
Analysis of Mechanical and Physical Properties on Magnesium Tricalcium Phosphate Composite by Powder Metallurgy

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Abstract

This work is on the synthesis of biodegradable Magnesium metal matrix composites using powder metallurgy technique for the application of bone plate implants, which exhibit excellent biocompatibility; whereas Magnesium alloys show good compatibility but their mechanical properties are not that good enough for using as degradable materials for bone implants. Magnesium metal matrix composites containing ZK30 Magnesium alloy with five weight fractions of (2, 4, 6, 8, 10wt.%) Tri-Calcium Phosphate (TCP) [Ca₃(PO₄)₂] have been produced using powder metallurgy followed by hot extrusion for consolidation. The mechanical properties such as Hardness, Density, Porosity, Tensile and Compression tests were investigated. The micro hardness of Mg composites is found decreasing on increasing wt.% of TCP particles, also it can vary depending upon the quantity of TCP particles. The ZK30 Mg alloy and Mg composites have higher micro hardness than human bone. The composite density with weight fractions appears to have improved experimental density in most cases, whereas the porosity is found less. The ZK30/4wt%TCP holds a higher ultimate tensile strength of 241.462MPa whereas ZK30/10wt%TCP gives a minimum of 151.169MPa. However, for ZK30/4wt%TCP an increase in tensile strength is observed due to excellent inter atomic bonding between the ZK30 Mg alloy matrix and the reinforcement. A reasonably good ultimate compressive strength of 241.462MPa was recorded for ZK30/2wt.%TCP. However, the tested Mg alloy and the composites show higher tensile and compressive strength than human bone. The SEM observation in tensile and compression tests depict ductile fracture for ZK30 Mg alloy and brittle fracture for Mg composites. The micro hardness, tensile strength and compressive strength of Mg composites decreased on increasing wt.% of TCP particles. The Magnesium composite showed appropriate mechanical properties; thus, it is found a good choice for bone plates implants.

Keywords: Magnesium composites, Tri calcium phosphate, Powder metallurgy

Introduction

Biomedical materials such as stainless steel; cobalt chromium alloys, pure titanium and its alloys, are permanent implant materials for bone fracture and load bearing implants of

damaged bone because of their high strength, toughness, ductility, and corrosion resistance [1,2]. The medical applications of biomedical metal alloys are restricted due to its two complications: stress shielding and second surgical intrusion. The elastic modulus of biomedical metal alloys (in the order of 100-200GPa) is very high related to cancellous bone (10-30GPa), which outcomes in loosening of implants, thickening of skeletons and disturbs healing process [3]. On comparison with biomedical metal alloys, biodegradable materials are capable of developing three-dimensional living structure of replaced bone with significantly good mechanical properties [4]. Moreover, this material does not need a second surgery with better degradation property [5].

Magnesium and its alloys have reserved a special position in orthopaedic application because of their biodegradable character, high stiffness and specific strength, excellent dimensional stability and damping capacities [6,7]. The elastic modulus of Mg and its alloys (40GPa) is closer to that of human bone (10-30GPa) minimises stress shielding effect [3]. The occurrence of great aggregate of Mg ions in the human body supports in biological mechanism and metabolic reactions, thus Mg and its alloys have excellent biocompatibility. The amount of Mg in human body is 35g per 70kg weight and the day-to-day necessity of Mg in human body is 375mg [8]. Density of Mg is 1.74g/cm^3 , is 36% lighter than aluminium and 78% lighter than steel [9] though the foremost shortcoming of Magnesium and its alloys are fast degradation rate [10]. Mg matrix composite reinforced with bioactive materials such as Hydroxyapatite (HAP), Calcium phosphate minerals (Ca-P), in turn have good biocompatibility, bioactivity and Osteo conductivity, these properties can mend the fast degradation rate of Mg alloys. The benefits include the corrosion rate and mechanical properties, which can be regulated by changing the quantity of metal matrix and reinforcement [11-13]. Mg composites can be implemented as an efficient implant material if it possesses additional mechanical properties to aid the damaged tissue, the degradation rate would be happening simultaneously to the healing progress and appropriate stabilisation of ions. ZK30 alloy possess 9% elongation at fracture improves shock absorbing capacity of alloy, besides Zn and Zr are non-toxic elements [11,14]. The common alloying element for Mg is Zn, which boosts the corrosion resistance of Mg alloys [15,16]. Zr is used for grain refinement thus improving the strength of Mg alloys [17]. The bioactive material such as TCP exhibits tremendous biocompatibility and biodegradability [18]. Furthermore, the properties of matrix materials can be improved by bioactive materials, which are capable of depositing Ca-P compounds to the surface [19]. It has been reported that the fast corrosion rate of AZ30 and Mg-Mn-Zn alloys are protected using Ca-P coating [20].

