

Characterizing the Compression Behavior of Al_2O_3/Si_3N_4 Nano Sized Particulate Reinforced Ceramic Matrix Composites

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Abstract

Objectives: Nano sized objects are exhibiting extra ordinary potential in all the aspects of properties. Objective of this work is to develop the composite of alumina reinforced with nano sized silicon nitride particles to analyze the compression behaviour of the developed composite materials against compacting pressure and % of reinforcement. **Methods:** Powder metallurgical techniques were used to manufacture the sample specimens of composites. The specimens were prepared with various proportions Si_3N_4 reinforcement ranges from 1 wt% to 20 wt%. Alumina was functionalized with 5 wt% of Poly Vinyl Alcohol (PVA) at 80°C using water as plasticizer to enhance the dispersion and flow behaviour essential for forming the material. The composites were cold formed in two cycles where compacting pressure was maintained as 510 MPa and 725 MPa. The sintering temperature was maintained as 1400°C for soaking period of 30 minutes. **Findings:** The results revealed that the reinforced composites showed 35% more compressive strength than unreinforced monolithic material. It was found that the reinforcement content of silicon nitride increased the compressive strength of the composite as expected. The barrelling behaviour was not observed during compression. The compressive strength of monolithic alumina at 725 MPa was 0.7 times greater than of 510 MPa. It was observed that 12.5% of reinforcement experienced maximum peak load of failure. The 1400°C for sintering was observed as not sufficient to make plastic flow in powder metallurgical preforms. **Application/Improvements:** The betterment in result can be achieved by increasing the sintering temperature to 1800°C for soaking time 30 minutes. This study reveals that this particular combination of ceramic matrix composites exhibit better results in compressive behaviour. This can be further analyzed for wear and can be used as outstanding material in hybrid ceramic bearings.

Keywords: Ceramic Matrix Composites, Compression Behaviour, Hybrid Bearings, Powder Metallurgy, PVA

1. Introduction

Ceramic Matrix Composites (CMC) are started to be used in applications where high strength, light weight wear resistance and thermal resistive behaviors are expected than conventional alloy materials. They are particularly used in Hybrid bearings, Aircraft generators, Biotechnology equipment, High speed machining and grinding spindles, High speed mills, Precision

instruments, Pumps and compressors. The Al_2O_3/Si_3N_4 composite that is proposed in this study is mainly for the application of Hybrid bearing in which the inner and outer races are made up of steels and the balls are made up of ceramic materials. The proposed composite can be used to replace the balls which are usually made by monolithic ceramic materials. The analysis is mainly aimed at compression behavior of the material which is considered as one of the predominant failure

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modes. Ceramic Matrix Composites are mostly manufactured by Powder Metallurgical (P/M) technique. The solid-state process minimizes the reactions between the ceramic matrix and the nano ceramic reinforcement and thus enhances the bonding between the reinforcement and the matrix. During ceramic processing several different additives must be introduced into the batch for producing particle dispersion and flow behavior necessary for forming. These additives unlike the powder or the solvent are added in a very minor quantity, most of which is eliminated in the subsequent processing steps.

Influence of nano particles with polymer, ceramic and metal matrices can be ensured with a short summary of few of the referred literatures. The addition of ZnO with Epoxy, nano silicate with Nylon6 has shown excellent resistance for crack propagation in structures^{1,2}. The yield strength, tensile strength and young's modulus are enhanced by the addition of Organoclay with poly propylene³. The nano graphene platelet with epoxy, multi walled carbon nano tube with epoxy have influenced the fatigue properties in positive way^{4,5}. In⁶ have concerned about the R-curve behavior of Reinforced Carbon-Carbon (RCC) panels with SiC surface coating⁶. Rodrigue Matadi Boumbimba et al. have discussed about the mechanical properties of PMMA/nanoclay composites under dynamic conditions. The dynamic behavior and glass transition temperature of amorphous polymer has been analyzed for varying temperature and clay concentration 3% wt and 5% wt⁷. The ternary composites which are made with nano fillers like Al_2O_3 with glass fiber reinforced epoxy PMC are developed the tensile, shear and bearing strength, nano CaCO_3 with poly propylene improved the fracture toughness^{8,9}. Basalt fabric and (graphite and nano SiO_2 individually and combindly) with epoxy are greatly increased the wear resistance of the material¹⁰. In¹¹ have analyzed a fatigue crack growth model to predict the crack growth rate of nano-composites. They suggested a formulation for it which can be helpful to assess the damage tolerance for small naturally occurring defect in nano-composites¹¹. Multi walled carbon nano tube with Epoxy, Rigid-silica nano particles and soft liquid rubber in epoxy, Carboxyl Terminated Butadiene acrylonitrile (CTBN-liquid rubber) with epoxy, Nano Poly Vinyl Alcohol with carbon fabric in epoxy polymer, Carbon Nano Fibers (CNF) with epoxy are improved the fatigue and fracture toughness under different mode of loading of PMC considerably¹²⁻¹⁶.

