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M.Sc. THESIS

PRODUCTION OF BIODEGRADABLE ZINC MATRIX COMPOSITE MATERIALS BY POWDER METALLURGY METHOD

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FOREWORD

I would like to thank my family members who have always supported me in this proces

August 2021 Amira HASSOUN

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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Explanation
T	**:** Temperature
t	**:** Time
º	**:** Degree

Abbreviation	Explanation
g	**:** Gram
mg	**:** Mili gram
mm	**:** Mili meter
ppm	**:** Parts per million
PVA	**:** Polyvinylalcohol
µm	**:** Micro meter
MA	**:** Mechanical alloying
Zn	**:** Zinc

ÖZET

YÜKSEK LİSANS TEZİ

BİYOBOZUNUR ÇİNKO MATRİSLİ KOMPOZİT MALZEMELERİN TOZ METALURJİSİ YÖNTEMİ İLE ÜRETİLMESİ

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Bu tez çalışmasında, biyomedikal implant amaçlı biyobozunur çinko (Zn) matrisli kompozit malzemeler üretilmiştir. Biyobozunur çinko matrisli kompozit numuneler geleneksel toz metalurjisi (presleme-sinterleme) yöntemi ile üretilmiştir. Biyobozunur malzemeler kemiğe yakın yeterli mekanik özelliklere, doku iyileşme hızına yakın biyobozunma hızına ve biyouyumluluğa sahip olmalıdır. Metal tozları, seramik esaslı katkılar ve polimer bağlayıcıdan oluşan karışım preslenerek ham numuneler üretilmiştir. Çinko (Zn) matrisli kompozit malzemeler 400 °C sıcaklıkta 1 saat süresince yatay boru tipi tüp fırında sinterlenmiştir. Ayrıca boşluk yapıcı madde kullanarak yüksek oranda gözenekli çinko esaslı kompozit numuneler üretilmiştir. Karakterizasyon kapsamında, numunelerin mekanik özellikleri ve mikroyapıları karakterize edilmiştir. Numunelerin mekanik özellikleri basma testleriyle belirlenmiştir. Numunelerin elektrokimyasal korozyon özellikleri yapay vücut sıvısında incelenmiştir. Ayrıca metal iyon salınımı ve ağırlık değişimi (biyobozunurluk) özellikleri yapay vücut sıvısı içerisinde incelenmiştir.

Ağustos 2021, 53. sayfa.

Anahtar kelimeler: Biyomalzeme, ortopedik implant, toz metalurjisi, Zn, biyobozunur metal

SUMMARY

M.Sc. THESIS

PRODUCTION OF BIODEGRADABLE ZINC MATRIX COMPOSITE MATERIALS BY POWDER METALLURGY METHOD

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In this thesis, biodegradable zinc (Zn) matrix composite materials were produced for biomedical implant applications. Biodegradable zinc matrix composite specimens were produced by traditional powder metallurgy (press-sinter) method. Biodegradable materials must show mechanical properties close to bone, biodegradation rate close to tissue healing rate, and biocompatibility. Mixture, which was consisted of metal powders, ceramic additives and polymer binder, was compacted and green specimens were produced. Zinc (Zn) matrix composite materials were sintered at 400 °C temperature for 1 hour in a horizontal tube furnace. In addition, highly porous zinc based composite specimens were produced by using space holder (pore former) materials. Mechanical properties and microstructures of the specimens were characterized. Mechanical properties were investigated by compression tests. Electrochemical corrosion properties of the specimens were investigated in simulated body fluid solution. In addition, metal ion release and weight change (biodegradation) properties were studied in simulated body fluid.

August 2021, 53. pages.

Keywords: Biomaterial, orthopaedic implant, powder metallurgy, Zn, Biodegradable metal

1. INTRODUCTION

1.1. BIOMATERIALS

Biomedical implant is a foreign device used inside the body, and is fabricated by using suitable biomaterial. In general, biomaterials are a class of advanced engineering materials. The biomaterials are widely employed in the repair, replacement of damaged parts of the living human body. Biomaterials are materials used for their mechanical, but not their biological properties. The aim of the biomaterials in the body is to change any damaged tissue by implantation of an implant [1-12].

Biomaterials can be divided into 2 groups

- Synthetic (fabricated) biomaterials
- Natural biomaterials

Natural Biomaterials

In general, the natural biomaterials are divided as polysaccharides (cellulose, alginate, glucose, chitin, chitosan) and proteins (silk, collagen, gelatine, fibrin) [4].

Synthetic Biomaterials

In general, the synthetic biomaterials are divided in two major groups; first group is polymers (organics) such as PLA, PGA, PEG and second group is metal and ceramic (inorganics). Advantages are availability and ease of fabrication. Mechanical properties (elastic modulus, hardness), geometry, wear resistance, chemical composition, electrochemical corrosion rate rate, biodegradation rate, porosity, pore size,

Biomaterials can be divide into four groups such as;

- Metals
- Ceramics
- Polymers
- Composite

Table 1.1 given below shows the main advantages and disadvantages of the biomaterials (metals, ceramics, polymers).

Table 1.1: Comparison of the biomaterials [7]

Material Class	Advantages	Disadvantages
Metals	Strong	Corrode in a physiological environment
	Wear resistant	High E
	Tough	High density
	Easy to fabricate	Not usually bioactive
		Not resorbable
Polymers	Resilient	Weak
	Tough	Low E
	Easy to fabricate	Not usually bioactive
	Low density	Nor resorbable
Ceramics	Biocompatible	Low tensile strength
	Wear resistant	Difficult to fabricate
	Lightweight composite	Low toughness
		Not resilient

Metallic biomaterials are most commonly used for the fabrication of the load bearing orthopaedic hard tissue implants. Cobalt, iron, titanium, chromium, molybdenum, nickel, and tantalum have been used for orthopaedic hard vtissue implants. Metallic biomaterials show high tensile strength, high electrochemical corrosion resistance, ease of fabrication, suitable ductility, suiytable toughness, high abrasion/wear resistance and highy fatigue resistance. Cobalt alloys, stainless steel alloys, and titanium alloys are the most used metallic biomaterials. While Co-Cr and stainless steel grades show high strength with high electrochemical corrosion behaviour, in general Ti and Ti alloys are better for their low elastic modulus and bioactivity. [1-6].

Table 1.2: Mechanical properties of metallic biomaterials [6]

Material	ASTM Standard	Condition	Elastic Modulus (GPa)	Yield Stress (MPa)	Tensile Stress (MPa)	High Cycle Fatigue Stress Limit (MPa)
Stainless Steel	F745	Annealed	190	221	483	221-280
	F55, F56, F138, F139	Annealed	190	331	586	241-276
		Cold Worked 30 %	190	792	930	310-448
		Cold Forged	190	1213	1351	820
Co-Cr Alloys	F75	Cast/Annealed	210	448-517	655-889	207-310
		Hot Isostatic Pressed	253	841	1277	725-950
	F799	Hot Forged	210	890-1200	1399-1586	600-896
	F90	Annealed	210	450-650	951-1220	-
		Cold Worked 44 %	210	1600	1896	586
	F562	Hot Forged	232	969-1000	1206	500
		Cold Worked, Aged	232	1500	1795	596-793
Ti Alloys	F67	Cold Worked 30 %	110	485	760	300
	F136	Forged / Annealed	116	896	965	620
		Forged, Heat Treated	116	1034	1103	620-589

In general, alumina (Al_2O_3), zirconia (ZrO_2), calcium phosphate, bioactive glass, hydroxyapatite (HA) are common ceramic biomaterials. Ceramic biomaterials can be used in the dental applişcations as dental implants, filling material for bone defects. In addition, ceramic biomaterials can be used in total hip or total knee orthopaedical implant applications for their high wear resistance and high strength.

Polymer biomaterial is an organic material which is very versatile than the metals or ceramics. Mechanical properties, electrochemical corrosion properties and chemical properties of the polymers can be changed in a very large scale depend on the intended biomedical applications.

The term composite biomaterials consist of 2 or more distinguished and separated phases on a macroscopic mixture scale. Composites consists of a matrix (continuous phase) and discontinuous phase (reinforcement). The matrix provide ductility and transmit the loads to the reinforcement. Usually, matrix can be produced from ceramic, polymers and metals. Composite materials produced for obtain a engineering material with desired mechanical or chemical properties. In general, bone tissue, cartilage tissue, wood, skin are examples for composite biomaterials. In general, properties of the composite biomaterials depend on the volume fraction of reinforcement/matrix and interface between the matrix and reinforcement. In addition shape and distribution of the reinforcement material is very important [4].

Calcium Phosphate Ceramics and Tricalcium Phosphate (TCP)

Calcium-phosphate ceramic*s* belong to the orthophosphate group and can be found in bones. In general the bone tissue consists of an inorganic phase of calcium-phosphates (apatites) and an organic component, which consists of water and collagen. There are monocalcium phosphates, dicalcium phosphates, tricalcium phosphates, and tetracalcium phosphates, in addition to the hydroxyapatite (HA). The stability raises with raising Ca/P ratios. Tricalcium phosphate *(*TCP), usually exists in 2 phases such as α-TCP or β-TCP. Tricalcium phosphate is usually studied as a coating with hydroxyapatite (HA).

Classification of Biomaterials Based on Activity

- Bioinerts
- Bioactives
- Biodegradables

In general, the bioactive biomaterials can be defined such as: no biological action to a biological system. Bioactive biomaterials react with lining tissues to form a chemical bond between an implant and surrounding living tissue. There is a high integration between the implant and living tissue [1-4].

