumina matrix, at a sintering temperature of 1500°C for holding time 20 minutes. Similarly, the optimum properties were found with reinforcement of 1 vol. % of MgO and 10 vol. % of ZrO_2 in the Al_2O_3 matrix were conducted using spark plasma sintering process. The highest relative density (99.68 %), minimum surface roughness (1.123 µm), highest microhardness (19.46 GPa) and minimum average grain size (0.595 µm). The highest fracture toughness (6.7 $MPa.m^{1/2}$) was found with reinforcement of 1 vol. % of MgO and 15 vol. % of ZrO_2 in the alumina matrix, at a sintering temperature of 1300°C and holding time 5 minutes.

Investigations with reinforcement of functionalized MWCNTs and ZrO_2 in the alumina matrix were conducted using microwave sintering process in which the powders were compacted at a pressure 100 MPa and sintered at 1450°C, 1500°C, and 1550°C and held for 20 minutes under pressure-less condition. Similarly, the reinforcement of MWCNTs and ZrO_2 in the alumina matrix was investigated were conducted using spark plasma sintering process in which heat and pressure were applied simultaneously at a pressure 60 MPa and sintered at 1250°C, 1300°C, and 1350°C, and held for 5 minutes. In the MW and SPS sintering process, the varying with reinforcement of functionalized MWCNTs (0.5 vol. %, 1 vol. % and 2 vol. %) and 3 mol % yttria stabilized zirconia (5 vol. %, 10 vol. % and 15 vol. %) in the alumina matrix and developed of MWCNTs-ZTA ceramic composites. The optimum properties were found with the reinforcement of 1 vol. % of functionalized MWCNTs and 10 vol. % of ZrO_2 in the alumina matrix were conducted using microwave sintering. The highest density (97.35 %), minimum surface roughness (1.134 µm), highest microhardness (16.31 GPa), and minimum average grain size (0.461 µm) were obtained. The highest fracture toughness (8.11 $MPa.m^{1/2}$) was found with reinforcement of 1 vol. % of MWCNTs and 15 vol. % of ZrO_2 in the alumina matrix, at a sintering temperature of 1500°C for holding time 20 minutes. Similarly, the optimum properties were found with reinforcement of 1 vol. % of functionalized MWCNTs and 10 vol. % of ZrO_2 in the Al_2O_3 matrix were conducted using spark plasma sintering process. The highest relative density (97.80 %), minimum surface roughness (1.125 µm), highest microhardness (17.65 GPa) and minimum average grain size (0.3947 µm). The highest fracture toughness (8.5 $MPa.m^{1/2}$) was found with reinforcement of 1 vol. % of MWCNTs and 15 vol. % of ZrO_2 in the alumina matrix, at a sintering temperature of 1300°C for holding time 5 minutes.

The mechanical properties and uniform disperse microstructure of SPS sintered samples were observed to be superior compared to the MW sintered samples. Among all the samples, highest density, minimum surface roughness, highest microhardness, and minimum average grain size were observed with the MgO-ZTA composite processed through SPS while highest fracture toughness was observed with the MWCNTs-ZTA composite processed through SPS. The minimum value of COF and wear rate was observed with the developed MgO-ZTA composite processed through SPS.

Keywords*:* Alumina; Zirconia; MWCNTs; Zirconia toughened alumina; Spark plasma sintering; Microwave sintering, Nanocomposites; Mechanical properties; Microstructure

1. INTRODUCTION

A composite material is a macroscopic fusion of two or more distinct materials with a recognizable interface. The Composite exhibits a notable fraction of both constituent phases in order to achieve the better conjunction of properties. The composite industries have started to perceive that the business use of composites guarantees to offer significantly larger opportunities than the aviation on the account of the unmitigated capacity of the transportation industry. Therefore, the composite applications have shifted from aircraft to other commercial utilization in recent years. The various reasons for the use of composites are:

- To enhance strength, stiffness and dimensional stability.
- To enhance toughness and impact strength.
- To increase heat deflection temperature and mechanical damping.
- To modify electrical properties and reduce cost.
- To minimize thermal expansion, the permeability of gases and liquids.
- To increase chemical, wear and corrosion resistance.

1.1 Classification of composites

Composites are commonly classified at two distinct levels as given below.

1.1.1 Based on the type of matrix material

Based on the type of matrix material, composites are classified into four main types. Fig. 1 represents the block diagram of composites based on the type of matrix material.

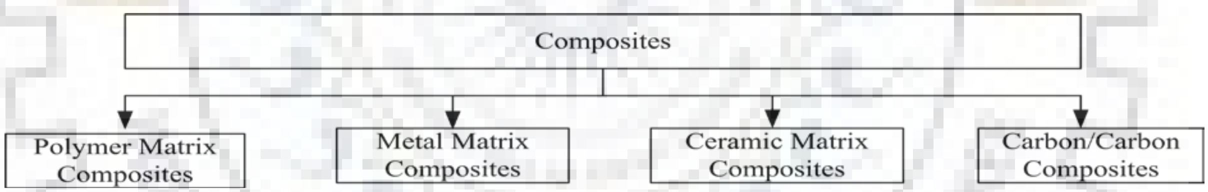

Fig. 1 Classification of composites based on the type of matrix material

(a) Polymer Matrix Composites

Polymer Matrix Composites (PMCs) use graphite, boron, and carbon as a fiber material. Nearly all PMCs use commercial fibers such as carbon-graphite and aramid fiber as a reinforcement. Thermoplastic, thermo-set materials and epoxy are used as matrix phases.

(b) Metal Matrix Composites

Metal Matrix Composites (MMCs) are advanced class of structural materials consisting of nonmetallic reinforcements incorporated into the metallic matrix. MMCs are widely used in engineering applications where the operating temperature lies in between 250ºC to 750ºC.

(c) Ceramic Matrix Composites

Ceramic Matrix Composites (CMCs) can be described as solid materials which exhibit very strong ionic bonding in general and in few cases covalent bonding. High melting points, good corrosion resistance, stability at elevated temperatures and high compressive strength, render ceramic-based matrix materials a favorite for applications requiring a structural material that doesn't give way at temperatures above 1500ºC.

(d) Carbon/Carbon Composites

Carbon/Carbon Composites (C/Cs) are developed specifically for parts that must operate in extreme temperature ranges.

1.1.2 Based on the geometry of reinforcement

Based on the geometry of reinforcement, the composites are classified into four main types. The block diagram of composites classification based on the geometry of reinforcement is shown in Fig. 2.