Bodo Fiedler et al., have studied about the fundamental aspects of nano reinforced composites. Mainly, the CNT's are dealt with polymer matrix. It is concluded from the expressions that the higher particle volume content leads to the agglomeration of particles. The agglomeration of particles can be avoided by functionalizing the particle/fiber with chemical reactions¹⁷. The research work is also being done in nano particle reinforced in metal matrix composites and ceramic matrix composites. The nano sized alumina particle in magnesium which improved wear resistance and tensile properties, nano sized Ni reinforced in Al_2O_3 which improved fracture toughness are few reviewed literatures which showed the effect of nano particle in MMC and CMC^{18,19}. In²⁰ have discussed about the effect of stress intensity factor and young's modulus ratio of particle and matrix of particle reinforced metal matrix composites on crack deflection angle. The finite element analysis using ANSYS software has been carried out to find out the displacement of nodes in crack surfaces. The variation in E_p/E_m affected the crack deflection angle in case of particle crack than the matrix crack²⁰. Nano SiC particles in aluminum alloy A356 increased the hardness and tensile properties²¹. Extensive studies demonstrated that reducing the particle size and avoiding agglomerates of the powder may effectively result in lowering sintering temperatures²².

In²³ have reviewed various assembly methods of graphene sheets with polymers in order to get the better dispersion and properties of composites with optimum level of fillers. In²⁴ have studied the mechanical properties and microstructure of Cu/ZrO₂ nano-composites formed by Friction Stir Processing. Hardness and abrasion behavior of the composite was outstanding compared with base metal property. In²⁵ have analyzed the hardness and microstructure of Magnesium alloy-Calcium Phosphate ($\text{ZK30-Ca}_3(\text{PO}_4)_2$) prepared by powder metallurgy techniques. It is observed that 8% addition of $\text{Ca}_3(\text{PO}_4)_2$ showed optimal level of reinforcement to have maximum hardness above which there was a reduction in hardness²⁵. In²⁶ have investigated the mechanical and tribological properties of Ni and Ni alloys with different ceramic reinforcements in various research articles. It is found that ceramic reinforcement has increased the properties to considerable level²⁶. In²⁷ have fabricated and analyzed the mechanical, wear and compressive properties of Aluminum reinforced with boron carbide. Optical Microstructure results revealed that boron carbide was

uniformly distributed and composites offered better properties when reinforcement % was increased²⁷.

In this work, the method of developing the ceramic matrix Al_2O_3 composites with nano reinforcement of Si_3N_4 is discussed in detail and the compression behaviour with respect to the process parameters and amount of reinforcement is analysed. Particulate type of reinforcement is generally done in Ceramic Matrix Composites. The size variation of the matrix and reinforcement particles, large volume fraction of the reinforcement lead to the segregation of the particles, porosity and poor dispersion which makes the material with comparatively poor mechanical strength. The Al_2O_3 was functionalized with Poly Vinyl Alcohol (PVA) to develop the composites.

2. Experimental Details

2.1 Materials

Aluminum Oxide Active (Al_2O_3) was commercially available and purchased from RANKEM (part of AVANTAR performance materials) with the molecular weight of 101.96. The silicon nitride Si_3N_4 nano particles were commercially purchased from SIGMA-ALDRICH. The size and other details of nano Si_3N_4 powder is given in Table 1. It is not an easy task to prepare a composite of both matrix and reinforcement from same group of materials through cold forming technique.

Table 1. Details of matrix and reinforcement powder

Description	Matrix - Alumina (Al_2O_3)	Reinforcement - nano Silicon Nitride (Si_3N_4)
Size of the particle	< 100 microns	< 50 nm
Molecular weight	101.96 g/mol	140.28 g/mol
Shape	Spherical	Spherical
Purity	99%	98.5+ %

2.2 Functionalization

The matrix material Al_2O_3 was initially functionalized with a hydroxyl group of material called Poly Vinyl Alcohol (PVA). PVA is a water soluble synthetic polymer with density 1.19 g/cm^3 . Functionalization is done to improve the bonding between the particles and to enhance the flow of particles during forming process. PVA is an odourless, colourless white powder. Water was used as plasticizer. In the PVA structure shown in Figure 1, the $-\text{C}-\text{C}-$ linkage

is referred as the vinyl backbone and the $-\text{H}$ and $-\text{OH}$ are referred as the side groups.