In the bioinert materials there is no any chemical bonding (reaction) at the interface between living tissue and the biomedical implant. Bioinert materials are separated from the living tissue by a fibrous very thin (connective tissue layer) layer [4].

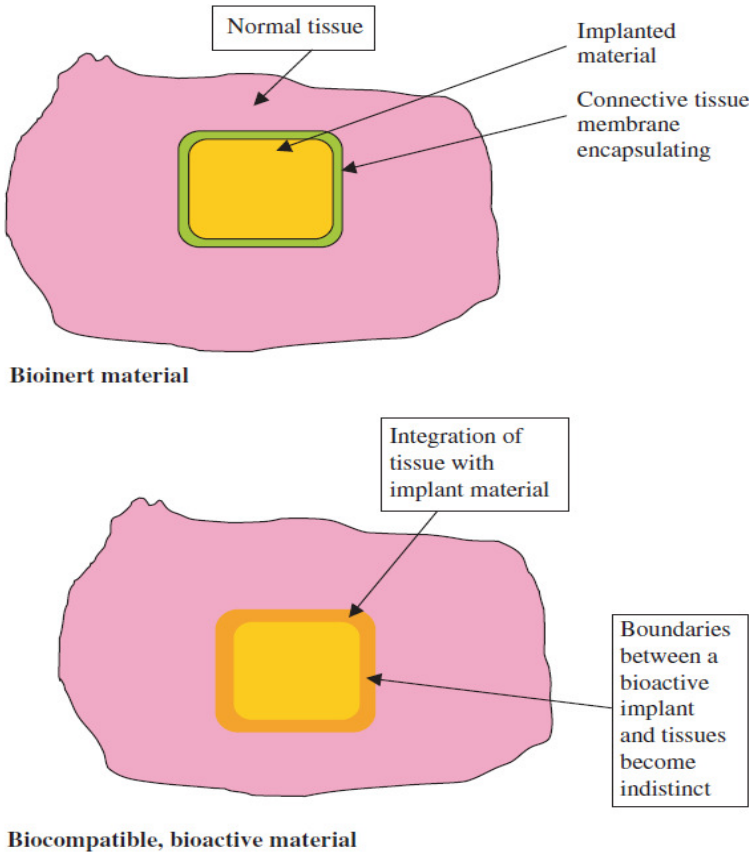


Figure 1.1: Implants in the human body [12]

Main Features of the Biomaterials

Biocompatibility

Biocompatibility is the property of a implantable biomaterial to exist inside the living body in contact with living tissues. Biomaterials for implant fabrication must show suitable biocompatibility, otherwise they can not be used inside the body.

Biodegradability (Bioresorption)

Biodegradable (bioresorbable) biomaterials are dissolved (resorbed) by natural or enzymatic mechanism or hydrolytic routes without the enzymes. Biodegradable materials are resorbed during the contact with the several body fluids [1].

Non-inflammatory

Inflammation (acute or chronic) can be decribed as response of the body to dangerous/toxic substances. Biomaterial for implant production must not stimulate undesired systematic or local reactions (allergy, toxicity) between implant materials and surrounding tissue inside the living body.

Nontoxicity

The biomaterials for implant fabrications must be nontoxic to the living human body. Aslo, electrochemical corrosion products, wear products or biodegradation products of the biomaterials inside the body must be also nontoxic [1].

Table 1.3 shows the main factors for material selection for the biomedical implant applications. In the first step, chemical composition (surface or bulk), density and elastic modulus are the main considered features for the implant materials. In the second level, adhesion, surface properties and hardness are the main properties. In the third level, biomaterial response type (bioinert, bioactive, biodegradable), geometry, thermal expansion, toughness, fatigue strength are the main parameters. In the fourth level, ease of fabrication is important for implant materials. Lastly, cost of the biomaterial is also important for biomedical implant applications.

Table 1.3: Material selection for implant applications [12]

Factors	Description		
	Chemical/Biological Characteristics	Physical Characteristics	Mechanical/Structural Characteristics
1st Level Material Properties	– chemical composition (bulk and surface)	– density	– elastic modulus – shear modulus – Poisson's ratio – yield strength – tensile strength – compressive strength
2nd Level Material Properties	– adhesion	– surface topology – texture – roughness	– hardness – flexural modulus – flexural strength
Specific Functional Requirements (based on application)	– biofunctionality – bioinert – bioactive – biostability – biodegradation behavior	– form & geometry – coefficient of thermal expansion – electrical conductivity – color, aesthetics – refractive index – opacity or translucency	– stiffness or rigidity – fracture toughness – fatigue strength – creep resistance – friction and wear resistance – adhesion strength – impact strength – proof stress – abrasion resistance
Processing & Fabrication	– reproducibility, quality, sterilizability, packaging, secondary processability		
Characteristics of host: tissue, organ, species, age, sex, race, health condition, activity, systemic response			
Medical/surgical procedure, period of application/usage			
Cost			

Table 1.4 given below shows the mechanical properties of the hard tissue (bone tisuue) and soft tissue in the human body. Elastic modulus of the implant materials must be close to bone tissue in order to prevent stress shielding effect. As shown in the table 1.4, elastic modulus of the cortical (dense) bone is about 12-17 GPa, while elastic modulus of the cancellous (porous) bone is about 0.4 GPa. Enamel is the hardest material in the body, and its elastic modulus is about 84 GPa. Elastic modulus values of the articular cartilage tissue and fibrocartilage are about 10 MPa and 160 MPa, which are very low values compared to cortical or cancellous bone tissue.

Table 1.4: Mechanical properties of hard and soft tissue [12]

Hard Tissue	Modulus (GPa)	Tensile Strength (MPa)
Cortical Bone (Longitudinal Direction)	17.7	133
Cortical Bone (Transverse Direction)	12.8	52
Cancellous Bone	0.4	7.4
Enamel	84.3	10
Dentine	11.0	39.3
Soft Tissue	**Modulus (MPa)**	**Tensile Strength (MPa)**
Articular Cartilage	10.5	27.5
Fibrocartilage	159.1	10.4
Ligament	303.0	29.5
Tendon	401.5	46.5
Skin	0.1–0.2	7.6
Arterial Tissue (Longitudinal Direction)		0.1
Arterial Tissue (Transverse Direction)		1.1
Intraocular Lens	5.6	2.3

1.2. COMPOSITE BIOMATERIALS

The term composite biomaterial can be described as a macro-combination (macromixture) of two or more different separated phases (materials). Composites consists of a matrix (continuous phase) and discontinuous phase (reinforcement). The matrix provide ductility and transmit the loads to the reinforcement. Bone tissue, cartilage tissue, wood, human skin are examples for composite biomaterials. Biological materials are generally composites. Bone, achieves its properties of low density and suitable strength by combination of apatite with collagen fibers [8-11]. Metal matrix composites (MMC) consist of two or more materials (phases) for obtaining the desired advantages of reinforcement material (particule or fibre) and the matrix material. Metals are employed as a matrix for the following features:

• High temperature resistance.

• High stiffness (elastic modulus) and tensile strengths.

• High toughness (energy absorption).

• High electric conduction and high thermal conduction

• Higher strength-to-density ratio,

• Ease of fabrication by traditional methods

In general, there are three kinds of metal matrix composites (MMCs):

(i) particle reinforced MMCs

(ii) short fiber or whisker reinforced MMCs

(iii) continuous fiber or sheet reinforced MMCs

Reinforcements

Metal matrix composites have several advantages than the traditional materials. Metal matrix composites show high flexibility. Also, combination of properties can be adjusted by varying the phases and their ratio. The most important properties of the reinforcement materials are their strength and Young's modulus [11].

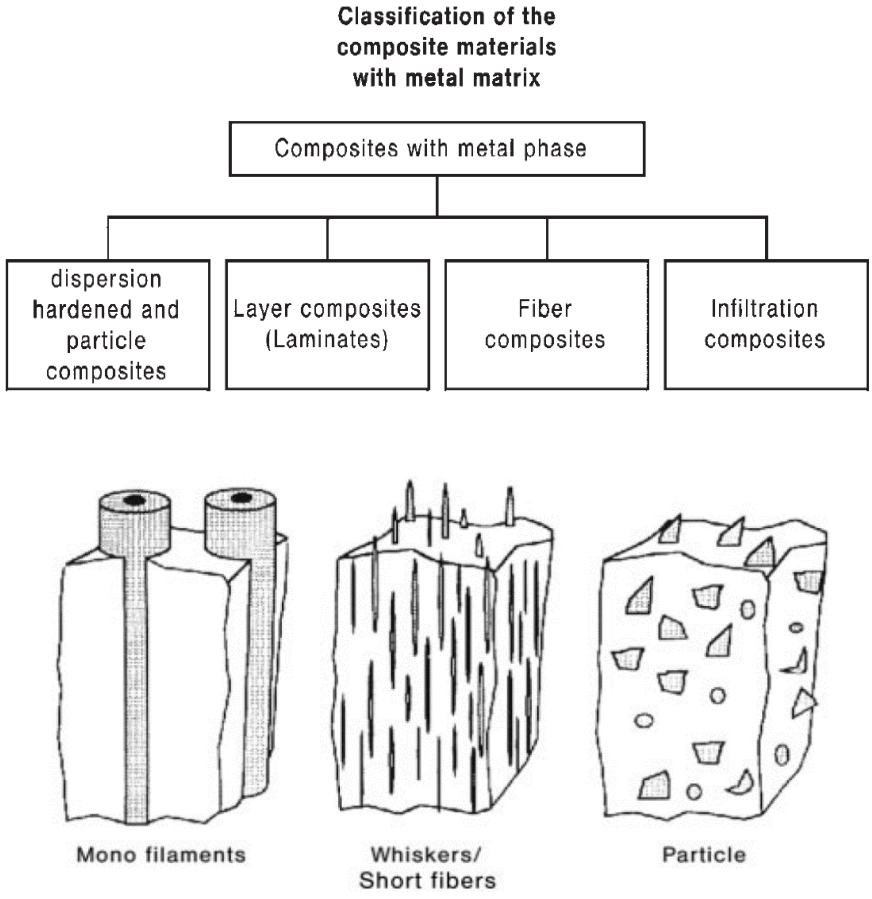


Figure 1.2: Metal matrix composites a) classification and b) shapes [10]

Figure 1.3 shown below schematically shows the elastic modulus to volume ratio of the reinforcement materials of platelets, fibers, and particles in a matrix material.