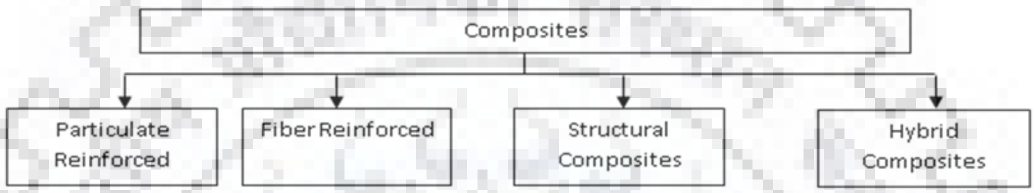

Fig. 2 Classification of composites based on the geometry of reinforcement

(a) Particulate reinforced composites

The dispersed phase for particle-reinforced composites is equiaxed (i.e., Particle dimensions are approximately the same in all directions) and the dispersed phase of fiber-reinforced composites have the geometry of fiber-reinforced composites have the geometry of a fiber.

(b) Fiber-reinforced composites

These are strong fibers embedded in a softer matrix to produce products with high strength to weight ratios. The matrix material transmits the load to the fibers, which absorb the stress.

(c) Structural composites

Structural composites are further classified as laminar structural composites and sandwich structures.

(d) Hybrid composites

A composite laminate comprises of the laminate of two or more composite material systems or a combination of two or more different fibers such as C and glass or C and armed into a structure. Hybrid composites consist of two constituents at the nanometer or molecular level.

1.2 Ceramic Matrix Composites

Ceramics are inorganic and non-metallic solids that are typically available in the form of powder materials. The basic reinforcements which are included in the ceramic matrices are carbon, glasses, glass-ceramics, oxides and non-oxides. Ceramic matrix composites (CMCs) can be processed either by conventional powder processing technique or by other more specific and customized techniques.

(a) Advantages of ceramic matrix composites

- Higher chemical stability

- Low density and light weight
- Excellent wear and corrosion resistance
- Improved toughness and stiffness
- Improved strength, and hardness at higher service temperatures

(b) Applications of ceramic matrix composites

The applications of ceramic matrix composite are used in various fields such as cutting tools, face seals, valving parts, actuators, slide bearings and rotary-vortex pumps.

1.3 Fabrication of ceramic composites through powder metallurgy

Powder metallurgy is a process of mixing and compressing different metal or ceramic powders to form finished and semi-finished components. After compressing, subsequent heating at elevated temperature in a furnace under a controlled atmosphere is done so as to obtain satisfactory strength, density without losing essential shape. The powder metallurgy process generally consists of four basic steps: powder manufacturing, powder blending, compacting, and sintering.

1.3.1 Powder compaction

Powder compaction is the process of compacting metal powder in the die through the application of high pressures. Typically, the tools are held in the vertical orientation with the punch tool forming the bottom of the cavity. The powder is then compacted into a shape and then ejected from the die cavity.

1.3.2 Sintering

Solid state sintering is the process of taking the material in the form of a powder and compact it into a mold or die. Once compacted into the mold, the material is placed under high heat for a long period of time. The un-sintered and sintered powder particles are presented in Fig. 3, which shows the un-sintered powders bounded together to form sintered powders.

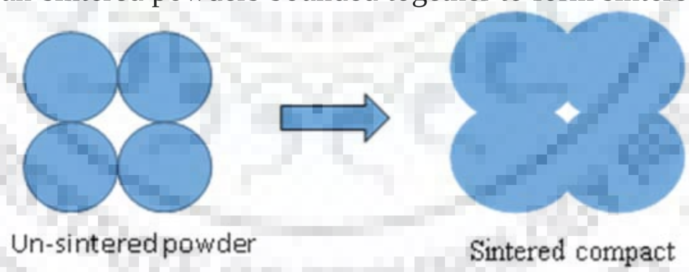

Fig. 3 Representation of un-sintered powder and sintered powder compact

(a) Advantages of powder metallurgy

- Freedom to start with raw materials with uniform purity characteristics
- Control of grain size with uniform structure
- Improved physical properties
- No needs high skilled personnel

(b) Disadvantages of powder metallurgy

- Difficult to secure exceptionally high purity power with satisfactory quality

- Less profit to manufacturing components in very small quantity
- Needs of the heavy expense of the tooling and equipment
- Oxidization of porous materials at elevated temperature

1.4 Advanced sintering methods

There are various advanced sintering methods like graphite resistance sintering, high induction graphite heating, microwave sintering and spark plasma sintering. Out of these four, microwave sintering and spark plasma sintering are discussed.

1.4.1 Microwave sintering

Microwave sintering can achieve rapid heating uniformity and does not subject the specimen to cracking or thermal stress. Because microwave has a strong ability to penetrate deep into the interior of the sample, first the temperature at the center of the sample rises rapidly to reach the ignition point and triggers combustion synthesis. Fig. 4 represents the schematic diagram of Microwave sintering furnace.

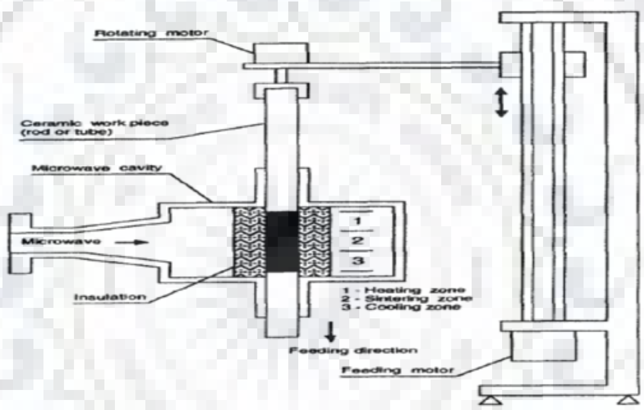

Fig. 4 Schematic of microwave sintering furnace

(a) **Advantages of microwave sintering**

- The sintering temperature is significantly reduced.
- 70 % energy savings than the conventional sintering.
- Sintering time is shortened as compared to conventional radiant heating.
- Densification process is accelerated both inside and outside the compact.

1.4.2 Spark plasma sintering

Spark plasma sintering (SPS) is a new method of compacting and sintering nano-crystalline powders with fine grain growth and effective shrinkage in less time as well as obtaining cleaner grain boundaries for effective interface formation. The current plays two roles in SPS i.e. promote enhanced diffusion rate during phase growth and inter-metallic diffusion and source of heating by Joule’s effect. When the powders are placed in the die, the current is passed through the sample and through resistance; the sample is heated as shown in Fig. 5. The sintering is done in the vacuum, so as to protect the placed materials from chemical oxidation.