Vinyl binders with the $-\text{C}-\text{C}-$ backbone are very flexible binders. The polar $-\text{OH}$ group is hydrophilic which promotes initial wetting and dissolving of the PVA in a polar liquid such as water. Hydrogen bonding of the $-\text{OH}$ side group to the surface of a particle provides adhesion and the dipolar attraction of $-\text{OH}$ side groups produces intermolecular bonding. PVA is a binder which has a strong affinity for adsorption on oxide particles dispersed in water.

Batch calculation for mixing was performed on the basis of percentage of weight of matrix, reinforcement and functionalizing agent or binder. 5% of PVA was used as standard amount of binder in all the batches. Water was added during the process as required. The PVA was mixed with water and heated to 80°C and stirred manually during heating. When the PVA was completely dissolved in water, the alumina was added to that and again stirred manually for 10 mins. The alumina was reached a wet formable state. The reinforcement was then added and stirred for 10 mins and the mixture was packed air tightly. The uniformly mixed powder is then heated up to 150°C for evaporating the volatile matter present in the mixture.

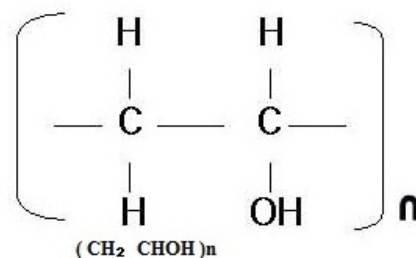


Figure 1. Molecular structure of PVA.

2.3 Specimen Preparation

The punch and die set up was designed to prepare the preform of 10 mm diameter. The external surface of the punch and the inner surface of the die were mirror finished to avoid wall frictional problems during forming. Springs were provided to eject the preform after releasing the load. The off axial loading was avoided by having a groove on the top of the die through which the load was applied. The material chosen for die and punch was EN30. The punch was hardened after fabrication. The bushes were used in die holes to guide the punch and to enhance smooth surface for easiness of compaction.

The static load was applied gradually. The experimentation was designed in such a way that the effect of compacting pressure in influencing the compression strength of the material to be studied. The entire experiment was divided into two cycles. Each cycle stands for one compacting pressure of forming preforms. In cycle 1, the static compacting pressure was maintained as 510 Mpa and in cycle 2, it was maintained as 765 Mpa. After forming, the green compacts were stored in air tight packs. In cycle 1, monolithic alumina and the preforms with 1 to 5 wt% of Si₃N₄ composites were fabricated (6 preforms). In cycle 2, monolithic alumina and the preforms with 7.5, 10, 12.5, 17.5, 20 wt% of Si₃N₄ composites were fabricated (6 preforms).

3. Results and Discussion

Compression behavior of the monolithic and nano Si₃N₄ reinforced Al₂O₃ composites was analyzed. In subsequent sections, the effect of binder/functionalizing agent and reinforcement on compression strength will be discussed.

3.1 Compression Behavior

In first cycle, where the compacting pressure was maintained as 510 Mpa, the compression strength of the material was increased with respect to the increment in reinforcement percentage. Silicon nitride reinforced composite preforms have shown better compression strength than monolithic Alumina. The uniform rate of increment is observed in each preforms where reinforcement gradually increased as 1, 2, 3, 4 and 5 %. The preform of 4% Si₃N₄ reinforcement observed as having 1.7 times greater compression strength than monolithic alumina. The preforms of 4 and 5 % reinforcement showed same compression strength. In cycle 2, where compacting pressure maintained as 765 Mpa, similar to previous cycle, the composite's compression behaviour dominated the monolithic alumina. The increment rate of compression strength was not uniform as like previous cycle. Even in this cycle, increment of reinforcement content in each preform was quite higher than previous cycle. The fluctuating pattern was observed in compression strength after the reinforcement of 12.5% of silicon nitride. The 12.5% Si₃N₄ reinforced composite observed as having 2.2 times greater compression strength than monolithic

alumina. This particular composition is the optimum level to which the nano sized silicon nitride particles can be added.