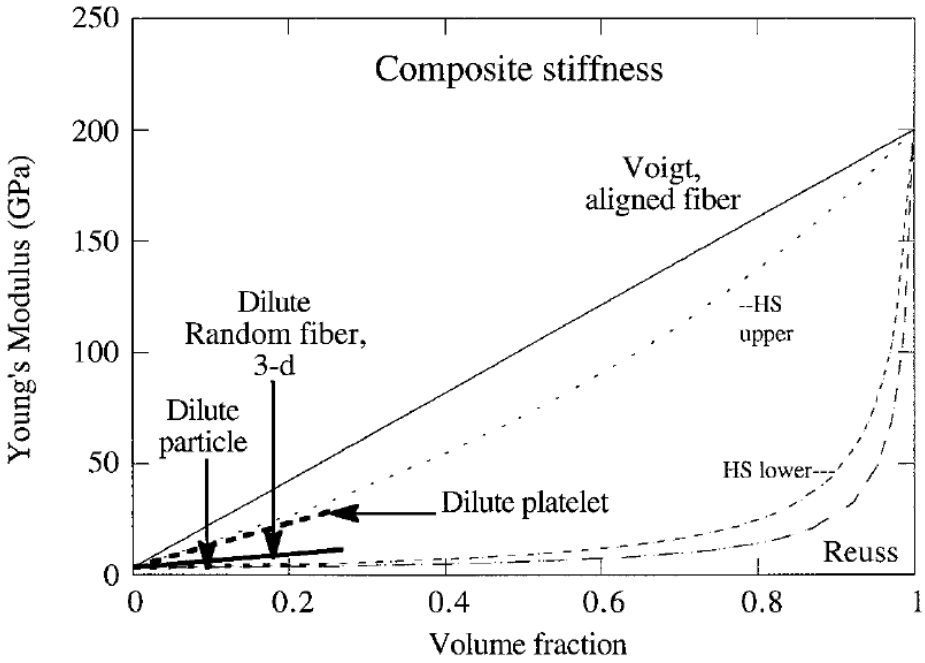


Figure 1.3: Elastic modulus and reinforcements [1]

In general stiffness (elastic modulus) of a composite biomaterial (usually polymer matrix) can be enhanced by the addition of a suitable particulate reinforcements. The shape (morphology) of the particulated reinforcement materials is very important. In the isotropic composite biomaterials, platelet (flake) reinforcements are the best effective for obtaining high Young's modulus, followed by fibres; the lowest effective morphology for high Young's modulus is the spherical reinforcement shapes [1].

Production of Metal Matrix Composites

The powder metallurgy route is the most important route in the production of metal matrix based biocomposites. In the powder metallurgy route metal powders and reinforcement materials (particles) are mixed. Then, high pressure is applied to obtain a compact (green specimen). For obtaining bonding between the metal particles, green compact is heated to about % 70-80 of their melting point (sintering). The sintering temperature must provide diffusion between the metal powders [6]. Ball milling (BA) or mechanical alloying (MA) is one of the most important route for production of metal matrix composites (MMC) reinforced by the dispersion ceramic based powders [9]

Figure 1.4: Carbon fiber reinforced-PEEK matrix compositea a) screws, b) hip stem [12]

1.3. ZINC ALLOYS

Zn (zinc) is a relatively abundante metal in the world (23rd element). However, production of the zinc is relatively high. Zn is 4th in the metals in production after Fe (iron/steel), Al, and Cu.

The industrial applications of the Zn can be grouped into 6 groups:

- Coatings
- Zn oxides (ZnO_2)
- Casting alloys
- Zn chemicals
- Alloying element (Mainly Cu-Zn)
- Wrought Zn alloys,

Zn coatings for electrochemical corrosion protection of steel products is the most widely used one. About 50% of Zn is used in the galvanizing of the steel products [13].

Table 1.5: Properties of Zn [13]

Atomic number	30
Atomic weight	65.38
Density	
Solid, 20°C	7.14 g/cm^3
Solid, 419.5°C	6.83 g/cm^3
Liquid, 419.5°C	6.62 g/cm^3
Velocity of sound, 20°C	3.67 km/s
Melting point	419.5°C
Boiling point, 1 atm	907°C
Heat capacity	
Solid, 25°C	25.4 J/mol
Liquid	31.4 J/mol
Resistivity	
Solid, 20°C	5.96 $\mu\Omega$·cm
Liquid, 419.7°C	37.4 $\mu\Omega$·cm
Thermal conductivity	
Solid, 18°C	113 W/(m·K)
Solid, 419.5°C	96 W/(m·K)
Liquid, 419.5°C	61 W/(m·K)
Linear coefficient of thermal expansion	
Polycrystalline	39.7×10^{-6} K^{-1}
a axis	14.3×10^{-6} K^{-1}
c axis	60.8×10^{-6} K^{-1}
Volume coefficient of thermal expansion	0.9×10^{-6} K^{-1}
Surface tension, liquid, 419.5°C	782 mN/m
Viscosity, liquid, 419.5°C	3.85 mN/m

Table 1.6 shows the main chemical reactions and their standard potential values of the zinc in the different corrosive conditions.

Table 1.6: Reactions of zinc [13]

Reaction	Equilibrium	Standard potential or equilibrium condition
Two dissolved substances		
1	$Zn^{2+} + H_2O = ZnOH^+ + H^+$	$\log (ZnOH^+)/(Zn^{2+}) = -9.67 + pH$
2	$ZnOH^+ + H_2O = HZnO_2^- + 2H^+$	$\log (HZnO_2^-)/(ZnOH^+) = -17.97 + 2pH$
3	$Zn^{2+} + 2H_2O = HZnO_2^- + 3H^+$	$\log (HZnO_2^-)/(Zn^{2+}) = -27.63 + 3pH$
4	$HZnO_2^- = ZnO_2^{2-} + H^+$	$\log (ZnO_2^{2-})/(HZnO_2^-) = -13.17 + pH$
Two solid substances		
5	$Zn + H_2O = ZnO + 2H^+ + 2e^-$	$E_0 = -0.439 - 0.0591\ pH$
One solid and one dissolved substance		
6	$Zn^{2+} + H_2O = ZnO + 2H^+$	$\log(Zn^{2+}) = 10.96 - 2pH$
7	$ZnO + H_2O = HZnO_2^- + H^+$	$\log(HZnO_2^-) = -16.68 + pH$
8	$ZnO + H_2O = ZnO_2^{2-} + 2H^+$	$\log(ZnO_2^{2-}) = -29.78 + 2pH$
9	$Zn = Zn^{2+} + 2e^-$	$E_0 = -0.763 + 0.0295 \log(Zn^{2+})$
10	$Zn + 2H_2O = HZnO_2^- + 3H^+ + 2e^-$	$E_0 = 0.054 - 0.0886pH + 0.0295 \log(HZnO_2^-)$
11	$Zn + 2H_2O = ZnO_2^{2-} + 4H^+ + 2e^-$	$E_0 = 0.441 - 0.1182\ pH + 0.0295 \log(ZnO_2^{2-})$
Stability of water		
(a)	$H_2 = 2H^+ + 2e^-$	$E_0 = 0.000 - 0.0591\ pH$
(b)	$2H_2O = O_2 + 4H^+ + 4e^-$	$E_0 = 1.228 - 0.0591\ pH$

Figure 1.5 shows the electrochemical corrosion products of the zinc in chloride environments with different concentrations.

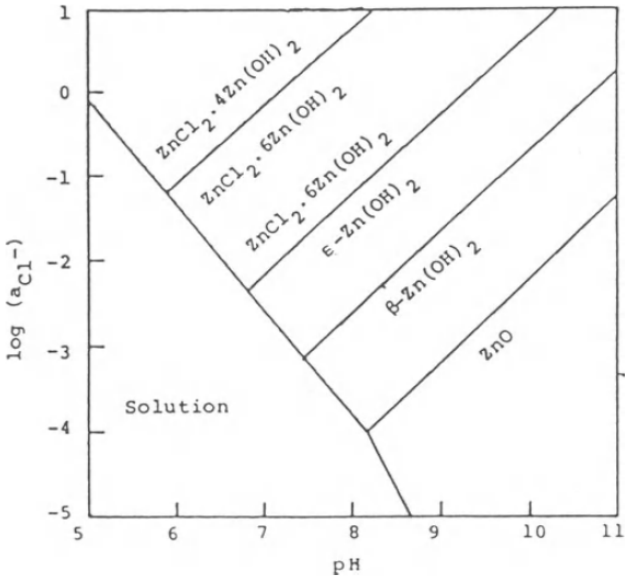


Figure 1.5: Corrosion products of Zn in chloride environment [13]

Figure 1.6 illustrates the Pourbaix diagram (E-pH diagram) of the zinc (Zn), which shows the thermodynamically stable phases of the zinc in different aquous environments. Thermodinamical stability of the phases of zinc alloysat specific conditions can be determined by using pH-potential values of the environment.

