TO DEVELOP BIODEGRADABLE Mg BASED METAL CERAMIC COMPOSITES AS BONE IMPLANT MATERIAL

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Abstract - Biodegradable materials for orthopedic implants have gained much attention due to their similar properties to natural bone. Magnesium based alloys are considered the best biodegradable material for bone substitute materials. However, magnesium alloys have very high corrosion rate. Research has been focused to fabricate and to make their composites to control their corrosion rates in human physiological environment and to develop the ability of formation of bone-like apatite layer on their surface. In the present study, Mg-Zn-Mn metal alloys were selected for making their composites with hydroxide apatite and bio glasses. Hydroxide apatite was prepared by coprecipitation method and borate based bioactive glasses were prepared by melting and quenching method. Samples from metal-ceramic composites were prepared by powder metallurgy route in various compositions. Further, samples were characterized for their phases, microstructure, corrosion behavior, mechanical properties and bioactivity. The composites showed bioactivity in SBF solution and their young's modulus values were obtained near to human bone. The degradation properties as studied in SBF solution revealed that mg based alloys composites having approximately 10% BAG and 10 % β – TCP resulted in reduction of the corrosion rate.

I. INTRODUCTION

Metals such as steel or titanium alloys represent traditional permanent bone implants but these implants need to be remove especially in young patients within one or two year after the first surgery[1]. It means, it requires post surgery and can make complications in patients. Biodegradable implants are the another approach to eliminate post surgery, which are slowly dissolve in the human organism and can be sustained up to bone fracture recovery. Magnesium alloys are considered the best suitable biodegradable implant materials [2]. These alloys have desirable biocompatibilities and mechanical properties as required in human body. There is one drawback with these materials that they have high degradation rate in the human body fluid or blood plasma and this may influence the mechanical properties resulting loss of integrity. Another factor is the fast release of hydrogen, restricting their extensive biomedical applications [3-11]. Bioactive surface coatings are generally used to improve the corrosion resistance of magnesium alloys but there is a chance that coating may be separated during application. Another approach to develop bioactivity and to increase the corrosion resistance of magnesium metal alloys is to add certain additives, which not only improve chemical resistance but also improve bioactivity [12-16]. Hence composites are the best alternative and have gained the great attention for research activities.

In the present study Mg-Zn-Mn metal alloys were taken as base materials. Composites were prepared by mixing prepared HAp and bio glass. Research work was carried out to observe the bioactivity and corrosion resistance along with the study mechanical properties of Mg based composites with doping HAp and bio glass for improved biocompatibility. This study verifies the bioactivities of HAp-added ZTA composites. All the dried gel and calcined powders were characterized by using X-ray diffraction, DTA/TGA and SEM. Densification and mechanical behaviour of sintered samples were observed. Bioactivities of all compositions were tested using SBF solution and then characterizing by FTIR.

II. EXPERIMENTAL

2.1. Materials preparation

Hydroxyapatite powder was produced by solution–precipitation method. Details of processing method is described by us elsewhere [17]. Analytical reagent grade of chemicals such as calcium nitrate [$Ca(NO_3)_2.4H_2O$], magnesium chloride [$MgCl_2.6H_2O$], sodium hydrogen carbonate[$NaHCO_3$], sodium hydroxide [NaOH], ammonium di-hydrogen orthophosphate [$NH_4H_2PO_4$] were used. Boro-silicate bio active glass[18-19] was prepared by the melt-quench technique, where the required materials were thoroughly mixed and further melted at sufficient temperature and subsequently quenched in water to get frit. The glass frit was further ground in planetary ball mill using zirconia pot and zirconia balls as grinding media with subsequent sieving with 37-micron sieve. Mg-Zn-Mn alloy was prepared in the laboratory by powder metallurgy route. For this purpose, 77.91wt% Magnesium, 20.07wt% zinc and 2.02wt% manganese metal powders were mixed homogeneously on a mortar pestle. Then the mixture was mixed in a planetary mill using tungsten balls and jar with the tungsten lining. Speed of the mill was kept very slow in the range of 10-15 r.p.m. The liquid media was taken as ethanol in the milling.

