T.C.
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INSTITUTE OF GRADUATE STUDIES
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M. Sc. THESIS

PRODUCTION AND SURFACE TREATMENT OF TI-CU ALLOY IN BIOMEDICAL IMPLANT APPLICATIONS

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FOREWORD

I would like to express my thanks to my teacher and supervisor Assoc. Prof. Dr. İlven MUTLU, who was always helped me.

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

December, 2017 Tuğçe ARABACI

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LIST OF SYMBOLS AND ABBREVIATONS

Symbol	Explanation
T	: Temperature
t	: Time
º	: Degree
α	: Alpha
β	: Beta

Abbreviation	Explanation
g	: Gram
mg	: Mili gram
mm	: Mili meter
nm	: Nano meter
ppm	: Parts per million
PVA	: Polyvinylalcohol
µm	: Micro meter
MA	: Mechanical alloying
OCP	: Open circuit potential

ÖZET

YÜKSEK LİSANS TEZİ

Biyomedikal İmplant Uygulamalarında Ti-Cu Alaşımının Üretimi ve Yüzey İşlemi

Tuğçe ARABACI

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Bu tezin amacı, Ti-5%Cu alaşımı biyomedikal implantların mekanik alaşımlama (MA)-toz metalurjisi yöntemiyle üretilmesidir. Numunelerin biyoaktivitelerini arttırmak için yüzey işlem yapılmıştır. Ayrıca alaşımların korozyon ve mekanik özellikleri incelenmiştir. Biyomedikal amaçlı titanyum alaşımlarının elastisite modülü düşük ve mümkün olduğu kadar kemiğe yakın olmalıdır. Titanyum alaşımlarından beta-Ti esaslı alaşımlar en düşük elastisite modülüne sahiptir. Geleneksel ve ticari beta-Ti alaşımlarının üretilmesi zordur ve başarılı bir sinterleme için yüksek sıcaklıklara ısıtmak gerekmektedir. Cu ilavesi alaşımın erime sıcaklığını düşürüp, alaşımın sinterleme kabiliyetini arttırmaktadır. Ayrıca Cu titanyum alaşımına antibakteriyel özellikler kazandırmıştır.

Bu tez çalışmasında Ti alaşımları mekanik alaşımlama yöntemiyle hazırlanmıştır. Alaşımı oluşturan elementlerin erime sıcaklıkları arasında farklar varsa çözünürlük seviyeleri düşük ise döküm uygun bir yöntem olmamaktadır. Bu şartlarda, MA döküm ile üretilmesi zor alaşımları için avantaj sağlamaktadır. Metal tozlarına bilyeli değirmende (mekanik öğütücü) zirkonya (ZrO_2) bilyeler kullanarak mekanik alaşımlama uygulanmıştır.

Toz karışımlarına sinterleme öncesi ham mukavemet kazandırmak için bir miktar polivinilalkol (PVA) ilave edilmiştir. Karışım tek eksenli pres ile sıkıştırılıp ham numuneler üretilmiştir. Ham numuneler 1100-1250 °C arasında sinterlenmiştir**.** Oksitlenmeyi önlemek amacıyla sinterleme işlemi saf argon atmosferinde gerçekleştirilmiştir. Yoğunluğu düşürmek ve elastisite modülünü kemiğe yaklaştırmak için boşluk yapıcı tekniği ile yüksek oranda (yaklaşık %70) implantlar üretilmiştir. Boşluk yapıcı olarak üre (karbamit) kullanılmıştır. Boşluk yapıcı suda içerisinde bekletme ile uzaklaştırılmıştır. Toplam gözenekliliğin % 60-80 arasında olması hedeflenmiştir. Toplam gözenek miktarı ilave edilecek boşluk yapıcı miktarı ile kontrol edilmiştir. Numunelerin biyoaktivitelerini arttırmak için alkali yüzey işlem yapılmıştır. Bu amaçla numuneler 60 °C sıcaklıktaki NaOH çözeltisine daldırılmıştır. Alkali yüzey işlemden sonra numuneler kurutulmuş ve 600 °C sıcaklıkta 1 saat havada ısıl işlem görmüştür.

Numunelerin mekanik özellikleri (Elastisite modülü) incelenmiştir. Taramalı elektron mikroskobu (SEM) ve x-ışınları difraksiyon (XRD) analizi ile mikroyapı (gözenek parametreleri) incelemesi gerçekleştirilmiştir. Elektrokimyasal korozyon testleri yapay vücut sıvısı ortamında, elektrokimyasal hücre sisteminde, potansiyostat ile gerçekleştirilmiştir. Alaşımların korozyon özellikleri elektrokimyasal korozyon ölçüm teknikleri (Tafel eğrileri, potansiyodinamik polarizasyon, lineer polarizasyon direnci (LPR), çevrimsel polarizasyon ile değerlendirilmiştir. Çözeltinin pH ve flor içeriğinin numunelerin korozyon davranışına etkisi incelenmiştir. Numunelerden metal iyon salınımları ve ağırlık kaybı statik daldırma testleri ile belirlenmiştir. Statik daldırma esnasında gerçekleşen metal salınım miktarı endüksiyonla çiftlenmiş plazma-kütle spektroskopisi (ICP-MS) ile tespit edilmiştir.

Kasım 2017, 58 sayfa.

Anahtar kelimeler: Ti-Cu, İmplant, Gözenekli malzeme, Yüzey işlem, Korozyon.

SUMMARY

M.Sc. THESIS

Production and Surface Treatment of Ti-Cu Alloy in Biomedical Implant Applications

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Department of Bio and Nano Technology Engineering

Supervisor : Doç. Dr. İlven MUTLU

The aim of this thesis is production of antibacterial Ti-(5%)Cu alloy foam for dentistry. The alloy sample was manufactured by mechanical alloying (MA) and PM (powder metallurgy) method. Surface (sodium hydroxide) treatment was carried out in order to increase bioactivity of the specimens. In addition, corrosion and mechanical properties of the alloys were characterized. Elastic modulus of the titanium alloy implants should be low and similar with bone (beta-Ti is the lowest). Traditional and commercial Ti alloys need to heat up to high sintering temperatures. Alloying with copper was lowered the sintering temperature and enhanced sinterability. Titanium can be antibacterial with Cu alloying.

In this thesis, titanium alloys were produced through MA method. When there is a wide range of melting temperatures between alloy elements or there is a low solubility, casting does not seem to be good. The metal powders were ball-milled (mechanically alloying) in a ball-milling machine by using hard zirconia balls.