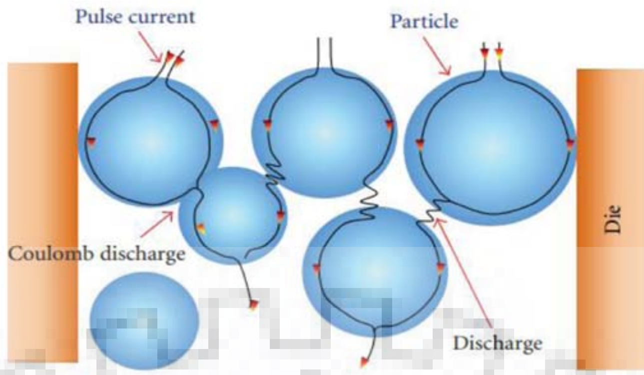

Fig. 5 DC pulse current flow through the particles

(a) Advantage of spark plasma sintering

- Fast sintering process and uniform suppression grain growth
- Low grain growth (nano-grain materials may be prepared)
- Compaction and sintering stages are achieved in one operation
- Binders are not necessary; High energy efficiency; Easy operation
- Better purification and activation of the powder particle surfaces

2. GAP AREAS OF RESEARCH WORK

The gap areas identified based on the literature review are as follows –

- Several investigations have been made on alumina toughened zirconia and also on zirconia toughened alumina ceramic-based nanocomposites, but very little work has been attempted on 3 mol % partially yttria-stabilized zirconia for retaining stability at elevated temperatures during the sintering process.
- Many researchers have worked on zirconia toughened alumina ceramic based nanocomposites. However, no work has been attempted on zirconia toughened alumina with the addition of magnesia to reduce the activation energy and to reduce sintering temperature.
- Much work has been carried out to develop ceramic-based composites using conventional sintering. However, very little work has been done to develop ceramic-based composites using spark plasma sintering and microwave sintering, which are recently developed and novel techniques.
- Many researchers have attempted to reinforce nano ceramic powder into a micro level matrix. However, very little work has been done to reinforce nano ceramic powder into a nano level matrix.
- Certain investigations have been carried out to explore the beneficial effects of the addition of carbon nanotubes (CNTs) in ZrB_2 based ultra-high temperature ceramic composites; yttria doped tetragonal zirconia composites, etc. However, no attempt has been made to investigate the effect of CNTs on zirconia toughened alumina ceramic-based nanocomposites.

3. OBJECTIVES OF THE PRESENT INVESTIGATIONS

Based on the literature review and the gap areas identified, the objectives of the proposed work are framed as follows -

(a) Development of zirconia - alumina ceramic composite with addition of magnesia
- To develop zirconia toughened alumina ceramic-based nanocomposite (with a small amount of magnesia) through the spark plasma sintering.
- To develop zirconia toughened alumina ceramic-based nanocomposite (with a small amount of magnesia) through the microwave sintering.
- To compare the properties like density, surface roughness, hardness, fracture toughness of the above two composites and select the best one for further investigations.

(b) Development of zirconia - alumina ceramic composite with addition of CNTs
- To develop zirconia toughened alumina ceramic-based nanocomposite (with a small amount of CNTs) through spark plasma sintering.
- To develop zirconia toughened alumina ceramic-based nanocomposite (with a small amount of CNTs) through microwave sintering.
- To compare the properties like density, surface roughness, hardness, fracture toughness of the above two composites and select the best one for further investigations.

(c) To make tribological studies on the developed composites
- Pin on disc tribological studies
- Coefficient of friction at different-2 load and sliding speed
- Wear rate at different-2 load and sliding speed
- Worn out surface analysis

(d) To characterize their microstructure through XRD, Fe-SEM, EDS, etc.

(e) To compare the overall properties of the two composites developed and to optimize their processing parameters.

The flow diagram of the developed MgO-TZA and MWCNTs-ZTA composite varying with MgO, MWCNTs and ZrO_2 reinforced in the alumina matrix using MW and SPS sintering through powder metallurgy route is shown in Fig. 6.

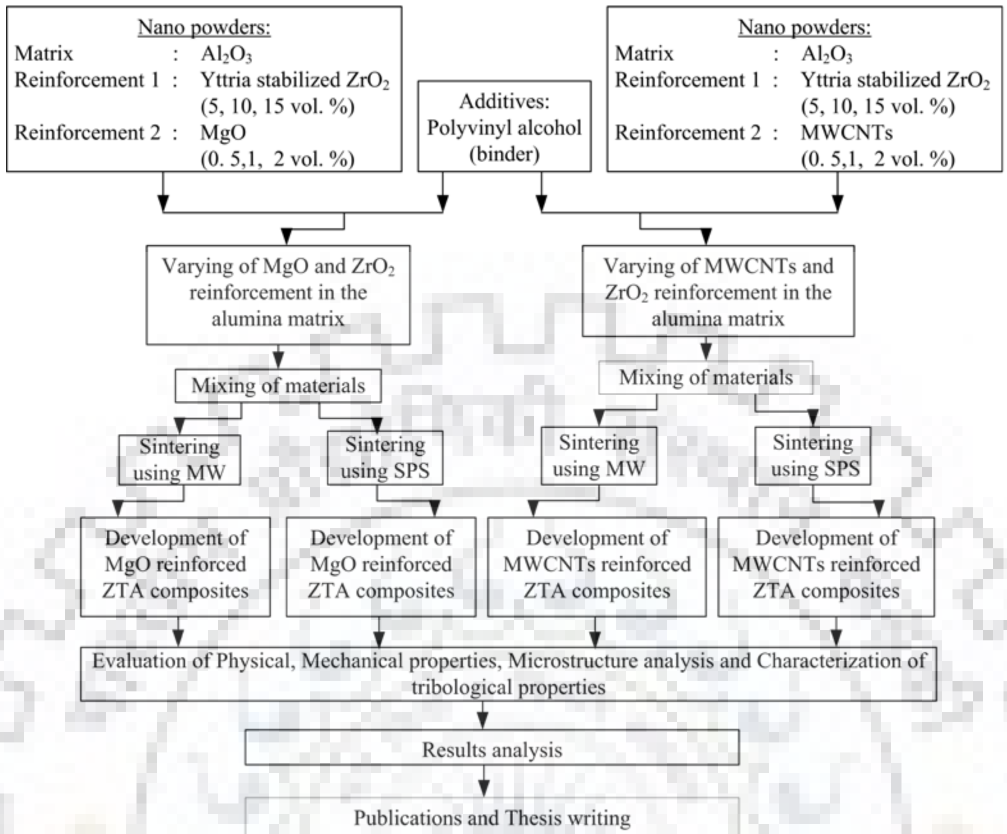

Fig. 6 Flow diagram of present work plan using MW and SPS sintering processes through powder metallurgy route

4. EXPERIMENTAL WORK

4.1 Selection of materials

The materials for the matrix as well as reinforcement are selected so as to achieve the desired properties of the composites.

4.1.1 Selections of matrix material

Most of the commercial work on CMCs has focused on alumina as the matrix material. The composites of alumina-based ceramics have excellent properties of chemical inertness and high abrasion resistance, high-hot-hardness against extreme environments. Alumina is used to make cutting inserts in comparison to carbide and high-speed steels, which is due to the inert behavior of alumina at elevated temperature.