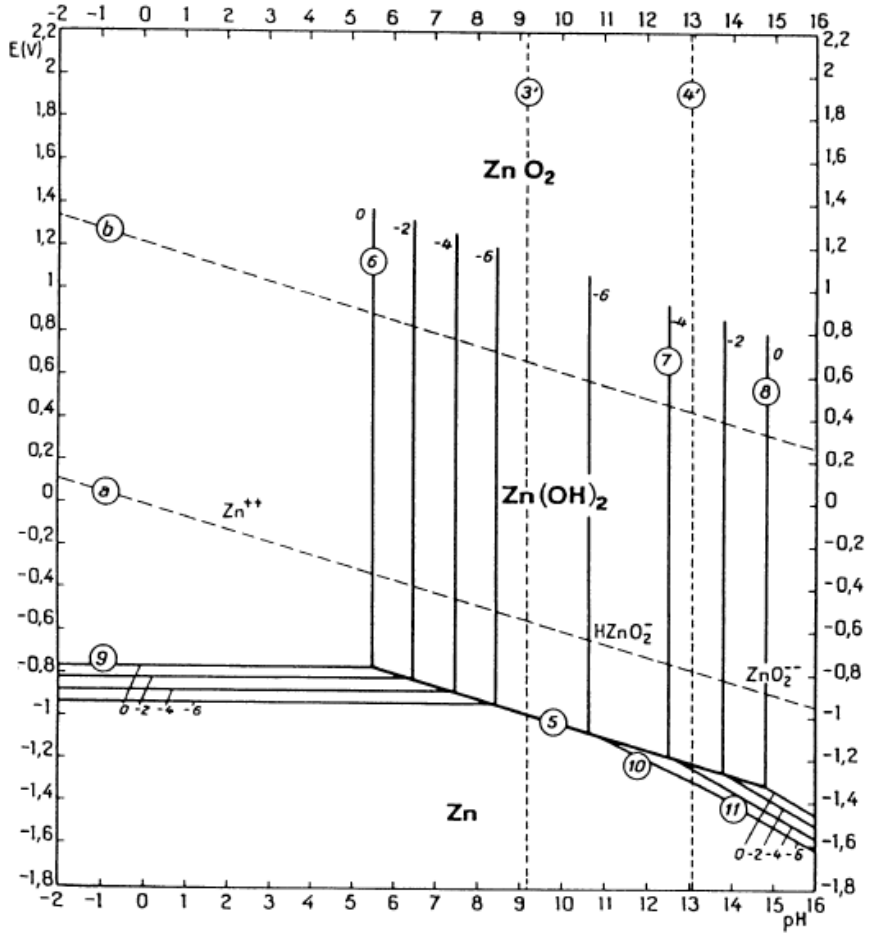


Figure 1.6: Pourbaix diagram of Zn [13]

1.4. LITERATURE REVIEW

Farhan [4] studied 3-dimentional printing of the biomaterials. PMMA/Zirconia biomaterials were prepared by the addition of different percent weight of Zirconia powder to the PMMA solution. The prepared samples were injected by using a syringe to get the desirable shape. Then it was sintered at different sintering temperature. Investigation of specimen microstructure was carried out by SEM. Phase structure was determined by XRD. The mechanical properties were determined by compressive tests. SEM pictures of the specimens were showed that pore content raises with PMMA level and decreases with the raise of sintering temperature.

Paksoy [6] studied characteristics of the cold gas dynamic sprayed titanium based coatings on cobalt alloys for biomedical hard tiisue orthopaedical implant applications. The aim of the study was enhancement on the bioactivity of the cobalt by formation of the very thin and dense titanium oxide layer on the surface by using the application of thermal oxidation. Cold gas dynamic spray (CGDS) process was preferred because of simplicity and high efficiency. SEM images showed that all the titanium coatings before thermal oxidation shows zero porosity. As a result, mechanical properties and bioactivity of Co-Cr alloys were enhanced by the Ti coating by using cold gas spray and thermal oxidation.

Bakın [7] studied bioactive coating for fuctionalization of the biomedical implant materials. In order to enhance the osseointegration, Ti is coated with CaP. To enhance biocompability, CaP coating is modified by doping. Effect of Mg-substitution on corrosion and bioactivity of CaP coatings on Ti6Al4V substrates via electrodeposition was studied. Characterizations of the coatings were examined by using XRD, FTIR and SEM. Corrosion properties were investigated by Tafel tests in the SBF environment.

Yürüker [8] studied development, production and characterization of boron carbide particle reinforced aluminium matrix composite materials mechanical properties and wear properties of the aluminium matrix composite specimens were determined. The wear behaviour of the composites was examined by metal-metal and metalabrasive wear tests. Metal-metal wear resistance of the investigated composites increased upon alloying of the matrix with Mg. Metal-abrasive wear resistance of the composites increased with increasing Mg content.

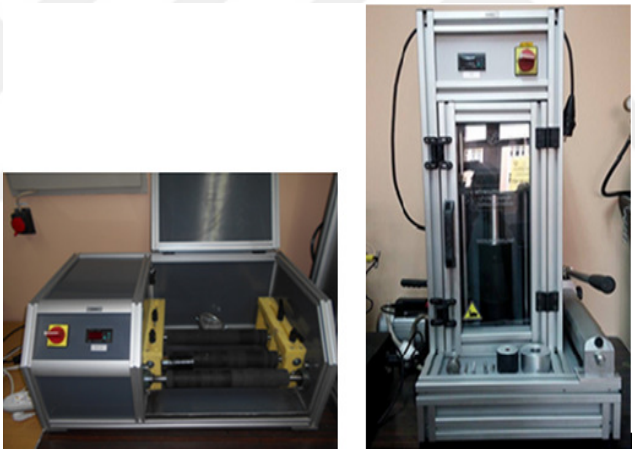
Kaftelen [9], studied development, fabrication and characterization of aluminium-based TiC and ZrC Particulate Composite materials. Very fine TiC particles were uniformly distributed in spherical droplets, whereas ZrC particles were clustered.

2. MATERIALS AND METHODS

2.1. PRODUCTION OF SPECIMENS

Non-Porous Sample Production by the Powder Metallurgy Method

In the experiments, initially non-porous biodegradable zinc alloys and zinc matrix composite specimens were manufactured by using Zn powders, Fe powders and tricalcium phosphate (TCP) powders. Zinc matrix composite specimens were manufactured by powder metallurgy route, which consisted of powder mixing, mechanical alloying, pressing and sintering stages. Compaction pressure was about 250 MPa. Sintering heat treatment of the green Zn specimens was carried out at 400 °C under vacuum. Figure 2.1 shows (a) ball mill (mechanical alloying) and hydraulic press, and (b) sintering furnace and vacuum pump.



(a)

(b)

Figure 2.1: a) Ball mill and hydraulic press, b) sintering furnace

In this study, zinc matrix composite specimens were manufactured by using Zn powders, Fe powders and tricalcium phosphate (TCP) powders. Zinc matrix composite specimens were manufactured by powder metallurgy route. In general, powder metallurgy method is suitable for the production of metal matrix composite materials. Casting is not suitable for the production of uniform metal matrix composites. In addition, wide metal alloy compositions can be obtained by using powder metallurgy-mechanical alloying method. There is no phase diagram (solid solubility) restrictions in the powder metallurgy-mechanical alloying method. Table 2.1 shows the amounts of alloying elements in the non-porous zinc (Zn) based specimens.

- Iron (Fe) was included in order to decreaase the biodegradation rate of the Zn based specimens. In general biodegradation rate of the pure Zn is higher than bone healing time.
- Iron (Fe) was also included in order to enhance the mechanical properties of the Zn based specimens. In general, pure zinc is very brittle metal.
- Copper (Cu) was included in order to enhance the mechanical properties of the Zn based specimens. In general, pure zinc is very brittle metal.
- Tricalcium phosphate (TCP) was included in order to enhance the biocompatibility of the Zn.

Table 2.1: Amounts of alloying elements in the non-porous Zn based specimens

Alloy	Zn	TCP	Fe	Cu
Zn-Fe	80		20	
Zn-Fe	85		15	
Zn-Cu	80			20
Zn-Cu	85			15
Zn-TCP	80	20		
Zn-TCP	80	15		
Zn-TCP-Fe	75	10	15	
Zn-TCP-Cu	75	10		15
Zn-TCP-Fe-Cu	70	10	15	5

Porous Sample Production by the Space Holder Method

In this thesis, highly porous Zn matrix composite foams were manufactured by powder metallurgy based space holder-water leaching technique, which provides open (interconnected) porous structure. Open porosity is very important in the biomedical implants, because open porosity enhances the osseointegration of the bioinert metals. Bone tissue grows inside the open pores and enhance the integration with implant. In addition open pores transmit body fluids. Moreover, increasing porosity of the metals decreases the elastic modulus of the metal-based implants. Elastic modulus of the orthopaedic implants must be low and close to bone in order to prevent stress shielding effect.