Metal powders mixed with poly-vinyl-alcohol (PVA), which provides binding. Mixtures were compacted in a press. Green specimens were sintered at 1100-1260 °C in argon atmosphere. In order to decrease the density, and to make the Young's (elasticity) modulus closer to human bony tissue, porous bone-like implants were manufactured. Carbamide (urea) was used as a space holder (pore former). Space holding agent was removed from the compacts by water leaching route. Porosity was in the range of 60-80 %. Total porosity (in %) was adjusted by space holder content. Surface (sodium hydroxide or alkali) treatment was carried out by in sodium hydroxyde for induce a bioactive surface. Activated samples were heat up to 600 °C.

Microstructure (pore structure and phases) of the sintered samples was examined. Corrosion (electrochemical) tests were carried out using a potentiostat in simulated body fluid electrolyte. Corrosion properties (rate and resistance) of the samples were tested by several corrosion (electrochemical) measurement techniques. Metal (Ti) ion release and weight loss behaviour of the samples were examined.

November 2017, 58 pages.

Keywords: Ti-Cu, Implant, Porous material, Surface treatment, Corrosion.

1. INTRODUCTION

Porous materials show a structure similar to human cancellous bones. Main advantage of the porous materials as a biomedical implant material is their ability to provide mechanical attachment to the surrounding bone. Main problem of the biomedical (orthopaedic or dental) implants is the difference of their Young's (elastic) modulus with the value of the bony tissue (stress shielding effect). High porosity (in %) lowers the elastic modulus and prevents stress shielding effect (which is the main problem in orthopaedic implants).

Copper (Cu) alloying provided good sintering capability to the pure-Ti and Ti-based alloys. Sintering process of the Cu-alloyed compacts was carried out at lower temperatures than the traditional Ti-based alloys. Machining (drilling, cutting or turning) properties of the alloys were increased by copper alloying. Cu alloying was also provided aging (precipitation hardening) capacity. In general, bacteries must be killed or eliminated from ithe surface of the mplants (Cu alloying can do this).

A bioactive layer (bone-like apatite) can be coated on the Ti-based alloy implants by using alkali (sodium hydroxide) surface treatment. Alkali (sodium hydroxide) surface treatment provides an active surface. This bioactive surface of the titanium-based implants leads to nucleation of apatite (in vivo bioactivity).

2. THEORY

2.1. BIOMATERIALS

In short, biomaterials can be defined as biocompatible (non-toxic) inorganic materials that are produced to replace a par tor a function of body, damaged organs or tissues of the living body in a safe, economical, aestetically manner [1-3].

In general, biomaterial science discipline consists of several individual steps as shown below. The bio-materials science is a multi-disciplinary science that consists of materials engineering, chemistry, biology, mechanical engineering, genetics, surgery and other disciplines.

Figure 2.1: The path from the science of biomaterials to clinical application [1]

Bio-compatibility therm can be desribed as suitable tissue response of materials. Biomaterials can be divided into 3 main groups as bioinert, bioresorbable, and bioactive [3].

Incompatible (Toxic) Materials

Toxic (incompatible) materials are release metal ions in toxic concentrations to the body fluids [3]. Releasing of some metallic ions occurs from biocompatible materials but in non-toxic levels. Biocompatible materials also called as biotolerant materials.

Bio-inert Materials

There is no any toxic ion release from bio-inert materials. There is no any bonding or any interaction with adjasent bone in bio-inert materials. Bioinert materials can be desribed and defined as any material that has minimum chemical bonding with adjasent tissue. Examples of bioinert materials are some stainless steels, titanium (Ti) alloys, alumina, and poly-ethylene. A fibrous film (capsule) forms on the bio-inert implants [3].

Bio-active Biomaterials

There is a chemical bonding between the bioactive materials and human bone. There is a chemical bonding between bioactive materials and tissue. Bioactive materials interacts/bonds with the adjasent bone tissue. Ion exchange causes bioactive film formation which is very similar (in composition) to the natural bone [3].

Bio-resorbable Materials

Bio-resorbable (bio-degradable) materials starts to degrade (dissolution or leaching) in the body after implantation and replaced by the adjasent tissue in a specific periode of time [3].

a) Metals

The most used material in biomedical applications is metallic biomaterials. Stainless steels, titanium and Co-Cr alloys have been used as biomaterials. Other alternative metallic biomaterials are tantalum, niobium, gold, platinum and magnesium. All the commercial metals are bioinert and do not show low elastic modulus close to bone [4].

b) Ceramics

Ceramics are brittle inorganic materials with high compressive strength, low tensile stress and bioinertness. Ceramics also have higher elastic modulus than the human bone tissue. The most common ceramic biomaterials are oxides (alumina and zirconia), calcium phosphate (hydroxyapatite). [4].

c) Polymers

Polymers are classified as natural and synthetic. Polymers can be divided as biodegradable and bioinert. Polyvinyl chloride, polyetheretherketone, polyethylene, polymethylmethacrylate, polytetrafluoroethylene can be used. Lactic acids is the most common example of biodegradable synthetic polymers. There are also wide range of natural polymer like chitosan, chitin, dextran.

d) Composites

Composite materials can be defined as macro-solution (mixture) made from several (2 or more) materials. In general, to produce composite materials metals, ceramics and polymers should be combined (mixed). Composite biomaterials are usually polymer matrix based. Composite biomaterials consits of a matrix (usually polymer) and a reinforcement material (laminated, fiber, particulate). Reinforcements can be vital or avital [4].

Table 2.1: Materials for use in the body [2]

Materials	Advantages	Disadvantages	Examples
Polymers (nylon, silicone rubber, polyester, polytetrafuoroethylene, etc.)	Resilient Easy to fabricate	Not strong Deforms with time, may degrade	Sutures, blood vessels, hip socket, ear, nose, other soft tissues, sutures
Metals (Ti and its alloys, Co-Cr alloys, stainless steels, Au, Ag, Pt, etc.)	Strong, tough, ductile	May corrode, dense, difficult to make	Joint replacements, bone plates and screws, dental root implants, pacer and suture wires
Ceramics (aluminum oxide, calcium phosphates including hydroxyapatite, carbon)	Very biocompatible, inert, strong in compression	Brittle, not resilient, difficult to make	Dental; femoral head of hip replacement, coating of dental and orthopedic implants
Composites (carbon-carbon, wire or fiber reinforced bone cement)	Strong, tailor-made	Difficult to make	Joint implants, heart valves

Biomedical Implants

In general, implant is a medical device that is placed (implanted) within the living body, beneath an epithelial surface (totally or partially). Implants are used to assist or enhance the functions of the human body [4].

The main requirements for implant/prosthesis materials are bio-compatibility, functionality, manufacturing capability, durability and safety.

Young's modulus of a biomedical prosthesis must be close to value of the Young's modulus of the living bony tissue. Difference between implants elastic (Young's) modulus and the human bones elastic modulus leads to stres-shielding effect. Dental prosthesis must be manufactured highly porous (to prevent stres shielding [4].