4.1.2 Selections of reinforcement materials

- Nano yttria was added in zirconia to retain stability in tetragonal phase at room temperature and yttria-stabilized zirconia was added in the alumina matrix. Hence, yttria (Y_2O_3), which belongs to the group of rare earth (RE) materials are used as reinforcement in the present work.

- The addition of MgO increases the hardness and MWCNTs increases fracture toughness that appears to be a good option as a secondary reinforcement, as it is a hard ceramic toughened and offers good wear resistance. Hence, MgO and MWCNTs are selected as secondary reinforcing materials.

4.2 Compaction and sintering

The powders were mixed manually using an agate pestle mortor for 40 minutes each sample. After mixing, the powders were dried at 50°C to remove the moisture content and were sieved to remove the agglomerated particles. The binder of polyvinyl alcohol was used to avoid cracking during the sintering process. Table 1 shows the process parameters and their ranges used in MW sintering and Spark plasma sintering.

Table 1 Process parameters and their ranges

Parameter	MW sintering	SPS sintering
Pressure	100 MPa (Hydraulic pressure)	60 MPa (Constant)
Temperature	1300°C, 1450°C, 1500°C and 1550°C	1250°C, 1300°C, and 1350°C
Heating rate	25 °C/min	100 °C/min
Holding time	20 minutes	5 minutes
Environment	Inert gas (Argon gas)	Vacuum

The sintered samples were getting the shape of 15 mm diameter, 3 mm height. The density of sintered samples was measured using Archimedes' principle. This method was used to weigh of samples in air and in distilled water using an electronic balance with the accuracy of 0.0001 g.

4.3 Development of composite with addition of MgO

MgO with (0.5 vol. %, 1 vol. % and 2 vol. %) and zirconia (5 vol. %, 10 vol. % and 15 vol. %) were reinforced in the alumina matrix to develop the MgO-ZTA ceramic composites using MW and SPS process through powder metallurgy route.

4.3.1 Development of composite using microwave sintering

MgO and zirconia reinforced in the alumina matrix successfully developed the MgO-ZTA ceramic-based composites using microwave sintering through powder metallurgy route. Each composition was weighed and mixed. After that, the powders were compacted at a pressure of 100 MPa and sintered. The properties such as density, surface roughness, microhardness, fracture toughness, phase analysis, and EDS dot mapping microstructure were investigated.

4.3.2 Development of composite using spark plasma sintering

MgO and zirconia reinforced in the alumina matrix successfully developed the MgO-ZTA ceramic-based composites using SPS through powder metallurgy route. Each composition was weighed and mixed. After that, the powders were pressed under the rapid heating. The properties such as density, surface roughness, microhardness, fracture toughness, phase analysis, and EDS dot mapping microstructure were investigated.

4.4 Development of composite with addition of CNTs

Functionalized MWCNTs (0.5 vol. %, 1 vol. % and 2 vol. %) and zirconia (5 vol. %, 10 vol. % and 15 vol. %) reinforced in the alumina developed the MWCNTs-ZTA ceramic composites using MW and SPS process through powder metallurgy route.

4.4.1 Development of composite using microwave sintering

MWCNTs and zirconia reinforced in varying proportions in the alumina matrix successfully developed the MWCNTs-ZTA ceramic-based composites using microwave sintering through powder metallurgy route. Each composition was weighed and mixed. After that, the powders were compacted at a pressure of 100 MPa and sintered. The properties such as density, surface roughness, microhardness, fracture toughness, phase analysis, and EDS dot mapping microstructure were investigated.

4.4.2 Development of composite using spark plasma sintering

MWCNTs and zirconia reinforced in varying proportions in the alumina matrix and successfully developed the MWCNTs-ZTA ceramic-based composites using an SPS process through powder metallurgy route. Each composition was weighed and mixed. After that, the powders were pressed under the rapid heating at the sintering temperature of 1250°C, 1300°C and 1350°C and for 5 minutes holding time under pressure of 60 MPa simultaneously. The properties such as density, surface roughness, microhardness, fracture toughness, phase analysis, and EDS dot mapping microstructure were investigated.

4.5 Characterization

4.5.1 Physical characterization

(a) Density

The compacts were cylindrical in shape, so the diameter and length are measured to calculate the volume, weight of the compacts are measured, then the density of the samples are calculated as ρ (s) using the Archimedes principle. The relative density is calculated using (Eq.1).

$$\text{Relative density } \rho(r) = \frac{\rho(s)}{\rho(t)} \qquad (1)$$

Where relative density ρ(r) is the ratio of sintered density ρ(s) to the theoretical density ρ (t) of the composite

(b) Surface roughness

Surface roughness was measured using Talysurf profilometer and it is a contact type device.

4.5.2 Metallurgical characterization

(a) FE-SEM

FESEM produces clearer, less electro-statically distorted images with spatial resolution down to 1.5 nm which is 3 to 6 times better than conventional SEM. The microstructure analysis of sintered samples was used to field emission scanning electron microscope (FE-SEM, Carl-Zeiss Ultraplus, Germany).

(b) XRD analysis

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

X-ray diffraction (XRD) (Smart lab, Rigaku Japan) technique was used for the structural and phase analysis of sintered samples. The XRD parameter has performed for the angle of a 2θ range of 15-80°, the scan rate of 0.5 °/min and ~0.1° step size for all sintered samples.

4.5.3 Mechanical characterization

(a) Hardness

The clear microstructure can be observed with a better surface finish of sintered samples. First of all, the sintered sample was polished through emery paper of 80 to 2000 grades and then followed by polishing on the clothes with alumina powders and then further followed by the diamond paste up to 1 μm roughness. Vickers hardness was measured using a microhardness test machine. The hardness parameters have performed to indentation load 200 gram and dwell time 10 sec.

(b) Fracture toughness

There are several indentation fracture equations for the determination of the fracture toughness by the Vickers indentation fracture method. Anstis equation is preferred to value of c/a ratio >2.5 and under the higher load which comes under the radial-median crack system. In my experimentation, I found to be given c/a ratio higher than 2.5 and under higher load of 98 N. The value of fracture toughness (K_{IC}) was calculated using the Anstis equation using the following relation (Eq. 2).

$$(K_{IC}) = 0.016\left(\frac{E}{H_V}\right)^{\frac{1}{2}}\frac{P}{C^{\frac{3}{2}}} \qquad (2)$$

Where the ‘P’ is the applied indenter load, ‘E’ is Young’s modulus, ‘c’ is the radial crack length, ‘a’ half of the indentation diagonal and ‘Hv’ is the Vickers hardness.