Zn powders and Fe powders and tricalcium phosphate (TCP) powder mixtures were ball-milled (mechanical alloying). The powder mixture was loaded in a container with ZrO_2 (zirconia) balls with 3 mm of diameter. Carbamide (urea) was used (about 70 vol. %) as a pore forming material (space holder). Average particle diameter of the urea was about 800 μm (710-1000 μm). Zinc powders and tricalcium phosphate (TCP) were mixed with 2.0 wt. % polyvinylalcohol (PVA) binder for green strength for handling purposes. Mixtures were compacted at about 200 MPa. The shape of the specimens was cylindrical. Diameter of the specimens was 10 mm. Specimens have a height of 17-20 mm. Compacted green samples were immersed into the water to remove the space holder (carbamide). Immersion period was about 13 hours in water. Polyvinylalcohol was thermally removed from the green body at about 390 °C. Zn-Fe-TCP based green compacts were sintered at 400 °C under vacuum. Table 2.2 shows the amounts of alloying elements in the porous Zn matrix composite specimens.

Table 2.2: Amounts of alloying elements in the porous Zn based specimens

Alloy	Zn	TCP	Fe	Carbamide
Zn-TCP	7.50	1.00	1.50	6.00

Figure 2.2 shows the Zn (left) powder having mean particle diameter of about 30-40 μm, carbamide (middle) powder having mean particle diameter of 800-900 μm, and metal-coated carbamide (right) powders. As the density of metals is higher than the cabamide, metal coating of the carbamide particles provides uniform density in the powder mixture and compacts (green specimens).

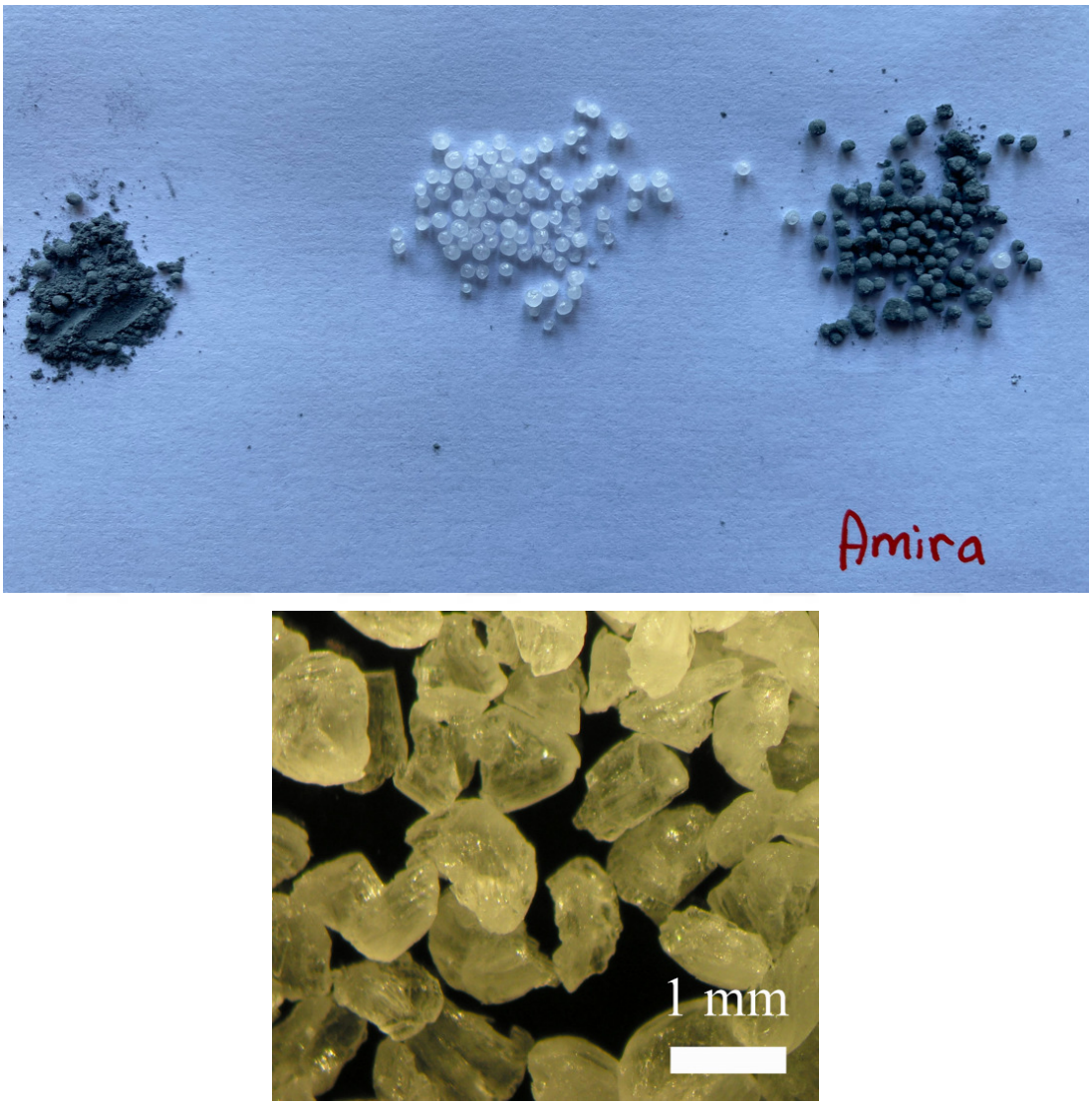


Figure 2.2. a) carbamide (left), metal (middle), metal-coated carbamide (right), b) carbamide

Figure 2.3 illustrates the main steps of the powder metallurgy based space holder method used for the production highly porous Zn matrix composite foams. Powder metallurgy based space holder route produces an open (interconnected) porous structure. Open structure can not be produced by using other methods like casting. Casting based methods produce closed porous structures, which is not suitable for implant applşications. In addition, powder metallurgy method is suitable for the production of the metal matrix composite specimens.

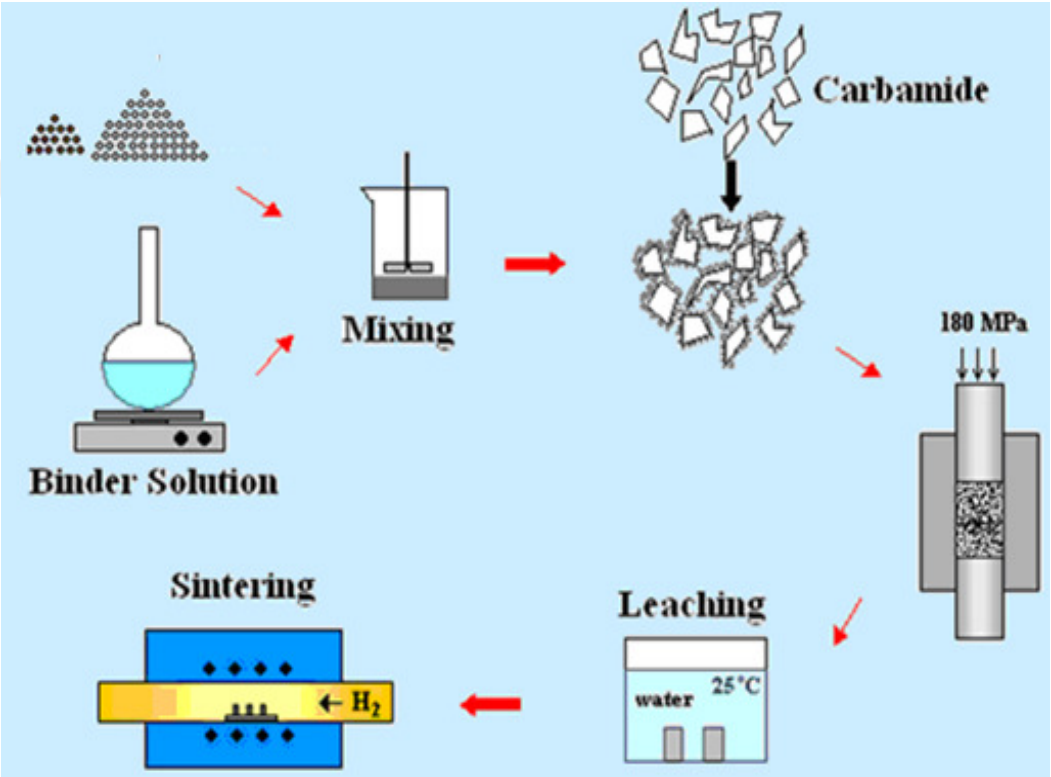


Figure 2.3: Main steps of the space holder method.

2.2. CHARACTERIZATION

Microstructure

Microstructure (powder morphology, powder size, sintered microstructure, sinterability and microstructural phases) of the Zn matrix composite specimens was studied by SEM. Densities (% porosity) of the Zn matrix composite samples were determined by using gravimetric (geometrical) method.

Mechanical Properties

Mechanical properties were determined by destructive compression tests and nondestructive ultrasonic tests.

Destructive Compression Test

Compression-tension device was employed to study the mechanical properties (Devotrans, Turkey). Figure 2.4 shows the photograph of the compression tests device.