2.2. Preparation of composites and their characterization

The compositions for making metal ceramic composites were selected in three different manners as details are given in Table 1.Further the samples were prepared in pellets and bar shapes by using hydraulic press and die with a punch pressure of approximately 200MPa. Prepared samples were sintered in an inert gas
atmosphere furnace at a temperature of 600^0C with a holding time of 1 hour. Rate of heating was kept 100^0C per minute.The crystalline phases were analyzed by X-ray diffractometry using model Rigaku (Mini FlexII). Concerning the apatite-forming ability evaluation, the samples of composites were immersed for various time upto twelve weeks, in simulated body fluid (SBF) with an ion concentration nearly equal to that of human blood plasma. The surfaces of samples were observed by FTIR (Model Tensor 27) as well as under SEM (Model INSPECT S50). Elastic constant of composites bars was measured by elastosonic (model 38DLPlus, Olympus). Variations of Na^+ and Ca^{++} ions concentrations in SBF solutions was observed by microprocessor flame photometer (model-1381) along with

Table 1. Composition of Metal alloys – HAp- Bioglass composites

Sample No.	Alloy	Hap(wt%)	Bio-glass (wt%)
1	0.95Mg-0.025Zn-0.025Mn	-	-
2	0.95Mg-0.025Zn-0.025Mn	5	-
3	0.95Mg-0.025Zn-0.025Mn	-	5
4	0.95Mg-0.025Zn-0.025Mn	5	5
5	0.95Mg-0.025Zn-0.025Mn	10	-
6	0.95Mg-0.025Zn-0.025Mn	-	10
7	0.95Mg-0.025Zn-0.025Mn	10	10
8	0.9Mg-0.05Zn-0.05Mn	-	-
9	0.9Mg-0.05Zn-0.05Mn	5	-
10	0.9Mg-0.05Zn-0.05Mn	-	5
11	0.9Mg-0.05Zn-0.05Mn	5	5
12	0.9Mg-0.05Zn-0.05Mn	10	-
13	0.9Mg-0.05Zn-0.05Mn	-	10
14	0.9Mg-0.05Zn-0.05Mn	10	10

compressor unit (model-380). The corrosion rate of the samples was measured as the function of mass loss of the samples at various time periods when in-vitro testing of the atmosphere furnace at a temperature of 600^0C with a holding time of 1 hour. Rate of heating was kept 100^0C per minute.The crystalline phases were analyzed by X-ray diffractometry using model Rigaku (Mini FlexII). Concerning the apatite-forming ability evaluation, the samples of composites were immersed for various time upto twelve weeks, in simulated body fluid (SBF) with an ion concentration nearly equal to that of human blood plasma. The surfaces of samples were observed by FTIR (Model Tensor 27) as well as under SEM (Model INSPECT S50). Elastic constant of composites bars was measured by elastosonic (model 38DLPlus, Olympus). Variations of Na^+ and Ca^{++} ions concentrations in SBF solutions was observed by microprocessor flame photometer (model-1381) along with compressor unit (model-380).The corrosion rate of the samples was measured as the function of mass loss of the samples at various time periods when in-vitro testing of the samples were done. Also, Immersion tests were carried out for two weeks in SBF as corrosion medium. The corrosion rate can be given by the following equation [20].

$$C.R = \frac{K\,x\,W}{S\,x\,t\,x\,\rho}$$

Where the coefficient K = 8.76 X 104 gm/cc, W is the weight loss (gm), S is the sample area exposed to solution (mm^2), t is the exposure time (day) and ρ is the density of the material (gm/cc), while C.R is the corrosion rate. Here, surface area of given samples is constant at 141.75 mm^2 and density of the samples were determined by water displacement method.

III. RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns for Alloy, HAP, alloy-bioactive glass composites, alloy-HAP composites and alloy-bioactive glass-HAP were observed of unfired and fired samples The XRD patterns of all the above compositions show crystalline phases of Magnesium, Zinc while for HAP and the alloy-HAP composites the crystalline phases of β-TCP, hydroxyapatite and calcium ammonium phosphate hydrate were observed. XRD patterns specifically for fired sample show a particular phase of Magnesium-Zinc alloy as seen in figure 1. In table 2, results of elastic constants of composites are summarized. It can be seen that all composites have elastic constants similar to human bone. Figure 2 shows the FTIR transmittance spectra of samples after immersion in SBF for 14 days of the samples of 0.9Mg-0.05Zn-0.05Mn alloys with different weight percent of hydroxyapatite and bio glass as mentioned in the figure.

Table 2: Elastic constant value of all metal alloy ceramic composites

Sample No.	1	8	3	12	5	4	11	7	10
Elastic constant (GPa)	36.6	37.8	40.7	44.8	38.2	36.6	43.9	45.3	46.8

There are three major groups present in the spectrum which are OH^-, PO_4^{3-} and CO_3^{2-}. Bands in the range of 630-573 cm^{-1} are attributed to phosphate amorphous band while the bands at 1043cm^{-1} and 1165 cm^{-1} are caused by stretching mode vibration of PO_4^{3-} and CO_3^{2-} Stretching mode vibration can also be observed at about 1420cm^{-1}. The broad band at 3437cm^{-1} and 1637cm^{-1} are assigned to OH stretching and bending respectively. This broad band mainly comes from water due to strong H bonding inside the structure. A sharp peak at about 3644cm^{-1} indicating the presence of $Mg(OH)_2$ which is the corrosion product from magnesium matrix. The carbonate and phosphate bands are observed to be more broad and deep with the increasing of weight percentage of bioactive glass.

