Mechanical behavior of nanoparticulate TiO$_2$ reinforced magnesium matrix composite

Ganesh Radhakrishnan, Anirudh P V, and Anujan Kumar S
Department of Mechanical Engineering, Velammal Engineering College, Chennai – 600 066.

Corresponding author: ganeshrk1982@gmail.com

Abstract. In this study, nano-sized titanium dioxide particulate reinforced pure magnesium matrix composite has been fabricated by powder metallurgy technique for five different weight fractions of reinforcement such as 4 wt%, 8 wt%, 12 wt%, 16 wt%, and 20 wt% respectively. Samples of these compositions are iso-statically cold compacted into cylindrical specimens of diameter and length each 15 mm respectively, followed by sintering and hot extrusion with an extrusion ratio of 1.56:1. SEM micrographs of blended composite powders before compaction confirmed the uniform distribution of reinforcement throughout the matrix without any agglomeration. Microstructural analysis of extruded specimens revealed the refined matrix grains and grain boundary. The reinforcement may interrupt the matrix grain growth on grain boundaries during extrusion. Targeting for biomedical applications like bone implants, kneecap surgery etc., the mechanical behavior of the composite such as microhardness, and compressive strength have been studied. It was observed from the study that the mechanical properties have been significantly improved by adding reinforcement compared to pure magnesium and better mechanical behavior have been noticed for composite with higher contribution of reinforcement.

Keywords: magnesium matrix composite, nanoparticulate, titanium dioxide, biomedical, bone implants, mechanical behavior

1. Introduction

During the past few years, the researchers focused majorly on magnesium due to its attractive low density. Even though it has low density and high strength it suffers from certain barriers such as low strength, poor ductility, poor wear, and corrosive nature which hindered it from being used in aerospace, automobile industries and much more fields in its pure form. Currently, researchers are working on adding reinforcements to magnesium metal matrix to improve its mechanical properties. Recent reviews highlighted that there are about 60 different types of components, from instrument panels to engine components, in which magnesium alloys such as cast alloys-AZ63, AZ81, AZ91 etc., wrought alloys-AZ31, AZ61, AZ80 etc., Elektron, Magnox, Magnuminium, Mag-Thor, Birmabright, Magnalium and ceramic reinforcements such as SiC, Al$_2$O$_3$, Si, Ti, Zr are added to magnesium are being developed for use. The use of magnesium alloys in automobile parts is predicted to increase at an average rate of 15% per year. Magnesium alloys are used in aircrafts, missiles, automobile wheels, housings, ladders, cell phones, power tools, textile machinery, seat frames etc. The next major field focusing on the usage of magnesium alloys is the biomedical field. Biomedical field has been using materials such as 316L SS, CoCrMo, Ti Ti6Al4V in all implants division ranging from cardiovascular to otorhinology. Implant alloys are fabricated using methods like investment casting, powder metallurgy, thermo-mechanical process(TMP), superplastic deformation (SPD), equal channel angular pressing (ECAP), accumulative roll-bonding (ARB), high-pressure torsion (HPT) etc. Magnesium can be used for bone implant since the modulus of the metal and bone is similar (40-45GPa) and hence secondary...
surgery for removal of the implant will not be necessary. But since pure magnesium is poor in certain mechanical properties, titanium dioxide is added to magnesium as reinforcement in powder metallurgy technique and the properties are studied.

Similarly, many other interesting recent works such as nano particulate of Zinc oxide and Zirconium oxide reinforcement in sisal fiber composite [1], Al$_2$O$_3$ reinforcement in coconut bunch fiber composite [2] and boron carbide reinforcement in aluminum alloy [3] have published. The following are the studies on material currently used in biomedical applications. Jian Fang Li et al had worked on 316L SS by layering the alloy of Zr and ZrO$_2$ in plasma surface alloying apparatus. The cross-section microscopy, surface, phase structure were analyzed and the surface roughness, wear were also measured. It is found that ZrO$_2$ layers tremendously enhance wear resistance, improve adhesion and spreading of osteoblast cells [4]. Sheida Shri et al had studied on the growth of tantalum multi-layer thin films on CoCrMo alloy done by radio frequency magnetron sputtering system. The crystallography, hardness, Young's modulus, film thickness, hardness was studied. The result was that the substrate temperature and bias voltage influence alpha and beta-Ta formation [5]. M.M. Machado Lopez et al observed the property enhancement of 45s5 bioglass coating on Ti6Al4V alloy by a colloidal electrophoretic deposition process. The study included X-ray diffraction, chemical composition analysis, and coating evaluation. The result was that the corrosion resistance was increased and ensured good protection from ionic attack [6].