Figure 2.2: Examples of typical total hip implant components [1]

Dental Implant Materials

Dental prosthesis (dental implant) is a part where missing teeth are replaced. Dental implants are metal anchors located in the jaw bone to support the crown where the teeth are missing.

Dental implants are subjected to mechanical loads during the chewing and biting. The bitting force on the human teeth during chewing the foods is between 110-850 N and the chewing force is about 100 N [5, 6].

Another important parameter is biocompatibility. Dental implant materials should be tolerated to biological or chemical reactions in saliva and other body fluids. Titanium alloys, gold, stainless steel alloys (316L or 304), cobalt-chromium alloys (vitallium) have been studied [5, 6].

The strength of the Ti is high (with high strength/density ratio), whereas elastic modulus is low (100-110 GPa) than the different metal alloys like 316L and vitallium with elastic modulus of 200 and 240 GPa [5, 6].

Ceramic materials (hydroxyapatite (HA), tricalcium phosphate (TCP), bioglass-ceramics and bioglasses (45S5) can be thought as implant material. Unfortunately, HA and TCP are very brittle.

In general, ceramic implants have low tensile strength values insufficient. Moreover, ceramics have high solubility, leads to hydrolysis in water and becoming brittle. Zirconia provides good view (very similar to natural teeth), biocompatibility and strength. Bur, zirconia implants are very brittle [5].

There are two types of dental implants for missing teeth [5, 6],

- Root type
- Periosteal type

a) Root-Form Implant

The other name of the root-form (srew type) dental implant is endosteal type dental implants. Overall shape, design, and size of the root-type implants are very similar to the shape and size of the human tooth root. The root-form implants are placed into the jaw bone [5, 6].

Figure 2.3: Root-form type dental implants [1]

b) Subperiosteal Implant

Sub-periosteal implants are composed of a metal framework. Subperioriosteal implants can be used if all teeth are not in place [5, 6].

2.2. TITANIUM ALLOYS

Titanium (Ti) is a transition element. Atomic number and atomic weight values of the titanium are 22 and 47.9 g/mol. Titanium is the fourth most abundant metal (0.6 % of the earth). The most important raw materials are ilmenite ($FeTiO_3$) and rutile (TiO_2). Production of Ti (Kroll's process) is very expensive [7-9].

Ti has low density, biocompatibility, strength and high corrosion resistance. Like other metallic materials (Fe, Ni, Ag, Nb, Ta, Co, Zr, Sn, Ce, and Cu) titanium crystallizes in two crystal structures (lattice). Pure titanium shows hexagonal closed packed (hcp) unit cell (alpha-phase) below the 883 °C (transus) and body centered (bcc) cubic unit cell (beta-phase) above the 883 °C, (beta transus temperature for pure titanium). Schematic unit cells of the structures of the Ti are shown in the Figure 2.4 below [7-9].

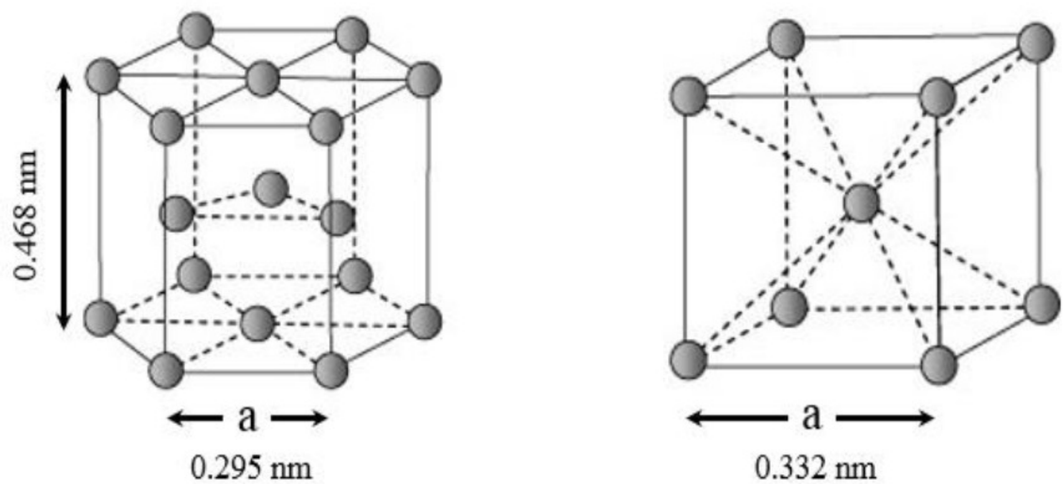


Figure 2.4: The unit cells of titanium alloys [7]

According to their unit cells, commercial Ti alloys can be divided into 5 groups as alpha (pure-Ti or cp-Ti), alpha-beta, near-alpha, metastable-beta and lastly stable beta titanium alloys.

Alpha-beta transormation temperature is lowered with increasing beta stabilizer elements. Alloying with beta-Ti stabilizing elements provide single beta-Ti phase region in the phase (equilibrium) diagrams.

Al and interstitial elements (O, C, and N) are categorized as alpha-Ti stabilizer elements. Beta-Ti stabilizer elements are categorized into beta-Titanium eutectoid and beta-Titanium isomorphous elements.

Zr and Sn can be categorized (in alloy design) as neutral elements [7-9].

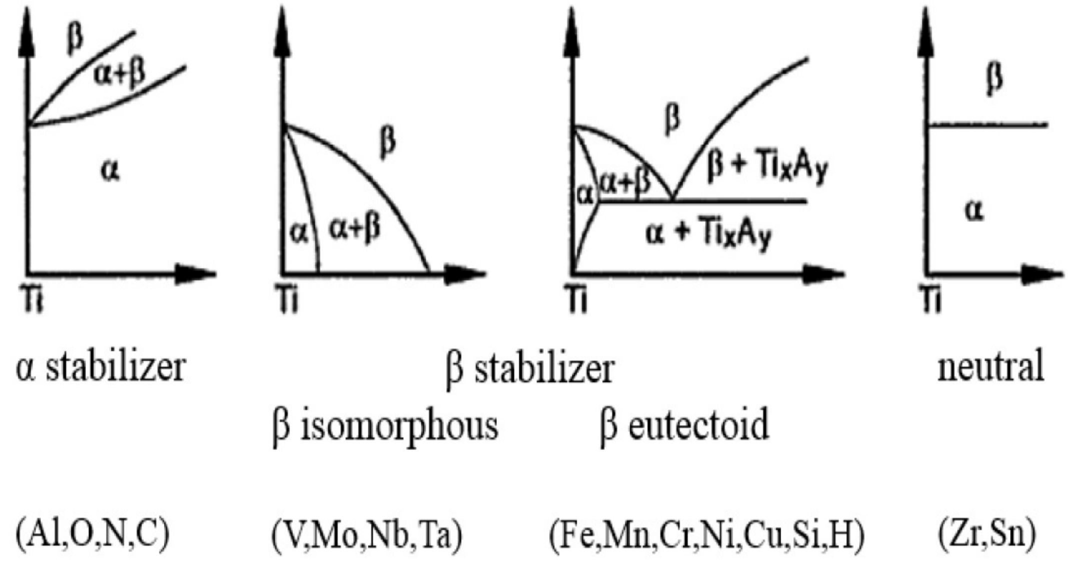


Figure 2.5: Phase diagrams of titanium alloys [7]

Mechanical (strength and elastic modulus) properties of the Titanium are related to the composition and the contents microstructural phases (alpha or beta). α-Ti phase show high creep resistance. Alpha-alloys can not be heat treated. Deformation of the beta-titanium is good, which is related to its bcc-based lattice structure [7-9].