The addition of silicon nitride more than 12.5% lead to the agglomeration of the particles in matrix and the potential of reinforcement was not distributed throughout the composite. The decrement in compression strength should have happened because of quicker nucleation and propagation of cracks at the interface of the matrix and agglomerated grains of silicon nitride. When the results of both the cycles compared, cycle 2 showed better compression strength than cycle 1. This is because of the well-known fact that the densification of the particles increased when compacting pressure was increased. The monolithic alumina preform of cycle 2 showed nearly 1.5 times greater compression strength of monolithic alumina in cycle 1. Barreling behavior of preforms was not observed during compression in both the cycles. Sudden fracture along the transverse direction has happened at the peak compression load. This showed the highly brittle nature of the ceramic materials. Table 2 and Figure 2 depict the results of compression test. Compressive strength calculated as follows:

Cold compressive strength = (Maximum compressive force/Area on which the load applied).

Table 2. Results of compression test

cycle	Composition (%)		Peak compression load (kN)	Compressive strength (Mpa)	
	Alumina	Si ₃ N ₄ (nano)+ PVA			
Compacting Pressure 509.55MPa	1	100	nil	0.72	9.172
		99	1	0.94	11.975
		98	2	1.12	14.268
		97	3	1.2	15.287
		96	4	1.28	16.306
		95	5	1.28	16.306
Compacting Pressure 764.33MPa	2	100	nil	1.04	13.248
		92.5	7.5	1.24	15.796
		90	10	1.28	17.600
		87.5	12.5	2.1	26.752
		82.5	17.5	1.9	24.204
		80	20	1.98	25.223

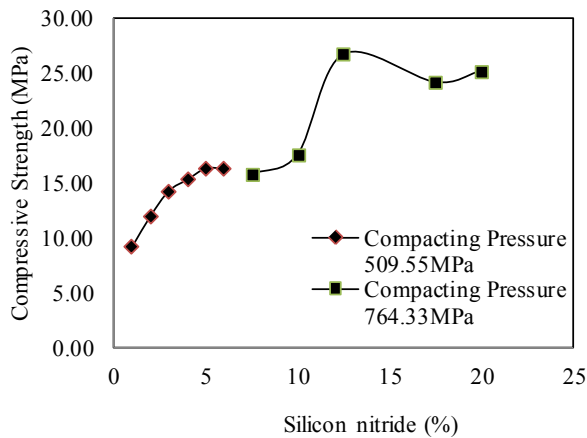


Figure 2. Effect of reinforcement and compacting pressure in compressive strength of sintered preforms.

3.2 Effect of Binder/Functionalizing Agent

Activated alumina particles were so dry and could not be processed through cold forming directly. The binding between particles could not be achieved initially. The preforms could be manufactured only after functionalizing the alumina particles with the functionalizing agent/binder Poly Vinyl Alcohol (PVA). Molecular binders are low- to high-molecular weight polymer molecules which may adsorb on the surfaces of particles and bridge them together, like PVA which has hydrogen bonds or form a polymer-polymer bonded network (film) among the particles. Since PVA has alcoholic compound in its molecular structure, water was used as plasticizer to dissolve PVA. The volatile content of plasticizer was evaporated in subsequent heat treatment processes. The binders are usually added to form a bonding matrix, which requires that they must be formable at an early stage and later capable of being hardened to form a structural bond. In green compacts, enough binding was achieved between matrix particles and reinforcement. Later the structural bonding after sintering could not be achieved to the greater extent because of the insufficient temperature maintenance during heat treatment. Sintering was done at 1400°C for the period of 1 hr. Sintering should have been done to at least 1600-1800°C, so that the plastic flow between the particles would be enhanced to have strong bond between particles. Binder has served the purpose in cold forming in an effective manner to form cylindrical preforms.

4. Conclusion

Nano sized Silicon Nitride (Si_3N_4) reinforced ceramic matrix (Al_2O_3) composites developed successfully. Role and effect of functionalizing agent/binder in preparing ceramic matrix composite were explained. Effect of compacting pressure and nano reinforcement in compression behavior of composite was explained. According to the results of test:

- When reinforcement of nano sized silicon nitride particles increases, the compressive strength of the material is also increased as expected.
- 12.5% of reinforcement was identified as optimum amount of reinforcement above which slight fluctuation in compressive strength was observed.
- When compacting pressure increased, the compressive strength of the material was increased because of the increased densification of compacts.
- Sintering temperature 1400°C was not enough to have strong structural bonding between particles. No sufficient plastic flow during heat treatment was observed. The temperature can be kept between 1600-1800°C for 1 hr.
- No barrelling behaviour was observed during the compression test. The sudden fracture in the direction perpendicular the loading direction was observed because of highly brittle nature of ceramic materials.

5. References

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