(c) Tribological studies

The dry sliding test was carried out using 320 grades of emery paper on the disc surface while the normal load range (35 N, 45 N, 55 N and 65 N) and sliding speed range 150 rpm, 250 rpm, 350 rpm, and 450 rpm were applied. The tribological tests were repeated varying with a higher normal load range (65 N, 75 N, 85 N and 95 N at higher sliding speed of 450 rpm. Among all the samples, tribological studies were performed on four optimized developed MgO-ZTA using SPS, MgO-ZTA using MW, MWCNTs-ZTA using SPS, and MWCNTs-ZTA using MW composites with 1 vol. % of MgO, 1 vol. % of MWCNTs and 1 vol. % of ZrO_2 reinforced added in the alumina matrix.

5. RESULTS

5.1 Investigations with the addition of MgO

5.1.1 Investigations using MW process

The optimum properties were found in the composition of 1 vol. % of MgO and 10 vol. % of ZrO_2 reinforced in the alumina matrix. The highest density (97.79 %), minimum surface roughness (1.511 μm), highest microhardness (18.09 GPa), and minimum average grain size (0.466 μm) were obtained. The highest fracture toughness (6.6 $MPa.m^{1/2}$) was found in the composition of 1 vol. % of MgO and 15 vol. % of ZrO_2 reinforced added in the alumina matrix, at a sintering temperature of 1500°C. The addition of 1 vol. % of MgO provided better pinning effect to inhibit the grain growth of Al_2O_3 and ZTA which leads to uniform dense and tough microstructure. The pinning effect was found caused by the formation of secondary phases. The presence of secondary phases plays significant roles in affecting the mechanical properties of ceramic composites. XRD confirms the constituent phases presents of major peaks were ZrO_2, α-Al_2O_3, and MgO. The MgO phase showed the minor peak of the secondary phase ($MgAl_2O_4$). The microhardness was increased added up to 1 vol. % of MgO and 15 vol. % of ZrO_2 reinforced in the alumina matrix. Nano-size zirconia was used to increase the fracture toughness and MgO was used to increase the hardness of the MgO-ZTA composite. Uniform microstructure was observed using an FE-SEM and obtained the sub-micron level of grain size.

5.1.2 Investigations using SPS process

The optimum properties were found with the compositions of 1 vol. % of MWCNTs and 10 vol. % of ZrO_2 reinforced in the Al_2O_3 matrix. The highest relative density (99.68 %), minimum surface roughness (1.123 µm), highest microhardness (19.46 GPa) and minimum average grain size (0.595 µm). The highest fracture toughness was found to be 6.7 $MPa.m^{1/2}$ the added with 1 vol. % of MgO and 15 vol. % of ZrO_2 reinforced in the Al_2O_3 matrix for the

holding time 5 minutes and sintering temperature of 1300°C. Nano-size zirconia was used to increase the fracture toughness and MgO was used to increase the hardness of the MgO-ZTA composite. XRD indicate the presence of major phases were ZrO_2, α-Al_2O_3, MgO, magnesia phase with minor peaks of the secondary phase $MgAl_2O_4$. Uniform disperse and suppressed grain growth microstructure was observed using an FE-SEM and obtained the sub-micron level of grain size. The developed composite has high hardness and tough to make it more suitable for applications such as ballistic armor and thermal barrier coating. Among all four developed composites, the maximum density and hardness added with 1 vol. % of MgO and 10 vol. % of ZrO_2 reinforced in the alumina matrix and developed MgO-ZTA composite using SPS was observed as shown in Fig. 7 and Fig. 8. Uniform disperse microstructure and suppressed grain growth was observed added with 1 vol. % of MgO and 10 vol. % of ZrO_2 reinforced in the alumina matrix using FE-SEM and obtained the sub-micron level of grain is shown in Fig. 9.

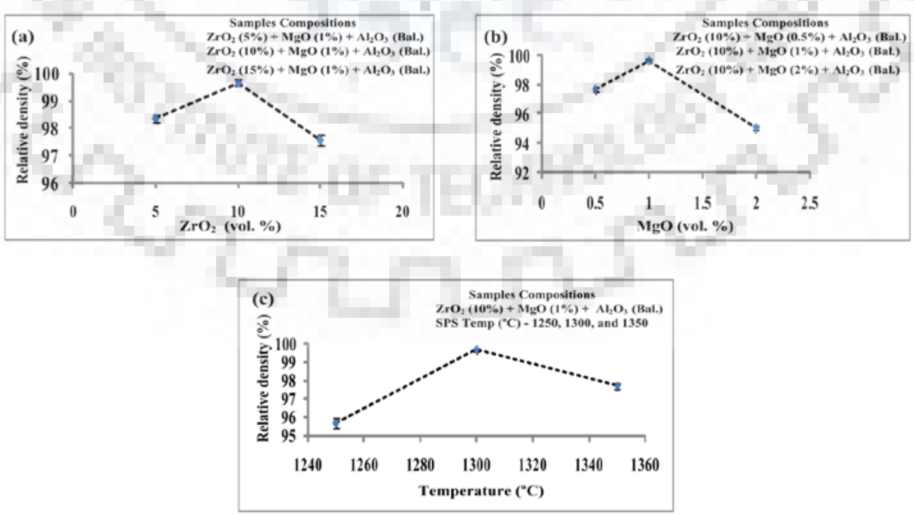

Fig. 7 Relative density of MgO-ZTA composite varying with (a) ZrO_2 (b) MgO and (c) sintering temperatures

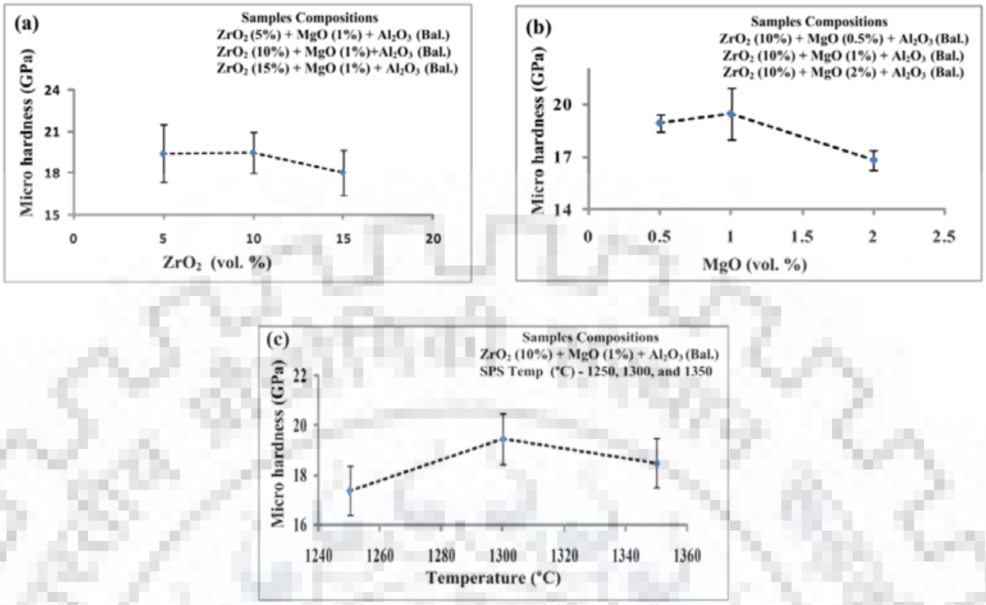

Fig. 8 Microhardness of MgO-ZTA composite varying with (a) ZrO_2 (b) MgO and (c) sintering temperatures