Several studies in magnesium reinforced with various particulates are discussed as follows. Manoj Gupta et al analyzed the Al and Mg-based nanocomposites synthesized using powder metallurgy and extruded for characterization studies. Density, microstructure characterization, X-ray diffraction analysis, tensile test, microhardness measurement was studied. It was observed that the hybrid reduced energy and time, hardness and work of fracture improved, and the processing time was considerably reduced [7]. Junko Umeda et al had studied on titanium particulate reinforced magnesium composite materials done by spark plasma sintering followed by hot extrusion. The optical microstructure, compression strength, tensile strength and X-ray diffraction were studied. The composite material resulted in increased compression strength but there was no improvement in tensile strength [8]. Ganesh Kumar Meenashisundaram et al had worked on titanium (IV) oxide nanoparticulate reinforced magnesium composite material done by disintegrated melt deposition technique followed by hot extrusion. The material characterizations studied were microhardness, compression, tensile, thermal expansion and fracture behavior. The composites resulted in increased hardness and fracture strain was increasing with increase in the addition of titanium (IV) oxide [9]. Cheng-Jie Li et al has worked on Mg-3Zn-0.2Ca-0.5Y alloy using extrusion of billet at different temperature after heat treatment. The compression strength, microstructural study, and tensile strength have been studied. It resulted in increased grain size with increase in extrusion temperature [10]. ShahrouzZamaniKhalajabadi et al have worked on magnesium titanatohydroxyapatite nanocomposites coated by magnesium oxide flakes and silicon by cold pressing with coating after heat treatment in argon atmosphere of cold pressed billets. The electrochemical, immersion, vitro biological and compression test were studied. The result was improved anticorrosion ability after surface modification [11]. AlirezaVahid et al had worked on magnesium reinforced with tantalum particles using sintering of compacted composite powder. Density, X-ray diffraction, microstructure study and thermal expansion behavior has been studied. The results of the above composites are increase in microhardness and compressive strength [12]. Dongfang Zhang et al has worked on hafnium coated magnesium alloy using sintering in tube furnace of hafnium coated magnesium. Crystal structure, electrochemical and corrosion test has been studied. The results are improved corrosion resistance with a change of microstructure and production of surface oxidation [13].
2. Experimental Procedure

2.1 Materials

Magnesium powder supplied by S D Fine-Chem Limited with mean particle size 177µm and >99.995% purity is used as the base material. Titanium Dioxide particles of mean size less than 45 µm and purity >99.5% supplied by Merck Life Science Private Limited is chosen as reinforcement.

2.2 Procedure

2.2.1 Particle Size Conversion

Titanium Dioxide particle with average size of 45 µm was converted to an average particle size of 100 nm using planetary mill which included a jar with 16 metal balls (ball to powder ratio is 5:1) for size conversion process. This process took 17 hours at 250 rpm in ball mill.

2.2.2 Elemental Mixture of Mg-TiO₂ Powders

Titanium Dioxide reinforcement was added to magnesium metal in five different weight fractions such as 4 wt%, 8 wt%, 12 wt%, 16 wt%, and 20 wt% respectively. This process of blending was carried out in the planetary mill at 200 rpm for 10 minutes for each composition.

![Sequence of operations](image-url)

**Fig.1** Sequence of operations – i) Particle size conversion ii) Elemental mixture iii) Compaction iv) Sintering v) Hot extrusion
2.2.3 Cold Compaction

The blended composite mixture was compacted at room temperature. The amount of powder weighed for each sample was 4.5 grams which produced a cylindrical billet of diameter and length of each 15 mm. This process was carried out in a Universal Testing Machine where the compaction die filled with weighed powders is fixed and a load of 50kN was applied using a punch. This load was held steady for 5 minutes to ensure that the load applied completely to produce a solid specimen.

2.2.4 Sintering

Sintering is a thermal treatment of fine-grained material at a temperature below the melting point of the base metal, for increasing its grain size and strength by bonding the particles together. The sintering process was done in two stages. In stage 1, the compacted specimens were sintered at 500°C for 4 hours in a muffle furnace at nitrogen atmosphere to prevent reaction of the specimen with air. A tray was prepared, and specimens were arranged in the tray in an individual crucible and placed inside the furnace. The gas was passed through a ceramic tube at 0.5 to 1 bar pressure into the chamber. Eight samples were heat treated at a time and took approximately 6 hours for one complete sintering process. The stage 2 sintering process is similar to stage 1, but the only difference is the heating temperature and the time of sintering were reduced. Sintering was done at 400°C for 1 hour at nitrogen atmosphere. The second stage sintering was done to refine grain and grain boundary. It took 1 hour to reach 400°C and the furnace was held at 400°C for 1 hour.