Figure 2.4: Compression test device

Nondestructive Ultrasonic Tests (NDT)

Elastic modulus of the Zn matrix composite specimens was also evaluated by non-destructive based ultrasonic testing (USM Go, General Electric). Measurements were carried out by pulse-echo mode transducer having 4 MHz probe. Figure 2.5 shows the photograph of the ultrasonic tests device.

$$E = \rho V_T^2 \frac{3V^2_L - 4V_T^2}{V_L^2 - V_T^2} \quad (2.1)$$

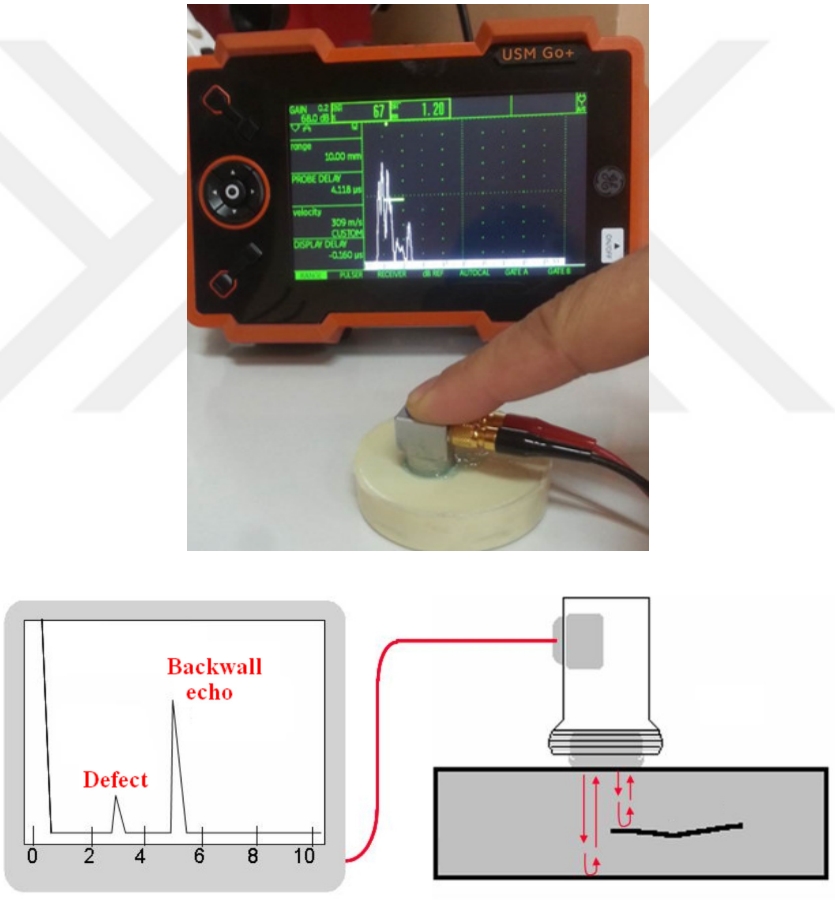


Figure 2.5: Ultrasonic test device

Biodegradation Properties

In order to study the weight loss, the Zn matrix composite specimens were immersed to the simulated body fluid (SBF) solution. Duration was up to 28 days.

Zn metal ion release was examined by using ICP-MS (Thermo Scientific) device. Gravimetric method was used for the measurement of the weight change.

Simulated body fluid (SBF) solution was prepared in the light of the literature. pH of the SBF solution was about 6.60. Amounts of the chemical reagents were given below in g/L:

- NaCl: 8.00
- CaCl2: 0.10
- MgCl2: 0.10
- KCl: 0.40
- KH2PO4: 0.60
- K2HPO4: 0.06
- NaHCO3: 0.35
- Na2SO4: 0.05
- Glucose: 1.00

Electrochemical corrosion tests were conducted in SBF (simulated (artificial) body fluid) using a potentiostat (Interface 1000, Gamry). High density graphite was counter electrode (cathode), saturated calomel electrode (SCE) was reference electrode and the sample was working electrode (anode). Evaluation of the corrosion results was carried out by software (Gamry).

3. RESULTS

3.1. MICROSTRUCTURE AND MECHANICAL PROPERTIES

Microsructure

In this study, biodegradable Zn matrix composite specimens for temporary implant applications were manufactured by the pressing-sintering route by using zinc (Zn) powders and tricalcium phosphate (TCP) powders. Figure 3.1 illustrates the images of the fine and irregular shaped zinc (Zn) powder, b) iron (Fe) powder, and c) tricalcium phosphate (TCP) powders.

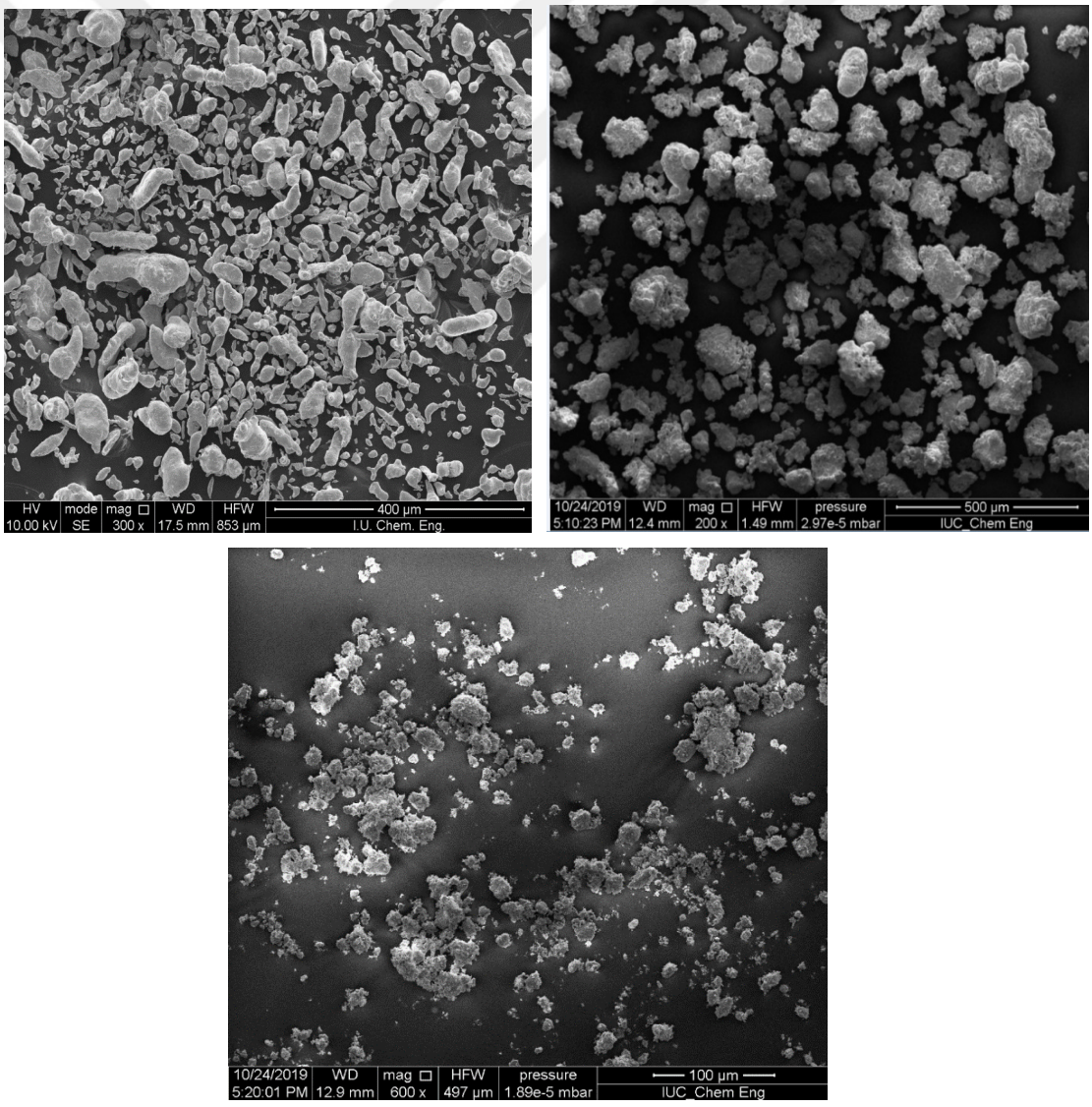


Figure 3.1: SEM picture of a) Zn powder, b) Fe powder, and c) TCP powder

Figure 3.2 shows the SEM image of the sintered zinc (Zn) matrix composite sample. As seen from the SEM image, sintering was suitable (sintering temperature and time). There is a suitable bonding between the Zn-Fe-TCP powders. As seen from the SEM image, there is an uniform microstructure.

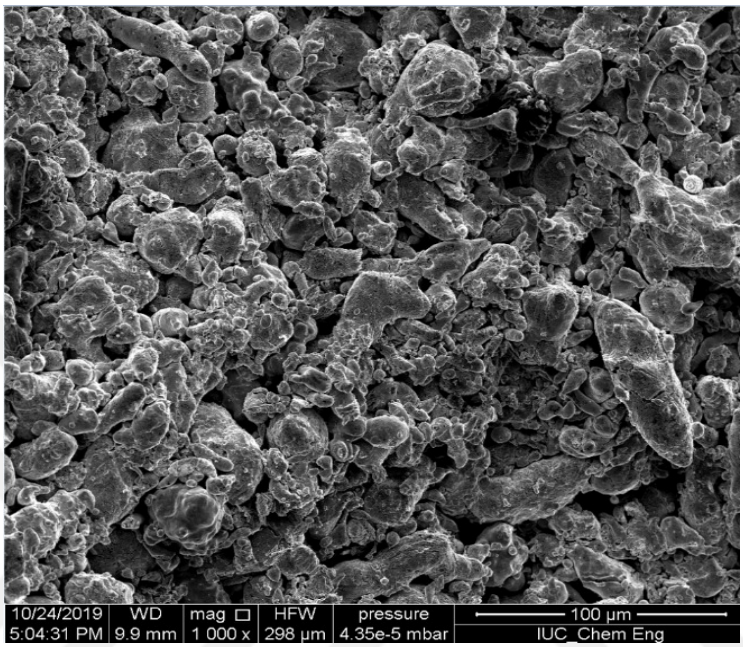


Figure 3.2: SEM picture of sintered Zn-Fe-TCP specimen

Figure 3.3 shows the photograph and optical microscope photograph of the sintered zinc (Zn) matrix composite sample.