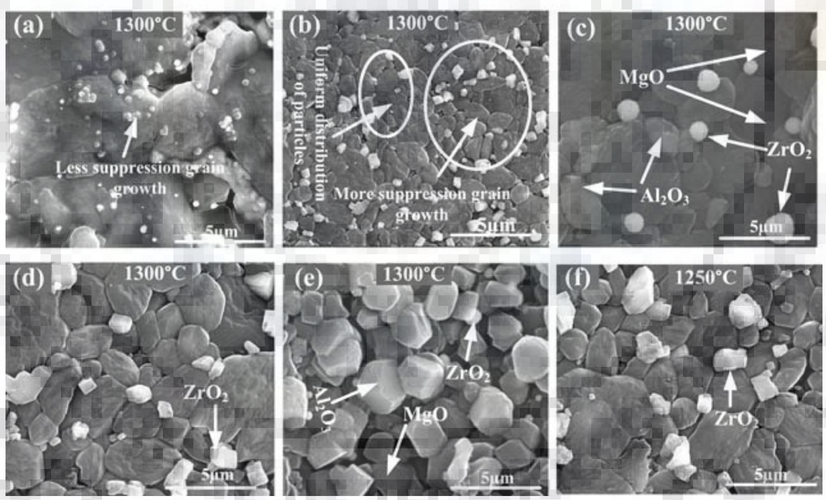

Fig. 9 FE-SEM microstructure of thermally etched MWCNTs-ZTA composite varying with (a) 5 vol.% of ZrO_2 (b)10 vol. % of ZrO_2 (c) 15 vol.% of ZrO_2 (d) 0.5 vol. % of MgO (e) 2 vol. % of MgO (f) 1 vol. % of MgO

5.2 Investigations with the addition of CNTs

5.2.1 Investigations using MW process

The optimum properties were found with the compositions of 1 vol. % of MWCNTs and 10 vol. % of ZrO_2 reinforced in the Al_2O_3 matrix. The highest density (97.35 %), minimum surface roughness (1.134 µm), highest micro-hardness (16.31 GPa), and minimum average grain size (0.466 µm) were received. The highest fracture toughness obtained in the composition of 1 vol. % of MWCNTs and 15 vol. % of ZrO_2 reinforced added in the alumina matrix was 8.11 MPa.m$^{1/2}$. The addition of 1 vol. % of MWCNTs provided better pinning effect to inhibit the grain growth of Al_2O_3 and ZTA which leads to a completely uniform dense and tough microstructure. The pinning effect was found due to the formation of secondary phases. The presence of secondary phases plays significant roles in affecting the mechanical properties of ceramic composites. The XRD confirms the constituent phases presents of major peaks were ZrO_2, α-Al_2O_3, and MWCNTs. The carbon phase showed the minor peaks in the form of the secondary phase $C_6Al_2O_{12}$, Al_2OC, and ZrC. Uniform disperse and suppressed grain growth microstructure was observed using an FE-SEM and obtained the sub-micron level of grain size.

5.2.2 Investigations using SPS process

The optimum properties were found with the compositions of 1 vol. % of MWCNTs and 10 vol. % of ZrO_2 reinforced in the Al_2O_3 matrix. It showed the highest density (97.80 %), minimum surface roughness (1.123 µm), the highest microhardness (17.65 GPa) and minimum average grain size (0.3947µm), while the highest fracture toughness was found to be 8.5 MPa.m$^{1/2}$ the added with 1 vol. % of MWCNTs and 15 vol. % of ZrO_2 reinforced in the Al_2O_3 matrix for the holding time 5 min and sintering temperature of 1300°C. The X-ray diffraction pattern confirms the constituent phases presents of major peaks were ZrO_2, α-Al_2O_3, and MWCNTs. The carbon phase showed the minor peak in the form of the secondary phase $C_6Al_2O_{12}$, Zr_2Al_3, $ZrAl_3C_4$ and ZrC. The property of microhardness was increased added up to 1 vol. % of MWCNTs and increased the fracture toughness added up to 15 vol. % of ZrO_2 in the alumina matrix. The fracture toughness was increased varying with MWCNTs and ZrO_2 reinforced added in the alumina matrix. Among all four developed composites, the maximum fracture toughness added with 1 vol. % of MgO and 15 vol. % of ZrO_2 reinforced in the alumina matrix and developed MWCNTs-ZTA composite using SPS was observed as shown in Fig. 10. Uniform disperse and suppressed grain growth was observed added with 1 vol. % of MgO and 15 vol. % of ZrO_2 reinforced in the alumina matrix and obtained the sub-micron level of grain size using FE-SEM is shown in Fig. 11.

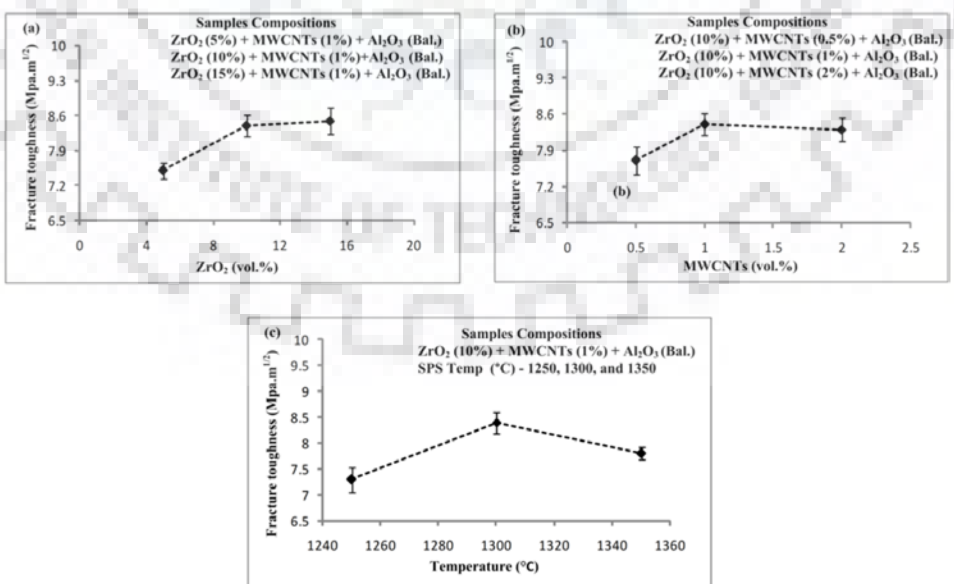

Fig. 10 Fracture toughness of MWCNTs-ZTA composite with varying amounts of (a) ZrO_2 (b) MWCNTs and (c) sintering temperatures