With the increase of sintering temperature in the order of 300 to 400°C, it is found that the micro hardness of composite in 15% SiC and Al₂O₃/Al-Mg composites decrease. Meanwhile the hardness increases when the sintering temperature is raised to 500°C. Meanwhile there are differences found when the composite is at 30%, the increased sintering temperature gives decreased micro hardness in SiC/AlMg composites but the micro hardness increases in Al₂O₃/Al-Mg composites [21]. In the study carried out the influence size of HA reinforcement on mechanical properties and biodegradation of Mg-3Zn/HA composites are noted. The composites are prepared using spark plasma for the sintering. This is used for orthopaedic implants, which are opted for temporary usage. The study emulates the size factor, as the cylindrical shaped HA(CHA) showcases better hardness elastic modulus when it is of smaller cylindrical shaped rather than round shaped (R-HA) [22]. The optimum composites matrix is found as 10% of reinforcement, when compared with 5% and 15% weight % reinforcement, in 10% the micro hardness is found to be 29% and Young's modulus 17%, Yield Tensile Strength (YTS) 138%, Ultimate Tensile Strength (UTS) 113% on comparison to unreinforced ZE41, the elongation is found as 5.3% [23]. Powder metallurgy and hot extrusion techniques were used to prepare the ZK61-HA composites. Significant improvement is noticed in compressive strength, hardness and compressive yield strength due to the presence of HA particle in the ZK61 Mg alloy matrix [24].

The objective of this research work is to prepare composites with Mg matrix composed of ZK30, the reinforcement is made with TCP particles of varied composition by powder metallurgy, which is followed hot extrusion for the needed consolidation.

The mechanical and physical properties of ZK30 Mg /TCP composite are studied for biomedical implants of bone plates.

Experimental Procedures

Materials and Methods

The matrix phase of ZK30 alloy comprises of 3wt.% Zn, 0.6wt.% Zr, and balance Mg, were prepared from high purity (Mg>99.95wt.%), (Zn>99.9wt.%) [14]. Five samples of different wt.% of TCP were processed to Mg composites along with ZK30 Mg alloy as control specimen. ZK30 Mg alloy, ZK30/2wt%TCP, ZK30/4wt%TCP, ZK30/6wt%TCP, ZK30/8wt%TCP, ZK30/10wt% TCP composites were synthesized using powder metallurgy. V blender was used for blending operation. Each blended samples of 150g was added to a cylindrical compaction chamber and pressed by a hydraulic vertical pressing machine of 150-ton capacity with a pressure of 23MPa. Compacted billets of 68mm diameter and 28 mm

length were attained. Sintering process were performed using muffle furnace of automatic relay in an argon atmosphere at a temperature of 450⁰C to have preferred atomic bonding between ZK30 alloy and TCP. With sufficient bonding the billets were cooled by natural convection. The cooled specimens were refined using turn table apparatus. Hot extrusion process was executed for the sintered billets. The extrusion die was lubricated with colloidal graphite followed by shielded with ceramic wool to prevent heat loss and oxidation. The extrusion setup was maintained at a temperature of 450⁰C and accomplished using hydraulic vertical pressing machine of 150-ton capacity. The extrusion procedure outcomes with a cylindrical rod of 12 mm diameter and 500 mm length.

Density and Porosity

Archimedes principle was carried out for determining the experimental densities and porosities. Each sample were prepared as 10 mm diameter and 10 mm length from extruded bars of ZK30Mg alloy, ZK30/2wt%TCP, ZK30/4wt%TCP, ZK30/6wt%TCP, ZK30/8wt%TCP and ZK30/10wt% TCP composites. The immersion fluid used was distilled water with weighing precision 0.0001g using electronic balance. Rule of mixtures was used for calculating theoretical densities.

Hardness

An automatic digital Vickers micro hardness tester (Shanghai MHVD - 1000AP/MP) was used for detecting the Vickers micro hardness of polished samples of ZK30Mg alloy, ZK30/2wt%TCP, ZK30/4wt%TCP, ZK30/6wt%TCP, ZK30/8wt%TCP and ZK30/10wt% TCP composites. The test was carried out along the transverse and longitudinal sections of samples at room temperature. The diamond indenter was used for the tests, the load applied for the test was 500g and with 10 seconds dwell time. The micro hardness value of each sample was found from an average of 2 indentations.

Tensile and Compression Study

Computer controlled universal testing machine (MTS insight 100 kN) was used for tensile test at room temperature with strain rate of $1 \times 10^{-3} \text{s}^{-1}$. Each sample for tensile test was prepared as per ASTM standard E8 with 4.75 mm diameter and gauge length of 25.40 mm. Computer controlled universal testing machine (UTM TUE CN-600) with 60-ton load capacity was used for compression tests at room temperature. Each sample for compression test was prepared as per ASTM standard E9 with 9.53 mm diameter and 25.53 mm length. The scanning electron microscopy technique was used to determine the cause of failure during tensile and compression tests.