Ti can be used in dental implants, orthodontic surgery, orthopaedic prosthesis (joint replacement), stents in biomedical field. Ti has high strength and low density. But, titanium is relatively expensive engineeringmetal. High price is a result of the reactivity of Ti with the oxygen from open-air. The use of inert atmosphere or vacuum is required during the production-manufacturing of the Ti and during the melting (die casting).

Reaction of titanium and titanium alloys with oxygen (from air) provides oxidation and formation of stable TiO_2 layer (rutile or anatase based). This oxide layer (TiO_2) provides high electrochemical corrosion resistance to the titanium and titanium-based alloys [9].

Table 2.2: Physical properties of Ti as compared to other structural metals [9]

	Linear Thermal Expansion Coeffi-cient (10^{-6} K^{-1})	Thermal Conductivity (W m^{-1} K^{-1})	Specific Heat Capacity (J kg^{-1} K^{-1})	Electrical Resistivity (μΩ m)
α Titanium	8.4	20	523	0.42
Ti-6Al-4V	9.0	7	530	1.67
Ti-15-3	8.5	8	500	1.4
Fe	11.8	80	450	0.09
Ni	13.4	90	440	0.07
Al	23.1	237	900	0.03

2.3. METAL FOAMS

In general, porous materials (metal foams or cellular solids) contain soo many micro-pores and macro-pores. Porous materials can be divided as low, middle and low porosity. Low and middle porosity materials have closed pores, while high porosity materials have open (interconnected) pores.

Cellular solids (porous materials) can be categorized as 2-dimensional (honeycomb-like) and 3-dimensional (foam-like) with poly-hedron structure. 3-dimensional foams, can be used in biomedical (dental or orthopaedical) applications. Porous materilas are widely exist around us [7].

Porous materials are new group of enginering materials. Porous materials (cellular materials) can have open (interconnected) porosity or closed (discrete) porosity. Open (interconnected) porous foams are used for filtering, while closed porous materials can be used for isolation, damping (in bumpers of the cars), packaging and lightweight structure (sandwich). Open porous foams have a potential to be used in biomedical applications.

Stress shielding (elastic modulus difference between implant and bony tissue) can be lowered by the incorporation (by using pore forming agents) of porosity. Increasing porosity (in %) content decreases the elastisity modulus of the materials. The open (interconnected) pores also provide mechanical attachment (called osseointegration) for the bone tissues and provide transmission of the blood or other body fluids [7].

Mechanical properties of the foams depends on their density (pore number, porosity %), amount and ratio of the open or closed (cells) pores, pore shape (morphology) and pore content (total porosity in %). Stres-strain curves of the foams consit of 3 regons; elastic region, plateau region and densification region [7].

Table 2.3: Porous metal fabrication processes and pore structures [10]

Pore Structure	Distribution of pores	Production method
CLOSED	Random pore distribution	Cymat/Hydro (Al, Mg, Zn)
		ALPORAS
		Sintering hollow spheres
		Alulight/Foaminal
	Graded pore distribution	Plasma spraying
OPEN	Homogenous pore distribution	Vapor deposition
		Orderly oriented wire mesh
		Ferromagnetic fiber arrays
		Rapid Prototyping
	Non-homogenous pore distribution	Sintering of metal powders and fibers
		Gas entrapment technique
		Space holder technique
		Replication method
		Combustion synthesis
		Slurry foaming technique
	Functionally graded pore distribution	Electric field assisted powder consolidation
		Rapid prototyping

2.4. POWDER METALLURGY

Powder metallurgy (PM) is the processing of metal powders (ferrous or non-ferrous) into engineering usefull components. Powder metallurgy method is the production and usage of metal powders. In general, powders are particles that are less than 1 mm (diameter). Usually, powders in the PM method are in the range of 10-250 µm.

Powder metallurgy (PM) includes sintering of the shaped (compacted) parts from powders in a high temperature furnace to develop strength without losing the designed shape obtained during compaction (pressing) [10].