2.2.5 Hot Extrusion

The extrusion process is done to improve the bonding between matrix and reinforcement, refine matrix grain and also to refine grain boundary. An extrusion die had to be fabricated that supports the dimensions of the specimen. The extrusion temperature range for magnesium is 250°C to 450°C. The reduction percentage was 20% in diameter i.e. 15 mm diameter was reduced to 12 mm through extrusion. And hence the extrusion ratio is 1.56:1. The taper angle of the die is 14° and length of taper is 10 mm. The specimen and die were pre-heated separately to prevent reaction of specimen with air during heating. The die was pre-heated to 200°C using band heater and the specimen was pre-heated to 350°C in muffle furnace. The pre-heating of die was done to provide a smooth extrusion and to reduce the load acting on die. The extrusion process was carried out in 100T hydraulic press. A tapered punch of 15 mm diameter and 50 mm length along with a 10 mm length taper similar to die’s taper was provided at end of the punch. This punch was fixed at the top die of hydraulic press and then pressure was applied with lubrication oil to reduce friction between punch and die walls during extrusion process. The dimension of extruded specimen is 12 mm in diameter and 18 mm in length.

2.3 Material characterization

2.3.1 SEM micrographs

SEM micrographs of the powder mixture was to investigate the uniform distribution of nano TiO₂ particulates in magnesium matrix. The SEM micrographs also to confirm agglomeration if any, particle size, grain and grain boundary refinement.
2.3.2 Density measurements

The mass density of extruded magnesium with 4, 8, 12, 16 and 20wt% TiO$_2$ was measured using Archimedes principle. Each sample was measured for 3 cycles to obtain accurate density values. Water was used as the standard liquid, which has a density of 1 g/cm$^3$.

2.3.3 Microhardness test

Using a microhardness tester-Wolpert Group with Vickers indenter, the Microhardness tests were conducted on flat and polished extruded specimens. Each sample was measured for 3 cycles to measure the hardness accurately.

2.3.4 Compression test

The compressive properties of extruded Mg (4, 8, 12, 16 and 20wt%) TiO$_2$ samples were determined at room temperature. The test specimen of 12 mm diameter and 20 mm length was used. Each sample was tested 3 times to ensure repeatable values.

3. Results and discussions

3.1 SEM micrographs

SEM analysis was conducted on the elemental mixture of Mg-TiO$_2$ to confirm the uniform distribution of TiO$_2$ reinforcement over Mg matrix in five different weight percentage. Only if there is a uniform distribution, the bonding improves by grain growth and hence the properties of the resulting matrix would be considerably improved. SEM analysis was conducted on the extruded specimen to obtain the micrographic images of each composition of nanocomposites. As shown in Fig.3 the structure and grain growth of the nanocomposites continuously improved with increase in the addition of TiO$_2$ reinforcement. The grain size of pure magnesium is large and has a lot of micro pores [24]. But the addition of nano TiO$_2$ refined the grain structure. Mg-TiO$_2$ composite exhibits very smooth surface with few micro pores on its surface. It can be seen that the reinforcement is uniformly distributed in the matrix. The reason for uniform distribution of reinforcement particles is due to the efficient strategy adopted while fabrication of the nanocomposites. It was evident from the micrographs that TiO$_2$ distribution was quite homogeneous. Hot extrusion is the reason for grain growth in the magnesium matrix. The micrographs also exhibited the presence of minimal porosity in the developed nanocomposites with the result of density measurement through Archimedes principle.
Fig. 2. SEM micrographs of Mg-TiO$_2$ powder mixture (a) Mg-4\%TiO$_2$, (b) Mg-8\%TiO$_2$, (c) Mg-12\%TiO$_2$, (d) Mg-16\%TiO$_2$ and (e) Mg-20\%TiO$_2$

3.2 Density and Porosity

| S. No | Materials       | Theoretical Density $\rho$ (g/cm$^3$) | Experimental Density $\rho$ (g/cm$^3$) | Porosity (%) |
|-------|-----------------|----------------------------------------|----------------------------------------|--------------|
| 1     | Mg-4\%TiO$_2$   | 1.839                                  | 1.837                                  | 0.1087       |
| 2     | Mg-8\%TiO$_2$   | 1.938                                  | 1.937                                  | 0.1012       |
| 3     | Mg-12\%TiO$_2$  | 2.039                                  | 2.037                                  | 0.1339       |
| 4     | Mg-16\%TiO$_2$  | 2.138                                  | 2.136                                  | 0.1183       |
| 5     | Mg-20\%TiO$_2$  | 2.239                                  | 2.236                                  | 0.1589       |