Results and Discussions

TGA of TCP

Calcium is identified as the alloying constituent for magnesium alloys, which is well compatible as it is a major constituent of human bone. In addition, the discharge of Mg and Ca ions can enrich the bone healing progression [25]. The specific properties will be retained since Calcium (1.55 g/cm^3) and Magnesium (1.74 g/cm^3) have similar densities [26]. The grain refinement, mechanical properties and corrosion resistance of Mg alloy is enriched by Ca [27]. Thermal stability of TCP was determined using Thermal Gravimetric Analysis (TGA). A thermal gravimetric analyser instrument was used for analysing, having a nitrogen atmosphere with a heating rate of 10°C/min from $0^\circ\text{C} - 1000^\circ\text{C}$. The weight loss owing to rise in temperature in nitrogen atmosphere was documented as the TGA of TCP. Fig 1 shows the thermograms of TCP. TGA of TCP curves marks in multi stages of degradation. The evaporation of moisture in the composite effects in initial stage of degradation, which begins at 0°C and concludes at 100°C . The degradation of TCP at 490°C with a weight loss of 2% confirms the second stage of degradation. The result evidently directs the stability of TCP up to 490°C which is adequate to accomplish the sintering and hot extrusion process at 450°C .

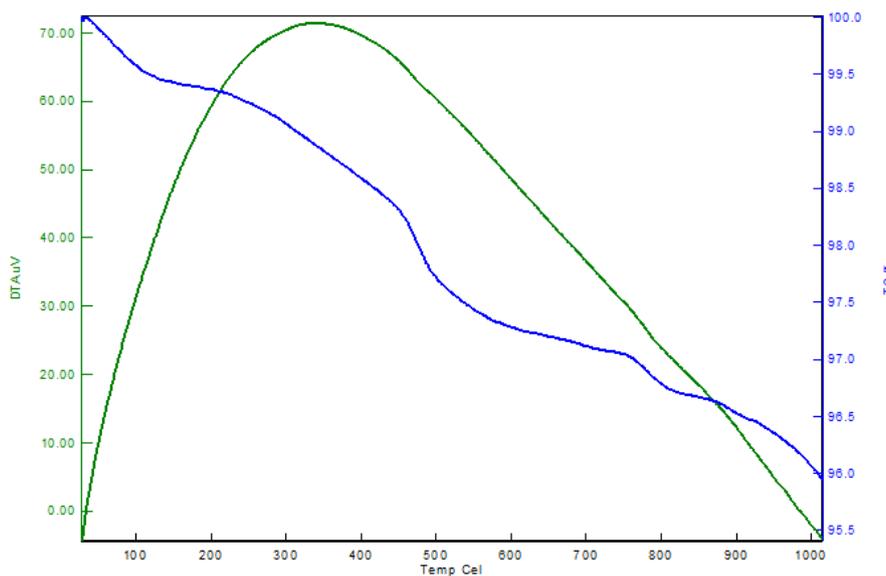


Fig.1. TGA of TCP

The theoretical, experimental densities and porosities of ZK30 Mg alloy and its composites are tabulated in Table 1. On comparison the experimental densities were nearer to theoretical densities of extruded ZK30 Mg alloy and Mg composites. The maximum experimental density was recorded for ZK30/8wt% TCP whereas minimum was noted for ZK30/2wt% TCP when compared with ZK30 Mg alloy.

Density and Porosity

Table 1 Density and porosity results

| Material | Theoretical density ρ (g/cm ³) | Experimental density ρ (g/cm ³) | Porosity (%) |
|-----------------|--|---|--------------|
| ZK30 Mg Alloy | 1.930 | 1.819 | 1 |
| ZK30/2wt.% TCP | 1.949 | 1.766 | 1.7 |
| ZK30/4wt.% TCP | 1.968 | 1.833 | 1.09 |
| ZK30/6wt.% TCP | 1.987 | 1.829 | 1.88 |
| ZK30/8wt.% TCP | 2 | 1.925 | 0.5 |
| ZK30/10wt.% TCP | 2.024 | 1.913 | 1.05 |

The theoretical, experimental densities and porosities of ZK30 Mg alloy and its composites are tabulated in Table 1. On comparison the experimental densities were nearer to theoretical densities of extruded ZK30 Mg alloy and Mg composites. The maximum experimental density was recorded for ZK30/8wt%TCP whereas minimum was noted for ZK30/2wt%TCP when compared with ZK30 Mg alloy. The introduction of TCP particles improved the experimental density of composites up to ZK30/8wt%TCP while a rise in experimental densities were observed due to decreased porosity percentage formation between ZK30 Mg alloy and TCP in ZK30/4wt%TCP, ZK30/6wt%TCP, ZK30/8wt%TCP and ZK30/10wt%TCP composites. In [8] the densities of Mg (1.738g/cm³) and its alloys (1.75-1.83g/cm³) were nearby to that of human cortical bone (1.75g/cm³) were witnessed. The obtained results confirm the formerly recorded measurements. On increasing wt.% of TCP particles the porosity of composites increased. The evaporation of various compounds from TCP during sintering and hot extrusion was attained from TGA study. The curve shown in Fig 1 was the source for increased porosity percentage. The excellent compatibility between Mg matrix and reinforcement phase results in minimum porosity [28].