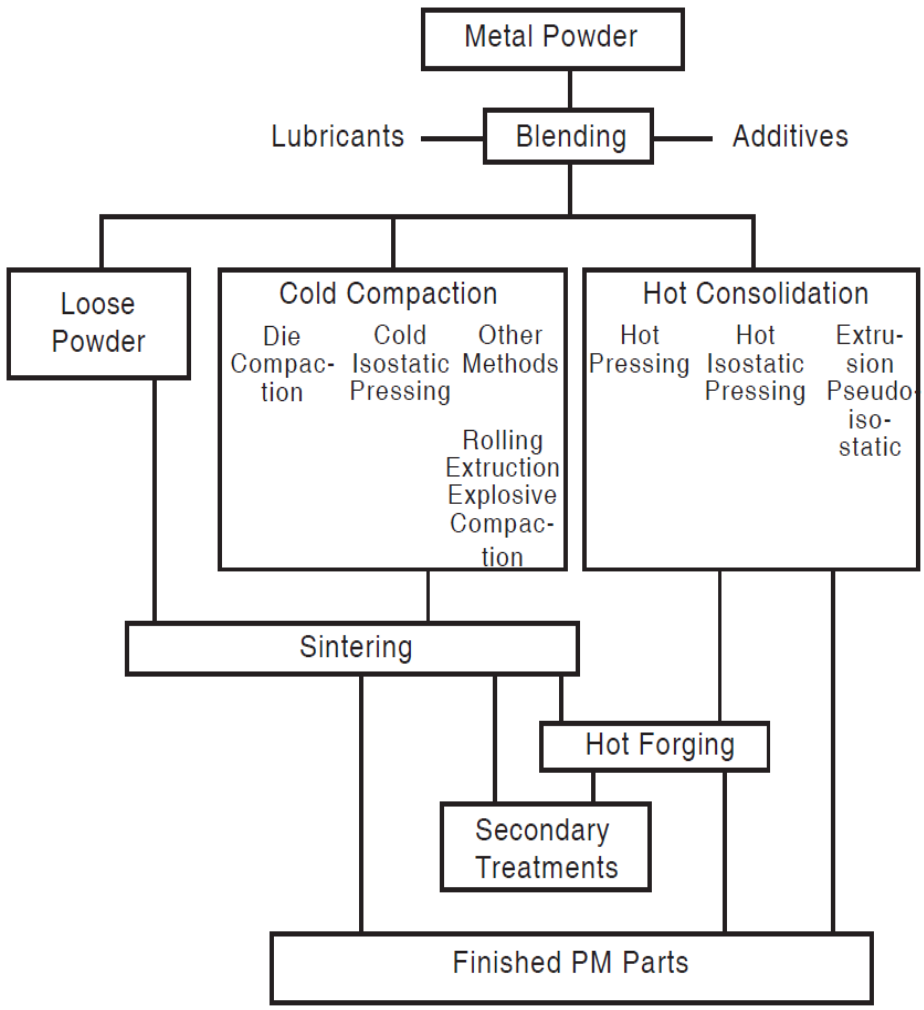


Figure 2.6: Steps of powder metallurgy [11]

The initial steps in PM, include blending, mixing, agglomeration, deagglomeration and lubrication. Blending and mixing (elemental metal powders or alloys) provide a homogenous mixture. Agglomeration used for easier flowing. Lubricant (stearates or other reagents) provides easier sample removal (ejection) from the die (mould) and longer die (tool) life [10].

a) Powder consolidation

Powder (particle) compaction (pressing) uses an external load (pressure) for shaping/forming the powders into a dens (about 90%) part. This compaction is carried out in rigid dies. Green density increase as the pressure increase.

In double action (top and bottom) compaction, the compaction pressure is exerted from both of bottom and top dies (punche). In the single action (top or bottom side) pressing method, density is highest at the top of the specimen. The PM parts usually contains too many pores [10].

b) Sintering

In order to produce useful engineering parts/devices for people, compacted (pressed) powder mixtures are diffusion bonded by heating to high temperatures. Sintering temperature is about 3/4 of the melting temperature of the metal or alloy [10].

2.5. CORROSION

Corrosion can be described as a destruction/degradation of a metallic alloy by a chemical or electrochemical-based reaction with its surroundings. Corrosion produces a deterioration of its properties. In general, physical effects are not called corrosion, but they are called errosion, wear and galling. Meanwhile, reactions of the polymers and ceramics are not included into the definition of the corrosion.

Corrosion processes (reactions) are usually electrochemical. Electrochemical corrosion process involves two reactions [15, 16]:

Anodic reaction:

$$M \rightarrow M^{+n} + ne^{-} \qquad (3.1)$$

Cathodic reactions:

$$2nH^{+} + ne^{-} \rightarrow H_2 \qquad (3.2)$$

$$2O + 2ne^{-} \rightarrow nH_2O \qquad (3.3)$$

$$M^{+n} + ne^{-} \rightarrow M \qquad (3.4)$$

For electrochemical corrosion, both anodic and cathodic reactions must be present. The electrode at which reduction (positive current enter from the solution) occurs is cathode (positive pole). The electrode at which oxidation (current leaves) occurs is anode (negative pole).

Electrochemical corrosion is possible (according to thermodynamical calculations) of most engineering conditions. But, it is important to determine how fast (kinetics of the reaction) the corrosion reaction will occur [15, 16].

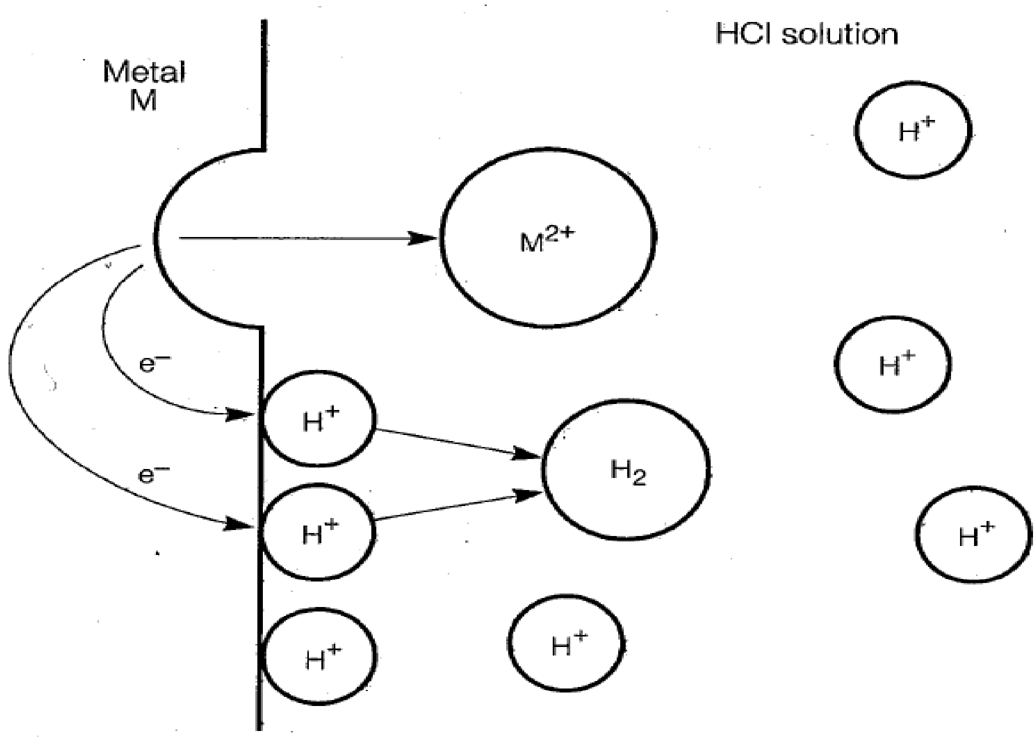


Figure 2.7: Schematic diagram of metal dissolution [17]

Passivation can be described as formation of a very thin, protective (from corrosion), oxide film which is a barrier (prevent contact) between corrosive solution (electrolyte) and metal, and this isolation leads to lowering the rate of anodic reaction (corrosion). Passivating metallic materials are actually active in the electromotive force (EMF) lists, but their electrochemical corrosion rate (weight change) is actually very low. Passive metals are noble in galvanic lists. Some engineering metals, like nickel, aluminum, titanium and stainless steels, show passivity [13-15].