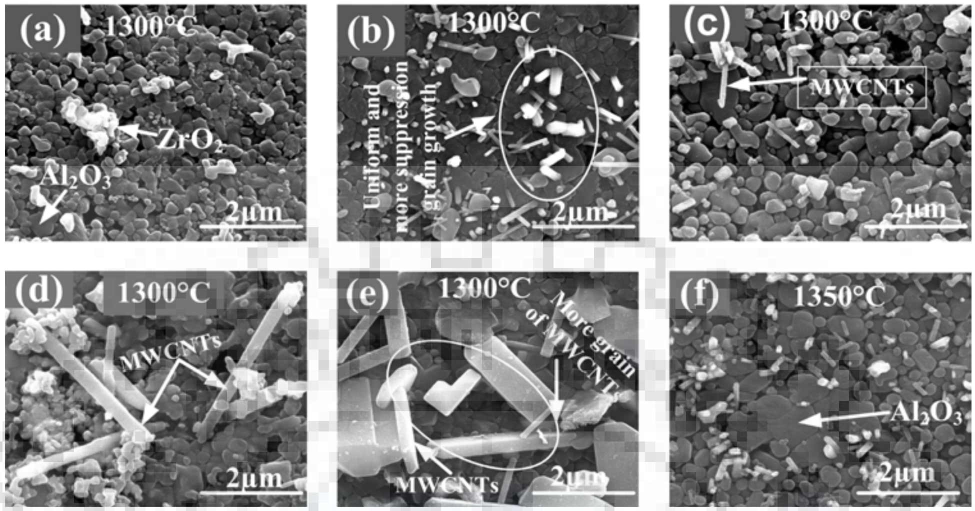

Fig. 11 FE-SEM microstructure of thermally etched MWCNTs-ZTA composite with (a) 5 vol.% of ZrO_2 (b)10 vol. % of ZrO_2 (c) 15 vol.% of ZrO_2 (d) 0.5 vol. % of MWCNTs (e) 2 vol. % of MWCNTs (f) 1 vol. % of MWCNTs and

5.3 Investigations on the tribological studies

The coefficient of friction and wear rate decreased with the increase of normal loads at sliding speeds 150 rpm, 250 rpm, and 350 rpm. The value of the coefficient of friction and wear rate decreases with the increasing of sliding speed with a variable normal load. The values of the coefficient of friction in the SPS sintered sample were lesser than that of the MW sintered sample with increasing of normal loads at a sliding speed of 450 rpm. The MW sintered samples were loose tribo-layer formed at the tribo surface than SPS sintered samples which were found in more uncovered tribo batches at the tribo surface in the MW sintered sample. The characterization tribological properties on the pin on disc of MgO-ZTA and MWCNTs composites through SPS process found better results compared MW process. Increased normal load due to adherent layer reduces the frictional force between tribo couple and results in reduced wear rate and coefficient of friction. COF and Wear rate has performed with optimize four develop MgO-ZTA using SPS, MgO-ZTA using MW, MWCNTs-ZTA using SPS, and MWCNTs-ZTA using MW are shown in Fig. 12 and Fig. 13.

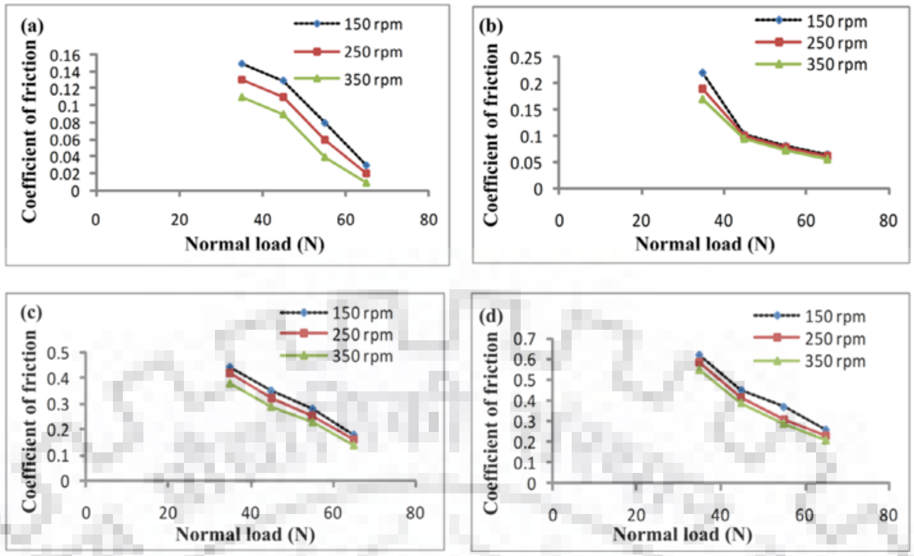

Fig. 12 COF values varying with normal loads at different fixed sliding speeds of 150 rpm, 250 rpm, 350 rpm for : (a) MgO-ZTA using SPS (b) MgO-ZTA using MW (c) MWCNTs-ZTA using SPS (d) MWCNTs-ZTA using MW

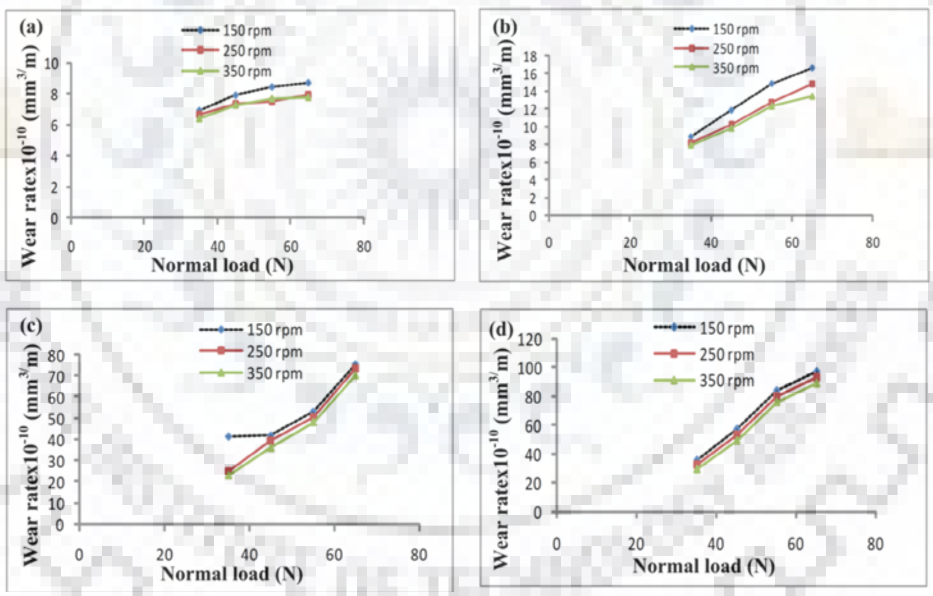

Fig. 13 Wear rate values varying with normal load at different fixed sliding speeds with a fixed value of 150 rpm, 250 rpm, 350 rpm for : (a) MgO-ZTA using SPS (b) MgO-ZTA using MW (c) MWCNTs-ZTA using SPS (d) MWCNTs-ZTA using MW