Hardness

The Vickers micro hardness of ZK30 Mg alloy and the Mg composites with different wt.% of TCP were shown in Fig 2. On comparison with ZK30 Mg composites, The ZK30 Mg alloy clenches a higher micro hardness of 94HV. A higher micro hardness of 93.56HV was recognized for ZK30/2wt%TCP although minimum of 77.99 HV was noted for ZK30/10wt%TCP. The obtained results show micro hardness of Mg composites decreased on

increasing wt.% of TCP particles, also it can vary depending upon the circulation of TCP particles. When Mg reinforced with Y_2O_3 particles the similar observations were declared [29]. The higher micro hardness of composite is due to fine and homogeneous distribution of particles whereas lower micro hardness is due to coarse and non-homogeneous distribution [30]. The cortical bone possesses a micro hardness of 49.8HV [31]. The investigated ZK30 Mg alloy and the Mg composites demonstrate results of excellent hardness.

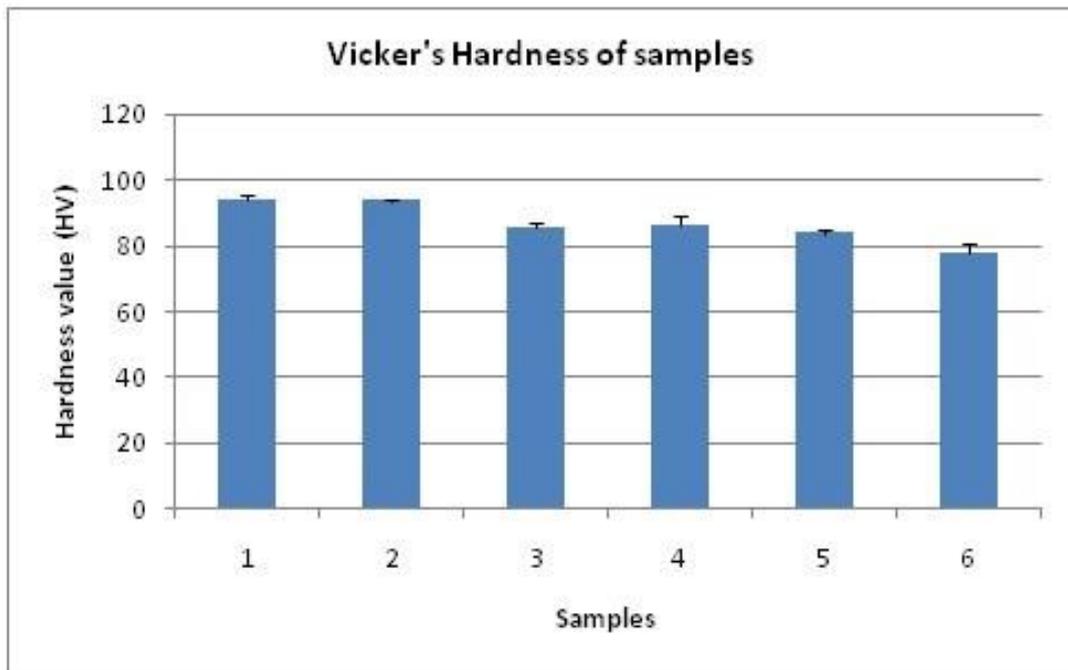


Fig.2. Graphical Representation of Micro Hardness of Various Mg/TCP Samples 1-ZK30 alloy, 2- ZK30/2wt%TCP, 3-ZK30/4wt%TCP, 4-ZK30/6wt%TCP, 5-ZK30/10wt%TCP

Tensile and Compression study

The room temperature of tensile test results is tabulated in Table 2 along with tensile stress strain curves of ZK30 Mg alloy and the composites with different wt.% of TCP are presented in Fig 3. The ZK30 Mg alloy holds a higher ultimate tensile strength of 271MPa whereas ZK30/10wt%TCP gives a minimum of 151.169MPa. The ZK30 Mg alloy shows an elongation of 7% and the ductility and shock absorbing capacity of the composites were enhanced by addition of TCP particles with an elongation of (0.75%-3.04%). The tensile strength of human bone varies between 90-190MPa [32]. The tested ZK30 Mg alloy and the Mg composites show greater tensile strength than human bone. The attained results indicate that the ultimate tensile strength and elongation of the material decreased on increasing the wt.% of TCP particles. However, for ZK30/4wt%TCP an increase in tensile strength is observed due to excellent inter atomic bonding between the ZK30 Mg alloy matrix and the