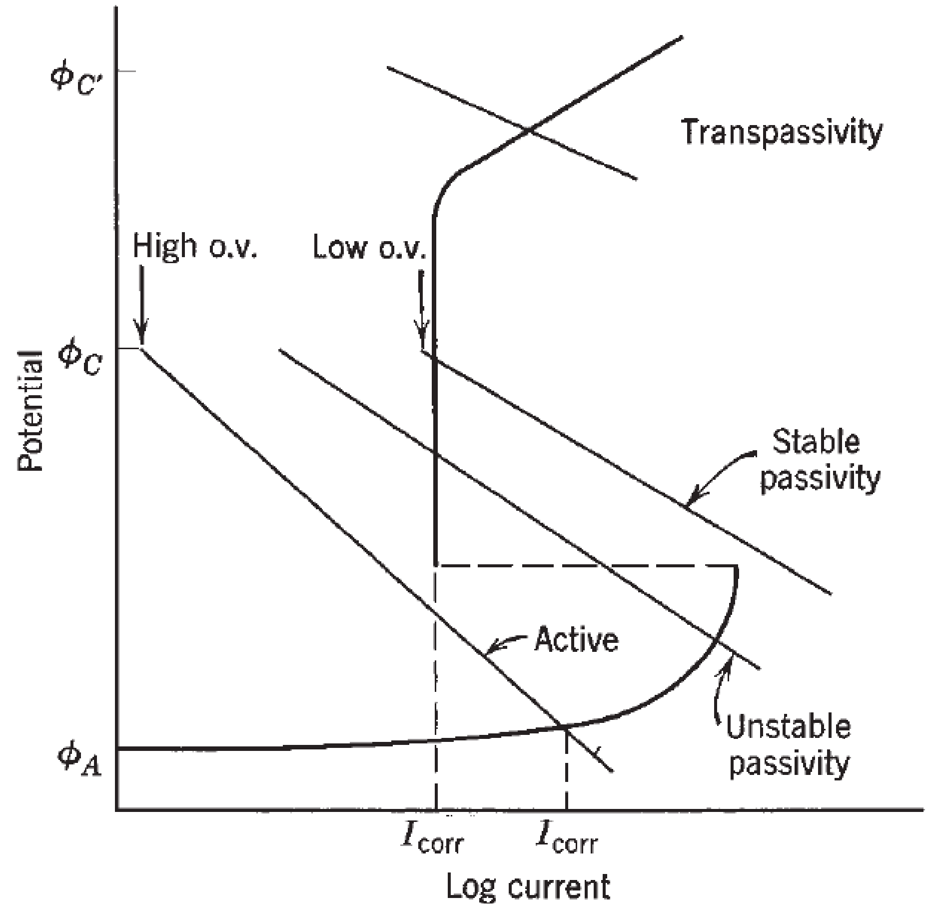


Figure 2.8: Polarization diagram for metal that is either active or pasive [18]

2.6. LITERATURE REVIEW

Osorio et al. [19] investigated and examined the corrosion behaviour of the titanium (Ti)-copper (Cu). Alloys were produced by die casting and then heat treated. 5-15 wt.% Cu values were added. After casting, the heat treatment was carried out at 900 °C. Electrochemical corrosion properties were investigated in sodium chloride (NaCl) environment.

Osorio et al. [19] found and concluded that, electrochemical corrosion rate (resistance) was increased with copper alloying. Martensite and Ti_2Cu based intermetallics have also an important role and impact on the corrosion rate.

Liu et al. [20] investigated and examined the impact of copper alloying. Anti-bacterial behaviour of the titanium-copper alloy was examined. 2, 5, and 25 % Cu contents were alloyed to the Ti. Anti-bacterial behaviour was studied and evaluated.

Liu et al. [20] found and concluded that, copper alloying provides anti-bacterial properties to the alloy. They found that, the optimum Cu alloying for antibacterial behaviour should be about 5% (in weight). They also observed some Ti-Cu based intermetallic particles in the microstructure of the samples. They also state that, high Cu release was observed for alloys with high Cu.

Zhang et al. [21] investigated the production and anti-bacterial property of titanium-copper. The samples were manufactured by the traditional PM route. Electrochemical corrosion rate was experimentally studied and examined.

Zhang et al. [21] found and concluded that, Cu (copper) provides antibacterial properties to the alloy. Some Cu-based intermetallic precipitates were observed in the microstructure. They found and concluded that, this precipitates (fine clusters) provide corrosion resistance.

Robin et al. [22] investigated the corrosion behaviour (rate) and the impact of pH value and fluoride (F^-) concentration of synthetical body fluid environment. Titanium has been tested and evaluated in saliva solution with pH of 2-7 and different fluoride contents.

Robin et al. [22] found and concluded that, corrosion resistance was decerased due to high fluoride content and lowering pH level (acidity).

Kim et al. [23] studied manufacturing of a Ti-based alloy for implant (orthopaedic) applications. Surface treatment (chemical based) was carried out to the Ti (titanium) alloy samples. Chemical treatment was carried out by immersing the specimens into sodium hydroxyde. After this chemical process, the titanium-based samples were heated up to high temperatures to produce a titanate film on the surface.

Kim et al. [23] concluded and found that, this active surface leaded to a bone-like apatite film in SBF environment.

3. MATERIALS AND METHODS

3.1. SPECIMEN PRODUCTION

In this thesis, biomedical Ti-5 wt.% Cu alloy foam was manufactured by powder metallurgy based space holder-water leaching technique, which provides open (interconnected) porous structure. Titanium (Ti) and copper (Cu) powders were used as a raw material for manufacturing (Alfa Aesar, USA). Average particle diameters of the metal powders were 34 μm.

The metal 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. Ball to powder ratio was 10:1. Mechanical alloying of the Ti and Cu mixtures was carried out for 3-4 hours. Speed of rotation was 400 rpm.

Carbamide (urea) was used (about 70 vol. %) as a pore forming material (space holder agent). Average particle diameter of the urea powders was about 800 μm (710-1000 μm). Metal powders were mixed with 2.0 wt. % polyvinylalcohol (PVA) binder for green strength for handling purposes.

Mixtures were compacted at 180-210 MPa. The shape of the specimens was cylindrical. Diameter of the specimens was 12.0 mm. Specimens have a height of 17-20 mm. Compacted green samples were immersed into the water to remove the space holder (urea). Immersion period was 10-15 hours at room temperature in water.

Polyvinylalcohol (binder) was thermally removed from the green body at 390-400 °C. After the debinding step, the green compacts were sintered at 1150-1250 ºC for 60-70 minutes in a tube (vertical) furnace. As the titanium alloys are very active, the sintering was carried out under pure argon atmosphere to prevent surface oxidation of the samples. Figure 3.1 shows the schematic illustration of the main steps of the space holder-sintering method for highly porous metallic foam production.