The presence of minimal porosity in the composite material can be due to better bonding between Mg-TiO$_2$ and the use of proper extrusion ratio. The results of density and porosity measurements conducted on the extruded specimen are shown in Table 1. Porosity is known to influence the mechanical properties to a great extent, therefore, pores must be eliminated through post sintering process and extrusion. The porosity of pure magnesium is higher when compared to reinforced magnesium [18]; the porosity level is low on an addition of 8 wt\% of TiO$_2$ with Mg. The density of composites increased with the increase in weight percentage of TiO$_2$ particulates. The density features revealed minimal oxidation of magnesium and absence of macro pores.
Fig. 3. SEM Micrograph showing distribution of nano-TiO$_2$ particulates in Mg-TiO$_2$ composites:
(a) Mg-4\%TiO$_2$, (b) Mg-8\%TiO$_2$, (c) Mg-12\%TiO$_2$, (d) Mg-16\%TiO$_2$ and (e) Mg-20\%TiO$_2$.
3.3 Microhardness

Table 2. Result of hardness.

| S. No | Composition     | Average Hardness in HV |
|-------|-----------------|------------------------|
| 1     | Mg-4%TiO₂       | 37                     |
| 2     | Mg-8%TiO₂       | 40                     |
| 3     | Mg-12%TiO₂      | 43.67                  |
| 4     | Mg-16%TiO₂      | 44.67                  |
| 5     | Mg-20%TiO₂      | 50                     |

The room temperature mechanical properties are depicted in Table 2. It is found that pure Mg reveals very low hardness and the composites displayed higher hardness compared to pure magnesium [24]. However, the addition of nano-sized TiO₂ particulates to pure Mg leads to significant enhancement in hardness. The improvement in hardness of nanocomposites may be due to the strengthening effects that have arisen from the refined grains. The synergetic effect of TiO₂ particulates in magnesium matrix revealed improved hardness values. The value of microhardness continuously increased with increase in addition TiO₂ reinforcement. An intending load of 0.1 kg for a dwell time of 15 s was used.

3.4 Compression test

The compressive strength of extruded Mg (4-20 wt%) TiO₂ samples were tested at ambient temperature. The test specimens of diameter 12 mm of five different compositions were used. The specimen was subjected to compression test at a ram speed of 3 mm per min. The test was carried out on five different compositions of Mg (4-20 wt%) of TiO₂ nanocomposites.

Table 3. Result of compressive strength.

| S. No | Composition     | Compressive strength in MPa |
|-------|-----------------|-----------------------------|
| 1     | Mg-4%TiO₂       | 292                         |
| 2     | Mg-8%TiO₂       | 307                         |
| 3     | Mg-12%TiO₂      | 312                         |
| 4     | Mg-16%TiO₂      | 321                         |
| 5     | Mg-20%TiO₂      | 330                         |
The variation in microhardness and compressive strength of the composite samples complement each other. At higher weight fraction of reinforcement, in spite of original variation in it, there is a drastic increase in compressive strength. This may be due to the restricted grain growth at a higher content of reinforcement.

Density and hardness increase with respect to the quantity of reinforcement added to the matrix. This is attributed to the fact such as the non-uniform crystalline structure and abrasive nature of reinforcement.

4. Conclusions:

Mg-TiO₂ nanocomposites were successfully synthesized through powder metallurgy method followed by sintering and hot extrusion. The technology route follows as conversion of macro
titanium particles to nanoparticles, preparing the elemental mixture, compacting the elemental mixtures into cylindrical specimens, sintering the specimens, extruding the specimens, and characterizing mechanical properties. Based on microstructural and mechanical characterization following conclusions can be drawn.

- Powder metallurgy method is an efficient technique to fabricate Mg-based composite since the method prevents oxidation of Mg and less porosity is achieved.
- SEM image confirms the uniform distribution of TiO$_2$ over Mg matrix and thus proves homogeneity of the composite.
- Density is observed to be increasing as the weight percentage of reinforcement increases and porosity is minimum due to the fine bonding of Mg and TiO$_2$ in the mixture and hence proves the minimum oxidation of Mg.
- Hardness has been considerably improved due to the synergetic effect of TiO$_2$ particles as the weight percentage of TiO$_2$ increases.

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