reinforcement. The decrease in tensile yield strength due to addition of bioactive material HAP was observed [33]. In [34] the root for declining ultimate tensile strength of material is due to the agglomeration of bioactive particle HAP was recorded. The reinforcement particles with micron dimensions can increase the tensile strength of Mg based composite but it disturbs plasticity [35]. The tensile strength along with plasticity can be enriched using reinforcement particle of nanometre scale [36]. Fig 4(a-f) portrays the SEM images of tensile fracture surface of ZK30 Mg alloy, ZK30/2wt%TCP and ZK30/8wt%TCP composites. The origin for failure of Mg alloys is due to quasi cleavage fracture [37]. The Mg alloy SEM observations in Fig 4(a,b) reveal about the formation of river like pattern due to cleavage fracture along with the occurrence of dimples marks as fine micro voids effects in ductile fracture. The lack of coalescence among micro voids creates dimple formation [38]. In Fig 4(c, d) for ZK30/2wt%TCP composites defines the existence of secondary cracks owing to particle agglomeration marks in brittle fracture with non-appearance of micro voids. On increasing wt.% of TCP (ZK30/8wt%TCP) the particle agglomeration increased which led to brittle fracture as seen in Fig 4(e, f). In [33] it was recorded that particle agglomerated due to the addition of HAP particles to Mg and forms brittle fracture. Also, ZM61-HAP composites retain parallel explanations [39].

Table 2 Tensile test results

| Material | Ultimate Tensile Strength (MPa) | Elongation (%) |
|----------------|---------------------------------------|----------------|
| ZK30 Mg Alloy | 271 | 7 |
| ZK30/2wt.%TCP | 214.14 | 2.022 |
| ZK30/4wt.%TCP | 241.462 | 0.953 |
| ZK30/6wt.%TCP | 195.828 | 3.04 |
| ZK30/8wt.%TCP | 183.851 | 1.006 |
| ZK30/10wt.%TCP | 151.169 | 0.759 |

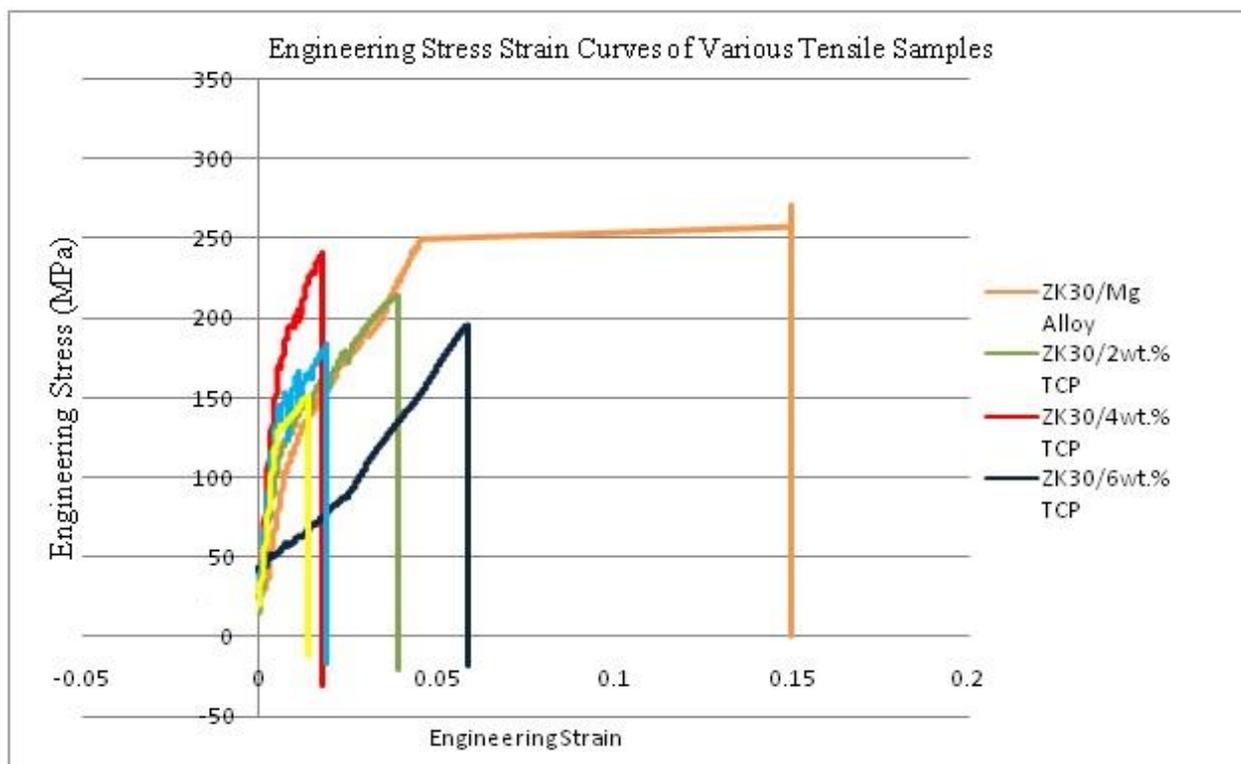
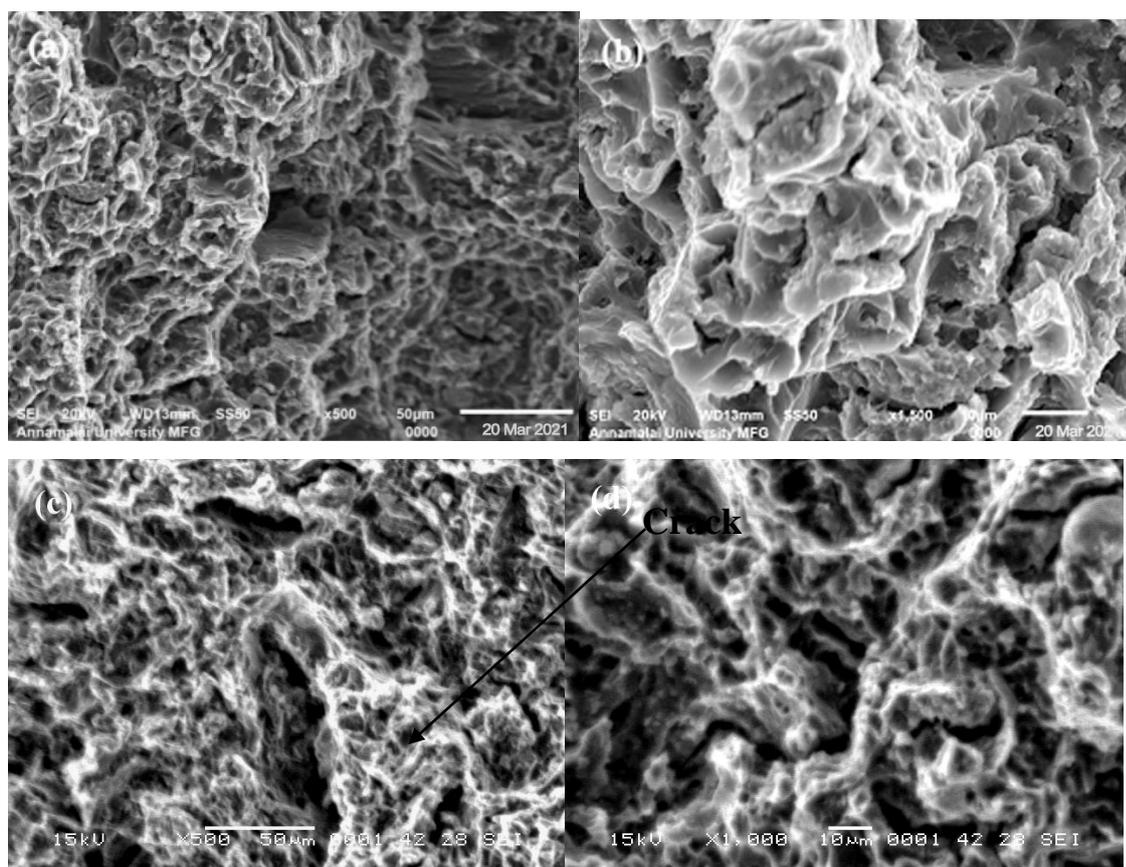