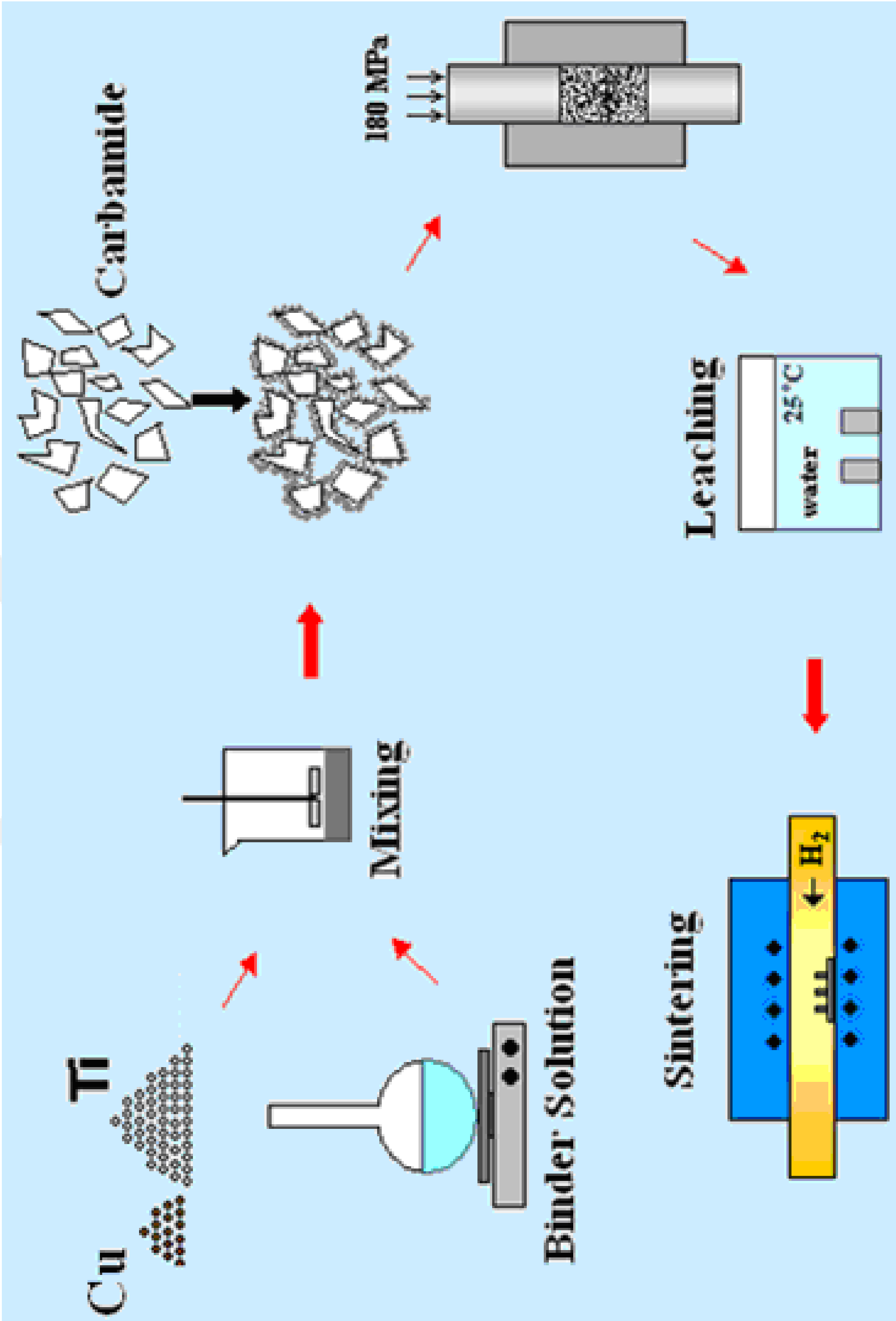


Figure 3.1: Space holder method.

(a)

(b)

Figure 3.2: a) Ball mill and b) hydraulic press

3.2. SURFACE TREATMENT

Alkali (sodium hydroxide) surface treatment was carried out by immersing the specimens into 10 M sodium hydroxyde solution. Soaking was carried out at about 55-60 °C for 24 hours. Then the samples were exposed to water. After that, the samples were heated up to 590-600 °C for 60-70 minutes. Heating was carried out under the open-air conditions. Then, immersion into SBF was carried out for active layer coating. Samples were removed from solution after 28 days.

Bone-bonding (bio-activity) properties of the metals can be investigated by observing the apatite precipitation on their surface in the SBF. Any apatite-like coating/precipitation on a material indicates the in vivo bio-activity of this material.

3.3. SIMULATED BODY FLUID PREPARATION

Simulated (artificial or synthetical) body fluid (SBF) solution produced in the light of the literature. Amounts of the chemical reagents were 8.00 g/L NaCl, 0.4 g/L KCl, 0.1 g/L $CaCl_2$, 0.1 g/L $MgCl_2$, 0.07 g/L Na_2HPO_4, 0.07 g/L Na_2SO_4, 0.70 g/L $NaHCO_3$, and buffer (tris) (Merck).

Artificial (synthetic) saliva was prepared according to the previous studies from the literature [4, 27-29]. Amounts of the chemicals were 0.4 g/L NaCl, 0.4 g/L KCl, 0.8 g/L $CaCl_2$, 0.7 g/L NaH_2PO_4, and 0.4 g/L carbamide. Solution with 0.25, 0.50, 0.75 and 1.00 wt. % F^- were produced (Merck). Effect of F (usually comes from toothpastes) content and pH was examined. Fluoride content of the solution was controlled by NaF addition. pH was controlled by lactic acid addition.

3.4. CHARACTERISATION

3.4.1. Mechanical Properties and Microstructure

FEG-SEM (field emission gun-scanning electron microscope) device was used in order to investigate the microstructure (pore morphology, pore size and microstructural phases) of the specimens (FEI Quanta FEG 450). Chemical composition was studied by using EDS analysis. Densities (% porosity) were determined by using gravimetric (geometrical) method. Young's (elastic) modulus was examined by performing compression tests (Devotrans, Turkey).

3.4.2. Corrosion Behaviour

Electrochemical DC corrosion tests were performed at room temperature conditions using a potentiostat (Interface 1000, Gamry). A three-electrode 1L glass cell was used during the measurements. Counter (auxiliary or cathode) electrode of the cell was high-density graphite. Reference electrode (RE) was a saturated calomel electrode. The sample was the working electrode (anode) of the cell. Data analysis was carried out by the Echem Analyst Software, Gamry.

Tafel curves (potantiodynamic polarization), open-circuit potential (OCP) and linear-polarization resistance (LPR) tests, were performed in order to evaluate electrochemical corrosion behaviour of the specimens. Open circuit potential tests were carried out for 2 hours. Tafel curves were plotted by polarizing the samples from -250 mV to +250 mV with respect to the OCP. In linear polarization resistance (LPR) tests the specimens were polarized from -20 mV to +20 mV (vs SCE).