6. CONCLUSIONS

Based on the present investigations, the following major conclusions can be drawn -

CONCLUSIONS ON THE ADDITION OF MAGNESIA USING MW SINTERING

- The optimum properties were found with the reinforcement of 1 vol. % of MgO and 10 vol. % of ZrO_2 in the Al_2O_3 matrix at a sintering temperature of 1500°C using MW.
- The highest density was found to be 97.79 %.
- The minimum value of surface roughness was found to be 1.511 µm.
- The highest microhardness was found to be 18.09 GPa.
- The highest fracture toughness was found to be 6.6 MPa.m$^{1/2}$ which was found with the reinforcement of 1 vol. % of MgO and 15 vol. % of ZrO_2 in the alumina matrix.

CONCLUSIONS ON THE ADDITION OF MAGNESIA USING SPS SINTERING

- The optimum properties were found with the reinforcement of 1 vol. % of MgO and 10 vol. % of ZrO_2 in the Al_2O_3 matrix at a sintering temperature of 1300°C using SPS.
- The highest density was found to be 99.68 %.
- The minimum value of surface roughness was found to be 1.123 µm.
- The highest microhardness was found to be 19.46 GPa.
- The highest fracture toughness was found to be 6.7 MPa.m$^{1/2}$ which was found with the reinforcement of 1 vol. % of MgO and 15 vol. % of ZrO_2 in the alumina matrix.

CONCLUSIONS ON THE ADDITION OF MWCNTS USING MW SINTERING

- The optimum properties were found with the reinforcement of 1 vol. % of MWCNTs and 10 vol. % of ZrO_2 in the Al_2O_3 matrix at a sintering temperature of 1500°C using MW.
- The highest density was found to be 97.35 %.
- The minimum value of surface roughness was found to be 1.134 µm.
- The highest microhardness was found to be 16.31 GPa.
- The minimum average grain size was found to be 0.461 µm.
- The highest fracture toughness was found to be 8.11 MPa.m$^{1/2}$ which was found with the reinforcement of 1 vol. % of MWCNTs and 15 vol. % of ZrO_2 in the alumina matrix.

CONCLUSIONS ON THE ADDITION OF MWCNTS USING SPS SINTERING

- The optimum properties were found with the reinforcement of 1 vol. % of MWCNTs and 10 vol. % of ZrO_2 in the Al_2O_3 matrix at a sintering temperature of 1300°C using SPS.
- The highest density was found to be 97.80 %.
- The minimum value of surface roughness was found to be 1.125 µm.
- The highest microhardness was found to be 17.65 GPa.

- The highest fracture toughness was found to be 8.5 $MPa.m^{1/2}$ which was found with the reinforcement of 1 vol. % of MWCNTs and 15 vol. % of ZrO_2 in the alumina matrix.

COMPARISONS OF ALL FOUR CASES

- The mechanical properties and microstructure of SPS sintered samples were observed to be superior compared to the MW sintered samples.
- Among all the samples, highest density, minimum surface roughness, highest microhardness, and minimum average grain size were observed with the MgO-ZTA composite processed through SPS.
- The highest fracture toughness was observed with the developed MWCNTs-ZTA composite processed through SPS.
- The minimum value of COF and wear rate was observed with the developed MgO-ZTA composite processed through SPS.

7. THESIS ORGANIZATION

Chapter 1 – Introduction

The chapter discusses the past and present stages of research regarding magnesia, CNTs, zirconia and alumina, MW and SPS sintering process.

Chapter 2 – Literature review

In this chapter, an extensive literature review is presented on factors affecting the process parameters of MW, SPS sintering and development of composites with magnesia, CNTs, zirconia and alumina.

Chapter 3 – Experimental procedure

In his chapter, MW and SPS sintering of alumina with MgO, CNTs, zirconia as reinforcement was done. Seven composites each with varying magnesia, CNTs, zirconia were developed by MW and SPS sintering.

Chapter 4 – Development of composites with addition of MgO

Six composite samples with alumina as matrix material and varying vol. % of MgO, CNTs and zirconia as nano reinforcement were sintered using MW.

Chapter 5 – Development of composites with addition of CNTs

Six composite samples with alumina as matrix material and varying vol. % of MgO, CNTs and zirconia as nano reinforcement were sintered using SPS.

Chapter 6 – Conclusions

8. PUBLICATIONS FROM THE PRESENT WORK

List of published papers	
1	**K.L. Meena**, D.B. Karunakar, Effect of ZrO_2 and MgO added in alumina on the physical and mechanical properties of spark plasma sintered nanocomposite, **International Journal of Refractory Metals & Hard Materials**81 (2019) 281–290.doi: 10.10 16/j. ijrmhm. 2019. 03.009.
2	**K.L. Meena**, D.B. Karunakar, Development of alumina toughened zirconia nanocomposites using spark plasma sintering, **Materials Today Proceedings**5 (2018) 16928–16935.doi: 10. 1016/j.matpr.2018.04.096.
List of communicated papers	
1	**K.L. Meena**, D.B. Karunakar, Effect of MWCNTs and ZrO_2 added in alumina on the physical-mechanical properties and analysis of microstructure using spark plasma sintering process, Communicated to **Metals and Materials International(under review).**
2	**K.L. Meena**, D.B. Karunakar, S. Aravindan, Development of alumina toughened zirconia nanocomposites using conventional sintering and microwave sintering – A comparison, Communicated to **Journal of Composite Materials (under review).**
3	**K.L. Meena**, D.B. Karunakar, Effect of MgO and ZrO_2 added in alumina on the mechanical properties and microstructure using microwave sintering process, Communicated to **Journals of Applied Science and Technology**.
4	**K.L. Meena**, D.B. Karunakar, Effect of MWCNTs and yttria-stabilized-zirconia added in alumina on the mechanical properties and microstructure using microwave sintering process, Communicated to **International Journal of Refractory Metals & Hard Materials.**
5	**K.L. Meena**, D.B. Karunakar, S. Aravindan, Tribological behavior of alumina toughened zirconia nanocomposite using microwave sintering and conventional sintering - A comparison, Communicated to **Tribology Transactions.**
6	**K.L. Meena**, D.B. Karunakar, Tribological behavior addition with MgO and MWCNTs in the ZTA composite using spark plasma sintering and microwave sintering - A comparison, Communicated to **Tribology Letters.**