Fig.3. Engineering Stress strain curves of various tensile samples



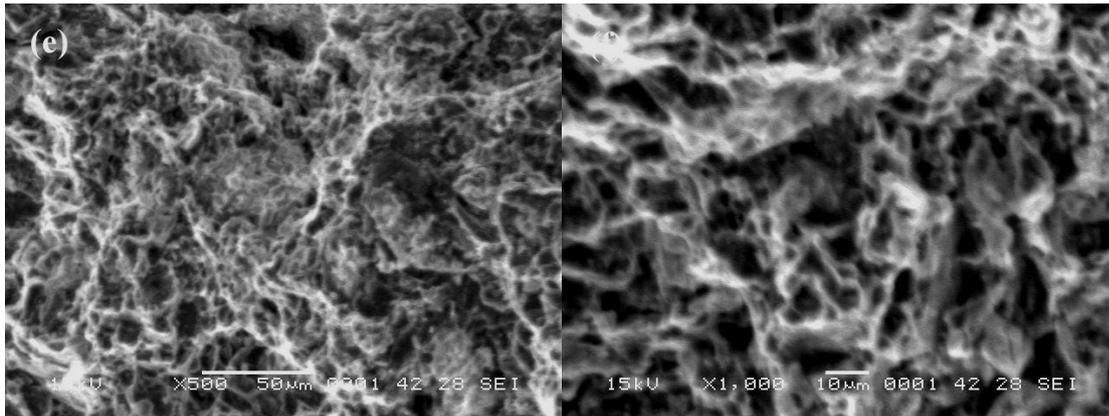


Fig.4. SEM images of tensile fracture surfaces of (a) ZK30 Mg Alloy x 500 (b) ZK30 Mg Alloy x 1500 (c) ZK30/2wt.%TCP x 500 (d) ZK30/2wt.%TCP x 1000 (e) ZK30/8wt.%TCP x 500 (f) ZK30/8wt.%TCP x 1000