The weight loss was taken continuously for 2 weeks and the result showed that as the immersion time increased, the amount of degradation products on the samples increased. In case of Alloy-10wt% HA-10wt%BAG sample, there were very low weight loss due to corrosion in SBF solution throughout the immersion test. With increasing time, the apatite layer grew thicker as shown in SEM micrographs, indicating better bioactivity of samples. Figure 4 shows that apatite particles have been deposited on the sample and more globular apatite was deposited after 2 weeks of immersion.

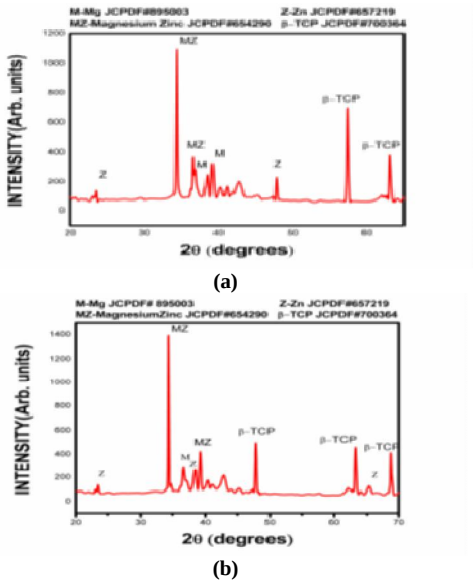


Fig 1. XRD patterns of sintered samples of (a) Alloy-5wt%HAp- 5wt % -bioactive glass composite and (b) Alloy-10 wt% HAp-10wt% bioactive glass composite

The surface of the Alloy-HAP-BAG sample was relatively flat and compact as compared to simple Alloy, Alloy-HAP composite or Alloy -BAG composite sample. This observation suggested that Alloy-HAP-BAG sample was more corrosion resistant than the simple Alloy, Alloy-HAP composite or Alloy -BAG composite. Variations of Na, Ca concentrations in SBF solutions as observed by microprocessor based flame photometer, due to soaking of metal-ceramic composites for various time periods is as shown in fig 4.18 and 4.19. As it can be observed for all of the samples that Na concentrations increased rapidly for first 7 days and further attains nearly a constant value. Whereas in the case of Ca, ion concentrations showed no values till day 3 in most of the samples but after that increased continuously till achieving a constant value till day 14. It's also observed that increasing the concentrations of bioactive glass and β-TCP in the alloy increased the ion leachability ate of the two ions observed. In FTIR results, the intensity of the Mg peaks of Alloy-HAP-BAG is lower than that of simple Alloy, Alloy-HAP composite or Alloy -BAG composite sample after 3 weeks of immersion; indicating that uniform layer of HAp has been formed all over sample. XRD patterns of both the samples soaked in SBF

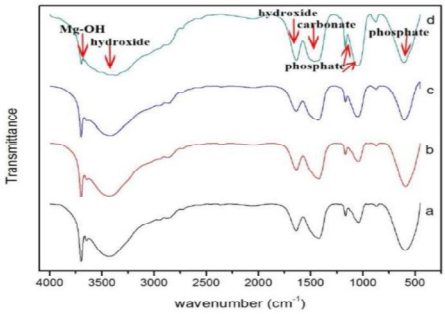
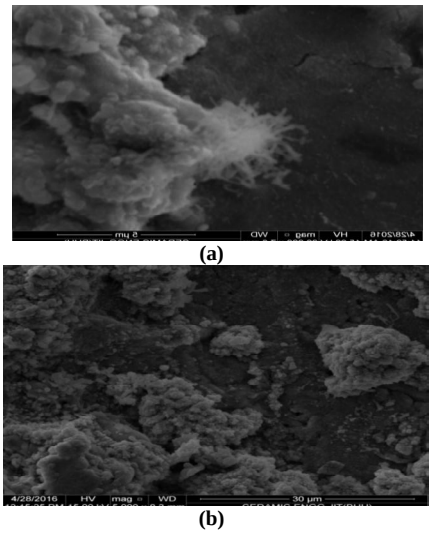