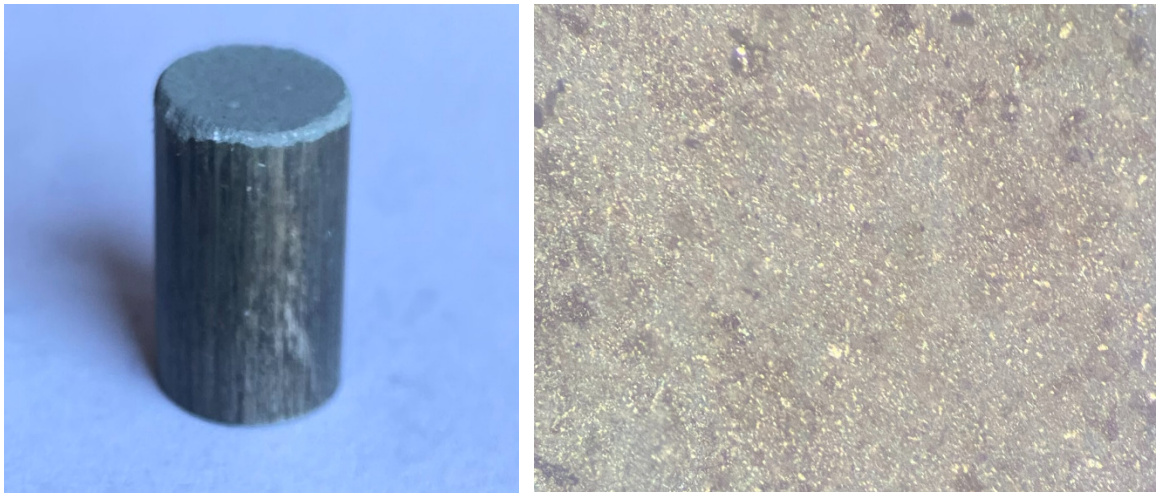


Figure 3.3: Photograph of sintered Zn-TCP specimen

Figure 3.4 shows the SEM image of the microstructure of the sintered highly porous zinc (Zn) matrix composite sample (foam). Mean macro-pore size was about 600 µm, which is suitable for biomedical implant applications.

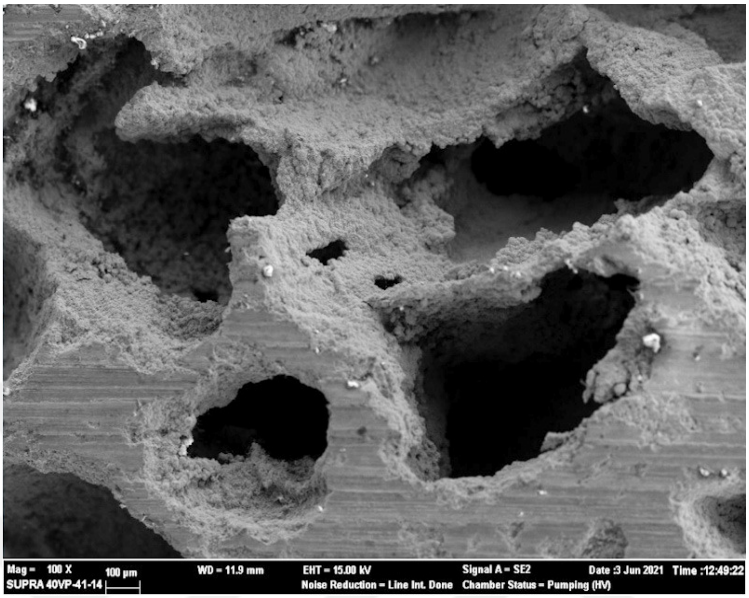


Figure 3.4: SEM image of the porous Zn alloy

Figure 3.5 shows the pictures of the sintered zinc (Zn) matrix composite samples with 10 mm diameter. As seen from the pictures, sintering process was suitable (sintering temperature and time). As seen from the pictures, there is no swelling or shrinkage. Also there is no any change in the dimensions of the specimen.

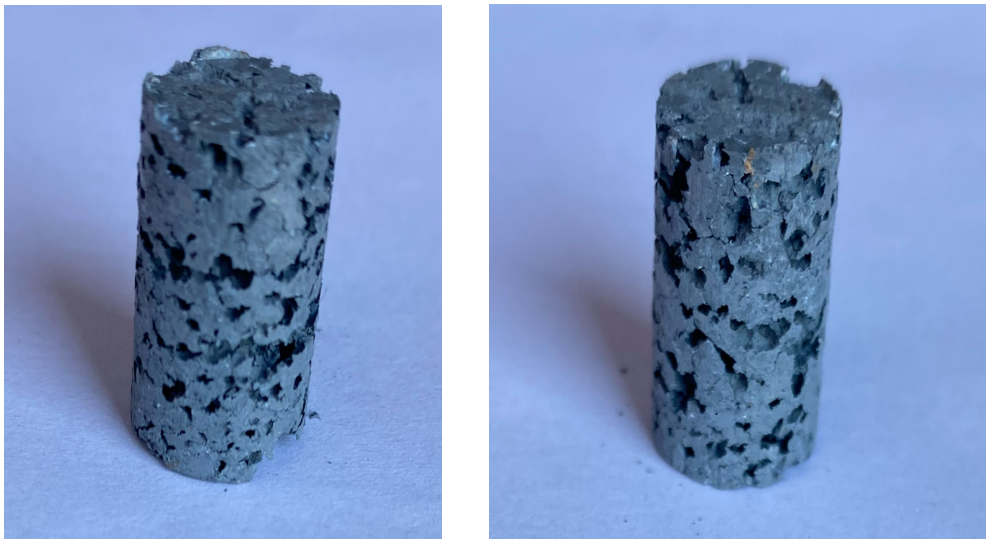


Figure 3.5: Pictures of the porous Zn alloy

Mechanical Properties

Table 3.1 shows the green density and sintered density values of the non-porous Zn matrix composite specimens.

Table 3.1: Green and sintered density values of Zn specimens

Alloy	Green Density (g/cm^3)	Sintered Density (g/cm^3)
Zn-20Fe	5.49	5.85
Zn-15Fe	5.42	5.67
Zn-20Cu	5.49	5.80
Zn-15Cu	5.35	5.61
Zn-20TCP	3.85	4.27
Zn-15TCP	3.93	4.30
Zn-TCP-Fe	3.96	4.37
Zn-TCP-Cu	3.93	4.20
Zn-TCP-Fe-Cu	4.19	4.60

Table 3.2 given below shows the green density and sintered density values of the highly porous Zn matrix composite foams.

Table 3.2: Green and sintered density values of porous Zn alloys

Alloy	Green Density (g/cm^3)	Sintered Density (g/cm^3)
Zn-TCP	2.50	3.00

Table 3.3 shows the ultrasonic (nondetsructive) and compression (destructive) elastic modulus values of the sintered non-porous zinc (Zn) matrix composite specimens. Difference between compression test values and ultrasonic test values was in the range of 5-10 %.

Table 3.3: Elastic modulus values of the Zn specimens

Alloy	Elastic Modulus (GPa) Ultrasonic	Elastic Modulus (GPa) Compression
Zn-20Fe	88	95
Zn-15Fe	84	90
Zn-20Cu	88	95
Zn-15Cu	83	90
Zn-20TCP	65	76
Zn-15TCP	73	78
Zn-TCP-Fe	83	80
Zn-TCP-Cu	75	84
Zn-TCP-Fe-Cu	84	90

Table 3.4 given below shows the elastic modulus values of the sintered highly porous zinc (Zn) matrix composite foams.

Table 3.4: Elastic modulus vales of the porous Zn alloys

Alloy	Elastic Modulus (GPa) (Compression)
Zn-TCP	2.50

Table 3.5 shows the change of the elastic modulus values of the sintered non-porous zinc (Zn) matrix composite specimens with immersion time in the simulated body fluid (SBF) solution.

Table 3.5: Elastic modulus values of the Zn specimens

Alloy	**Elastic Modulus (GPa)**			
	1 day	**3 day**	**7 day**	**14 day**
Zn-20Fe	94	90	85	79
Zn-15Fe	90	88	82	77
Zn-20Cu	94	90	83	82
Zn-15Cu	90	88	84	81
Zn-20TCP	75	70	68	57
Zn-15TCP	77	71	70	56
Zn-TCP-Fe	81	77	73	60
Zn-TCP-Cu	83	80	72	66
Zn-TCP-Fe-Cu	88	80	75	67

Table 3.6 shows the change of the elastic modulus values of the sintered highly porous zinc (Zn) matrix composite foams specimens with immersion time in the simulated body fluid (SBF) solution.

Table 3.6: Elastic modulus values of the porous Zn alloys

Alloy	**Elastic Modulus (GPa)**		
	1 day	**7 day**	**14 day**
Zn-TCP	2.50	1.50	0.50

Pore Properties

Figure 3.6 given below shows the mean pore diameter distribution of the highly porous porous Zn matrix composite specimens produced by using irregular shaped carbamide particles. As seen from the Figure 3.6, mean pore diameter was about 640 µm, which is suitable value for the biomedical implant applications.