The compressive test results and stress strain curves of ZK30 Mg alloy and the Mg composites are displayed in Fig 5 and Table 3. A higher ultimate compressive strength of 365.165MPa were exposed by ZK30 Mg alloy when compared with ZK30/2wt%TCP, ZK30/4wt%TCP, ZK30/6wt%TCP, ZK30/8wt%TCP, ZK30/10wt%TCP composites. The natural bone holds a compressive yield strength of 130-180MPa [40]. The achieved results specify that the on increasing wt.% of TCP particles the compressive strength of composite decreased owing to insufficient load transfer between the ZK30 Mg alloy matrix and the reinforcement. The mechanical properties of a composite can be enhanced by concentrating on aspects includes grain size and dislocations [41]. The strength of the material can be boosted by dispersion of solid particles in matrix material [42]. Fig 6 (a-f) represents the SEM pictures of compressive fracture surface of ZK30 Mg alloy ZK30/2wt.%TCP and ZK30/8wt.%TCP. In Fig6 (a-b) of ZK30 Mg alloy shows the cleavage planes with occurrence of minute formation of void nucleation owed to ductile fracture. The ZK30/2wt.%TCP in fig 6 (c-f) describe about the quasi-cleavage fracture as formation of river like patterns. On increasing wt.% of TCP particles for ZK30/8wt.%TCP the SEM observations in fig 6 (e-f) demonstrate the increased percentage of river like patterns with micro voids leads to ductile fracture. The Mg composites with ductile fracture were also obtained [43].

Table 3 Compressive test results

| Material | Elongation (%) | Ultimate Compressive Strength (MPa) |
|----------------|----------------|-------------------------------------|
| ZK30 Mg Alloy | 2.730 | 365.165 |
| ZK30/2wt.%TCP | 2.470 | 340.719 |
| ZK30/4wt.%TCP | 1.520 | 338.427 |
| ZK30/6wt.%TCP | 2.770 | 326.719 |
| ZK30/8wt.%TCP | 1.200 | 211.995 |
| ZK30/10wt.%TCP | 2.290 | 183.347 |

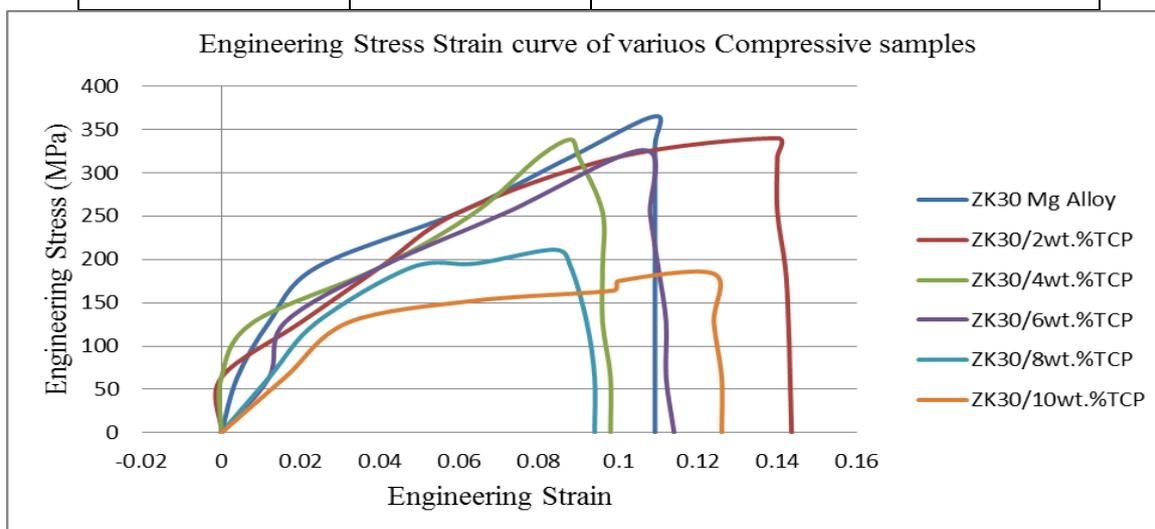
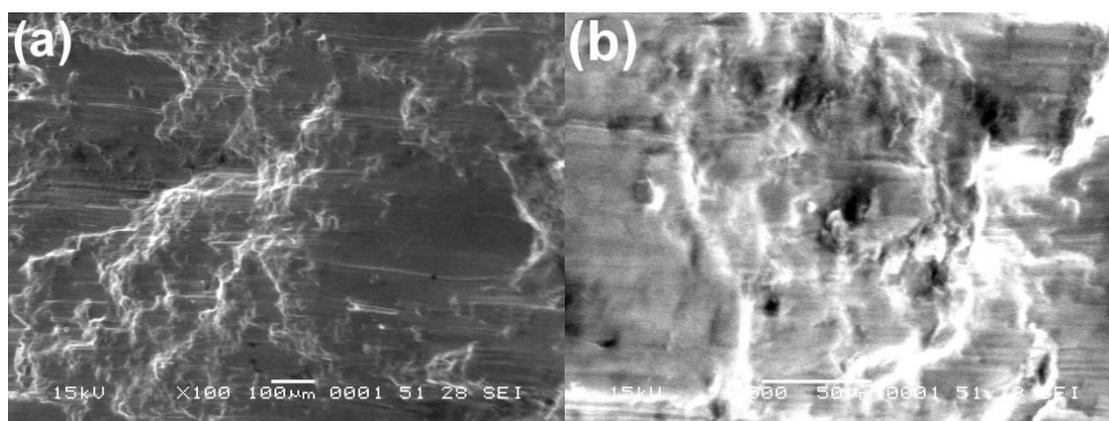