Fig 2. FTIR of samples of 0.9Mg-0.05Zn-.05Mn metal alloy with doping of a) 10wt% HAp b) 10wt% bioglass c) 5wt% each of HAp and bio glass and d) 10wt% HAp +10wt% bioglass

for 3 week showed the presence of HA, $Ca_3(PO4)_2$ and CaO phases. $Mg(OH)_2$ phase is more significant in Alloy, Alloy-HAP composite or Alloy-BAG composite sample, indicating more degradation has occurred. With increasing time, the apatite layer grew thicker as shown in SEM micrographs, indicating better bioactivity of samples. Fig. 3 showed that globular apatite particles have been deposited on the sample and more globular apatite was deposited after 2 weeks of immersion. Hydroxyapatite was formed only if the material is bioactive when immersed in SBF. It may be concluded that a thick globular apatite was when formed on the surface of Alloy-HAP-BAG sample, it acted as protection layer over its surface

thus increases the corrosion resistance in physiological medium.

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(a)

(b)

Fig.3. SEM micrograph of the samples of 0.9Mg-0.05Zn-0.05Mn alloy having (a)5wt% each of HAp and Bioglass and (b)10wt% each of HAp and Bioglass respectively immersed in SBF solution for 14 days

Whereas in the case of Ca, ion concentrations showed no values till day 3 in most of the samples but after that increased continuously till achieving a constant value till day 14. It's also observed that increasing the concentrations of bioactive glass and β-TCP in the alloy increased the ion leachability ate of the two ions observed. In FTIR results, the intensity of the Mg peaks of Alloy-HAP-BAG is lower than that of simple Alloy, Alloy-HAP composite or Alloy -BAG composite sample after 3 weeks of immersion; indicating that uniform layer of HAp has been formed all over sample. XRD patterns of both the samples soaked in SBF for 3 week showed the presence of HA, $Ca_3(PO4)_2$ and CaO phases. $Mg(OH)_2$ phase is more significant in Alloy, Alloy-HAP composite or Alloy-BAG composite sample, indicating more degradation has occurred. With increasing time, the apatite layer grew thicker as shown in SEM micrographs, indicating better bioactivity of samples. Fig. 3 showed that globular apatite particles have been deposited on the sample and more globular apatite was deposited after 2 weeks of immersion. Hydroxyapatite was formed only if the material is bioactive when immersed in SBF. It may be concluded that a thick globular apatite was when formed on the surface of Alloy-HAP-BAG sample, it acted as protection layer over its surface thus increases the corrosion resistance in physiological medium.

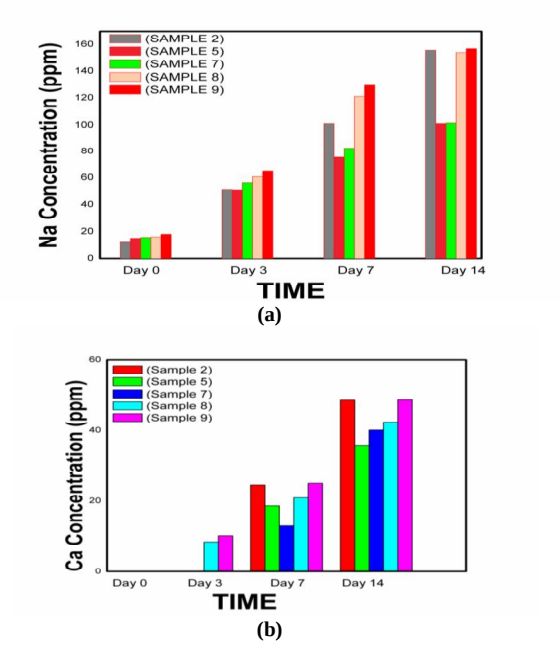


Fig.4. Shows variations in sodium concentrations in SBF solution due to soaking for various time periods

CONCLUSION

In this study Metal-ceramic composites were prepared by powder metallurgy route. The microstructure of the composites showed that the distribution of bioactive glass and β–TCP were evenly distributed on the surface. In–vitro studies revealed that the metallic alloy also has the ability of formation of carbonated apatite layer on the surface of the sample. Also, increasing percentages of BAG and β–TCP in the composite, increased the amount of porosity and apatite forming on the surface of the samples which resulted in better osteoconduction of the samples. The degradation properties in SBF solution were investigated through corrosion rates measurements by measuring the degradation masses. This scenario revealed that with approximately 10% BAG and 10% β–TCP composite with metallic alloy resulted in reduction of the corrosion rate for the initial immersion periods. The FTIR bands showed that the development of phosphate and carbonated bands on the surface of the samples after soaking in SBF solution occurred. Thus the composites were showing bioactivity and also it can be concluded that the more bioactivity was observed with 10% BAG and 10 % β – TCP in the 0.9Mg-0.05Zn-0.05Mn composites compared to the lower percentage as well as pure alloys and individual metal -ceramic composites.

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