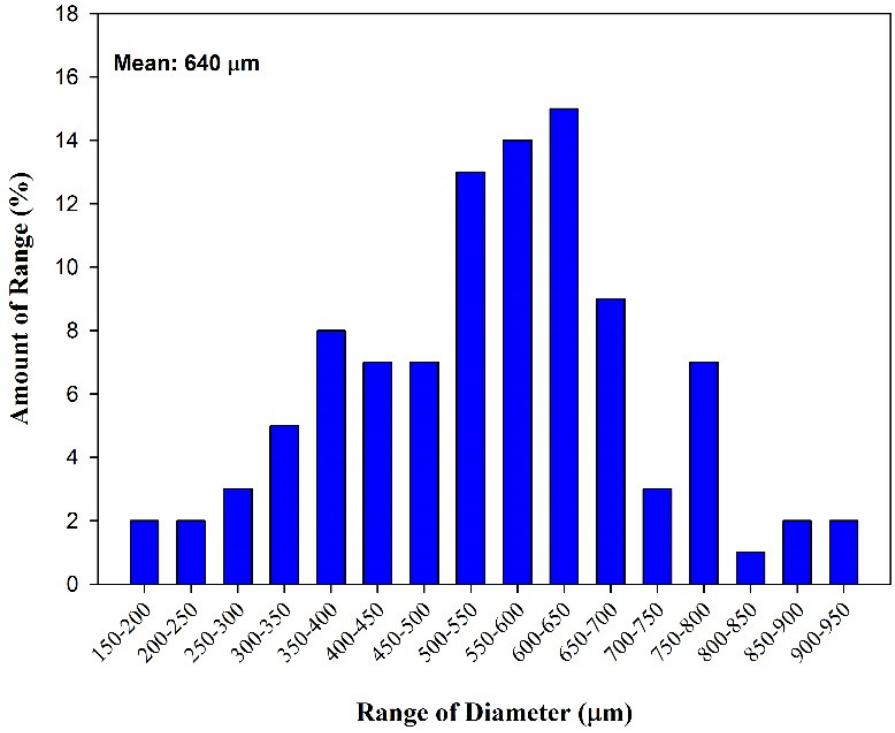


Figure 3.6: Mean pore diameter in porous Zn-TCP specimen

3.2. CORROSION AND BIODEGRADATION

Biodegradation behaviour of the specimens was studied by weight change and metal ion release measurements in simulated body fluid solutions. Metal ion (Zn^{2+}, $Cu^{2+}$and Fe^{3+} / Fe^{2+}) release values from the specimens were increased with increasing immersion time in the simulated body fluid (SBF) solution. Table 3.7 given below shows the amounts of the release of alloying elements from the Zn based specimens in the SBF solution.

Table 3.7: Amounts of release of alloying elements from Zn alloys in the SBF

Alloy	Zn (ppm)	Fe (ppm)	Cu (ppm)
Zn-20Fe	210	17	
Zn-15Fe	201	22	
Zn-20Cu	205		13
Zn-15Cu	198		11
Zn-20TCP	245		
Zn-15TCP	269		
Zn-TCP-Fe	220	22	
Zn-TCP-Cu	210		7
Zn-TCP-Fe-Cu	217	24	

Biodegradation behaviour of the specimens was also studied by weight change in SBF. Weight loss values of the zinc (Zn) matrix composite specimens were increased with increasing immersion times in the simulated body fluid (SBF) solution, as expected. Table 3.8 given below shows the weight change of the Zn alloys in the SBF solution.

Table 3.8: Weight change of the Zn alloys in the SBF

Alloy	Weight change (%)
Zn-20Fe	19
Zn-15Fe	21
Zn-20Cu	18
Zn-15Cu	20
Zn-20TCP	35
Zn-15TCP	34
Zn-TCP-Fe	33
Zn-TCP-Cu	31
Zn-TCP-Fe-Cu	28

In addition, the biodegradation behaviour of the specimens was studied by electrochemical corrosion tests in the simulated body fluid solutions. Table 3.9 given below shows the electrochemical corrosion rate values of the different Zn alloys in the simulated body fluid (SBF) solution. As shown in the Table 3.9, the highest electrochemical corrosion rate was in the Zn-15TCP specimen, while the lowest electrochemical corrosion rate was in the Zn-20Cu specimen.

Table 3.9: Corrosion rate values of the Zn alloys in the SBF solution

Alloy	Corrosion Rate (mm/year)
Zn-20Fe	0.16
Zn-15Fe	0.19
Zn-20Cu	0.16
Zn-15Cu	0.18
Zn-20TCP	0.40
Zn-15TCP	0.42
Zn-TCP-Fe	0.27
Zn-TCP-Cu	0.22
Zn-TCP-Fe-Cu	0.23

4. DISCUSSION

In this thesis, biodegradable zinc (Zn) matrix composite materials were produced for biomedical implant applications. Biodegradable zinc matrix composite specimens were produced by traditional powder metallurgy (press-sinter) method. Biodegradable materials must show mechanical properties close to bone, biodegradation rate close to tissue healing rate, and biocompatibility. Mixture, which was consisted of metal powders, ceramic additives and polymer binder, was compacted and green specimens were produced. Zinc matrix composite materials were sintered at 400 °C temperature for 1 hour in a horizontal tube furnace. In addition, highly porous zinc based composite specimens were produced by using space holder (pore former) materials. Mechanical properties and microstructures of the specimens were characterized. Mechanical properties were investigated by compression tests. Electrochemical corrosion properties of the specimens were investigated in simulated body fluid solution. In addition, metal ion release and weight change (biodegradation) properties were studied in simulated body fluid.

Biomedical implant is a foreign device used inside the living body, and is fabricated by using suitable biomaterial. In general, biomaterials are a class of advanced engineering materials. Metallic biomaterials are most commonly used for the fabrication of the load bearing orthopaedic hard tissue implants. In general, the biodegradable biomaterials are dissolved (resorbed) by natural or enzymatic mechanism or hydrolytic routes without the enzymes. In general the term composite biomaterial can be described as a macro-combination (macromixture) of two or more different distinguished and separated phases (materials). Composites consists of a matrix (continuous phase) and discontinuous phase (reinforcement). Metal matrix composites (MMC) consist of two or more materials (phases) for obtaining the desired advantages of reinforcement material (particule or fibre) and the matrix material. The powder metallurgy route is the most important route in the production of metal matrix based biocomposites.

In this study, Zn matrix composites were manufactured by using Zn powders, Fe powders and TCP powders. Zinc matrix composites were manufactured by powder metallurgy route. In general, powder metallurgy method is suitable for the production of metal matrix composite materials. Casting is not suitable for the production of uniform metal matrix composites. In addition, wide metal alloy compositions can be obtained by using powder metallurgy-mechanical alloying method. There is no phase diagram (solid solubility) restrictions in the powder metallurgy-mechanical alloying method. Fe was included in order to decreaase the biodegradation rate of the Zn based specimens. In general biodegradation rate of the pure Zn is higher than bone healing time. Fe was also included in order to enhance the mechanical properties of the Zn based specimens. In general, pure zinc is very brittle metal. Cu was included in order to enhance the mechanical properties of the Zn based specimens. TCP was included in order to enhance the biocompatibility of the Zn.

In this thesis, highly porous Zn matrix composite foams were manufactured by powder metallurgy based space holder-water leaching technique, which provides open (interconnected) porous structure. Open porosity is very important in the biomedical implants, because open porosity enhances the osseointegration of the bioinert metals. Bone tissue grows inside the open pores and enhance the integration with implant. In addition open pores transmit body fluids. Moreover, increasing porosity of the metals decreases the elastic modulus of the metal-based implants. Elastic modulus of the implants must be low and close to bone in order to prevent stress shielding effect. Powder metallurgy based space holder route produses an open porous structure. Open structure can not be produced by using other methods like casting. Casting based methods produce closed porosous structures, which is not suitable for implant applications. In addition, powder metallurgy method is suitable for the production of the metal matrix composite specimens.

Microstructure of the sintered zinc matrix composite samples were studied by SEM study. As seen from the SEM images, sintering was suitable (sintering temperature and time). There is a suitable bonding between the Zn-Fe-TCP powders.

Biodegradation and electrochemical corrosion properties of the specimens were studied in SBF solution. Weight loss values of the zinc matrix composite specimens were increased with

increasing immersion durations in the simulated body fluid solution. In addition, metal ion (Zn and Fe) release values were increased with increasing immersion time in the SBF solution. The highest electrochemical corrosion rate was in the Zn-15TCP specimen, while the lowest corrosion rate was in the Zn-20Cu specimen.

5. CONCLUSION AND RECOMMENDATIONS

In this thesis, biodegradable zinc (Zn) matrix composite materials were produced for biomedical implant applications. Biodegradable zinc matrix composite specimens were produced by traditional powder metallurgy (press-sinter) method. Biodegradable materials must show mechanical properties close to bone, biodegradation rate close to tissue healing rate, and biocompatibility. Mixture, which was consisted of metal powders, ceramic additives and polymer binder, was compacted and green specimens were produced. Zinc (Zn) matrix composite materials were sintered at 400 °C temperature for 1 hour in a horizontal tube furnace. In addition, highly porous zinc based composite specimens were produced by using space holder (pore former) materials. Mechanical properties and microstructures of the specimens were characterized. Mechanical properties were investigated by compression tests. Electrochemical corrosion properties of the specimens were investigated in simulated body fluid solution. In addition, metal ion release and weight change (biodegradation) properties were studied in simulated body fluid.

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