Fig.5. Engineering Stress strain curves of various compressive samples



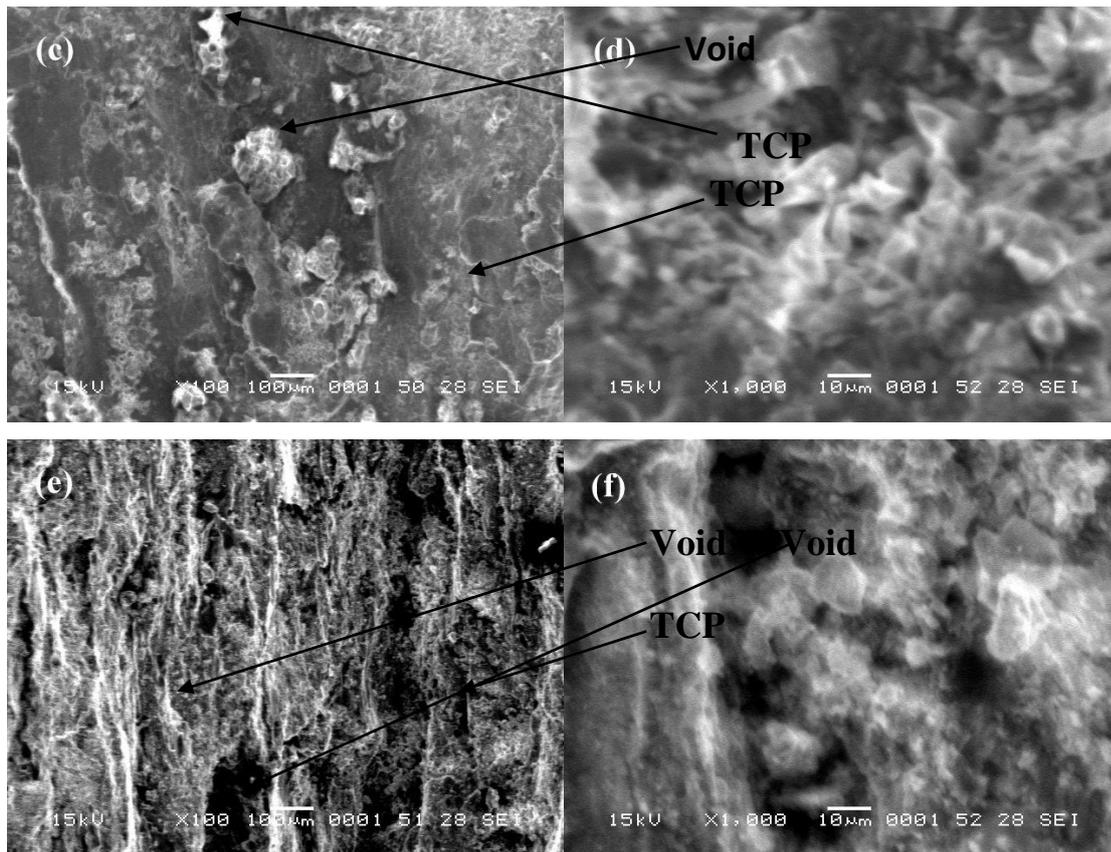


Fig.6. SEM images of compressive fracture surfaces of (a) ZK30 Mg Alloy x 100 (b) ZK30 Mg Alloy x 1000 (c) ZK30/2wt.%TCP x 100 (d) ZK30/2wt.%TCP x 1000 (e) ZK30/8wt.%TCP x 100 (f) ZK30/8wt.%TCP x 1000.

Conclusion

The specimens were prepared by powder metallurgy and are further subjected to hot extrusion process for preparing ZK30 Mg alloy and Mg composite comprising TCP reinforcements. The composite density appears to be improved to a certain range with minimum porosity. The ZK30 Mg alloy and Mg composites retain micro hardness higher than human bone. The ZK30 Mg alloy holds a higher ultimate tensile strength of 271MPa whereas ZK30/10wt%TCP gives a minimum of 151.169MPa. However, for ZK30/4wt%TCP an increase in tensile strength is observed due to excellent inter atomic bonding between the ZK30 Mg alloy matrix and the reinforcement. A higher ultimate compressive strength of 365.165MPa was exposed by ZK30 Mg alloy. However, the tested Mg alloy and the composites show higher tensile and compressive strength than human bone, the SEM observation in tensile and compression tests depict ductile fracture for ZK30 Mg alloy and brittle fracture for Mg composites. The micro hardness, tensile strength and compressive strength of Mg composites decreased on increasing wt.% of TCP particles. The results

evidently direct that the ZK30 Mg alloy/TCP composites have tremendous mechanical properties and appropriate for used bone plates implants.

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