In order to examine the localised corrosion (pitting) of the samples cyclic polarization test was performed. Polarization was performed from -500 mV (starting potential) to 0 mV (last potential). Figure 3.3 shows the shematic illustration of electrochemical corrosion measurement equipments and devices and the photograph of the set-up.

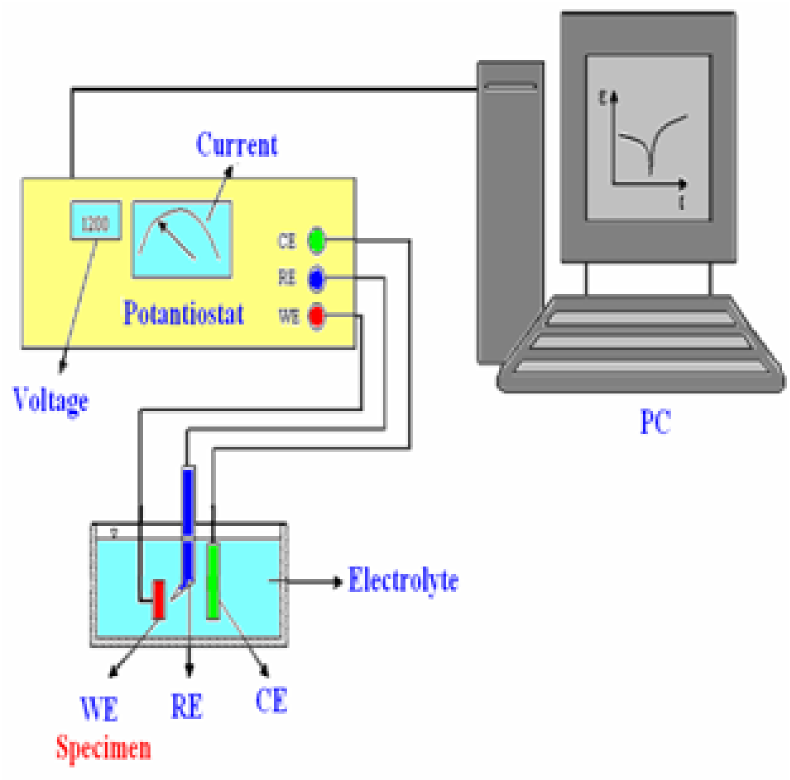


Figure 3.3: Electrochemical corrosion test system

3.4.3. Immersion Experiments

In order to study the weight change (loss) the alloys were immersed to the artificial saliva. Duration was 28 days. Ion release was examined by using ICP-MS (Thermo Scientific) device. Gravimetric (geometrical) method was used for the measurement of the weight change (loss).

3.4.4. Rapid Prototyping

Rapid prototyping (additive manufacturing or 3-dimensional printing) method was used in order to produce dental implant prototypes. Dental implant prototypes were produced by a 3-dimensional printing device (Formlabs). 3-dimensional printing (rapid prototyping) device was stereolithography based (SLA). Photopolymer liquid resin was used as raw material. Prototypes were produced layer by layer by selectively photopolimerization (curing) of the photopolymer resin using a a light source (usually UV). The UV light was scanned by mirror system to cure the liquid polymer resin into hardened plastic part. The SLA system was in upside-down (vertical) mode.

4. RESULTS

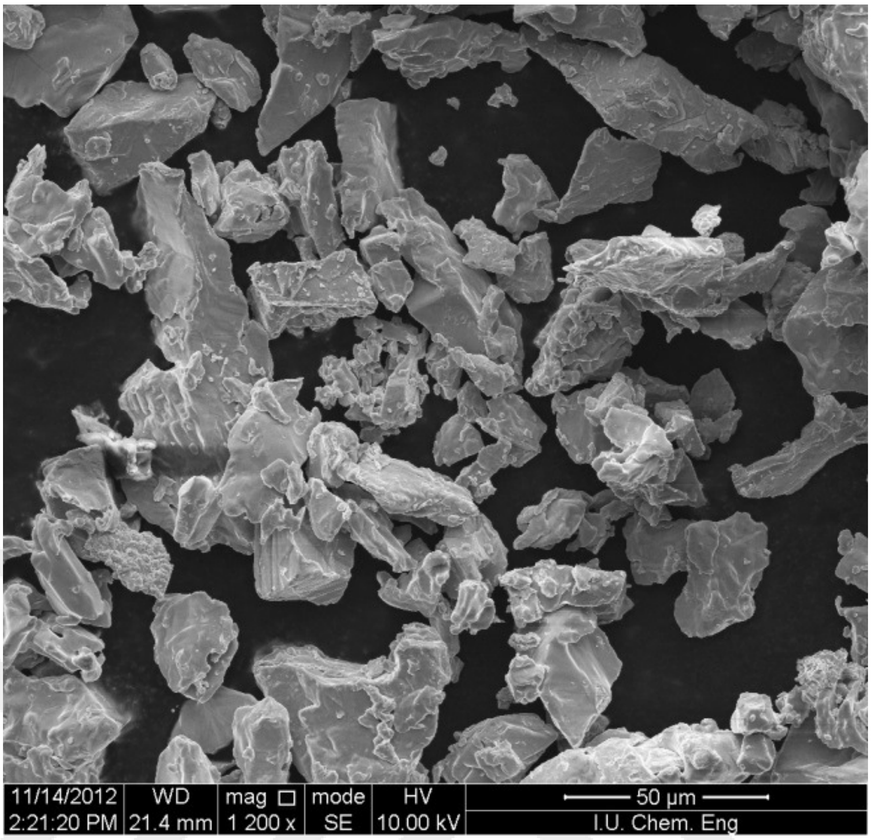
4.1. MICROSTRUCTURE AND MECHANICAL PROPERTIES

Figure 4.1 illustrates the SEM pictures of raw material powders and sintered specimen (a) titanium, (b) copper, (c) carbamide, and (d) photograph of the porous specimen after sintering. As seen from the SEM images, the pure Ti and pure Cu powders were irregular shaped.

Average pore (macro) diameter and morphology of the porous (about 70%) specimens depended on the first diameter and shape of the urea (pore forming agent) and the average diameters of this macro pores were about 450-500 µm. This value is proper for implant production and osseointegration [3-5]. Samples consisted of open (interconnected) porous structure. The surface and cell walls of samples consisted of a thin rutile-based oxide layer (TiO_2).

Sintering temperature of the alloy (compared to the commercial Ti alloys was lowered with Cu alloying. This was attributed and related to the formation of liquid (eutectic) phase provided by Cu-Ti reaction (according to phase diagram).

Young's modulus (elastic modulus) was of about 2-10 GPa. Increasing porosity (in %) was lowered the elastisity modulus, as expected. Elastic modulus of the porous samples was similar to cancellous (porous) bony tissue.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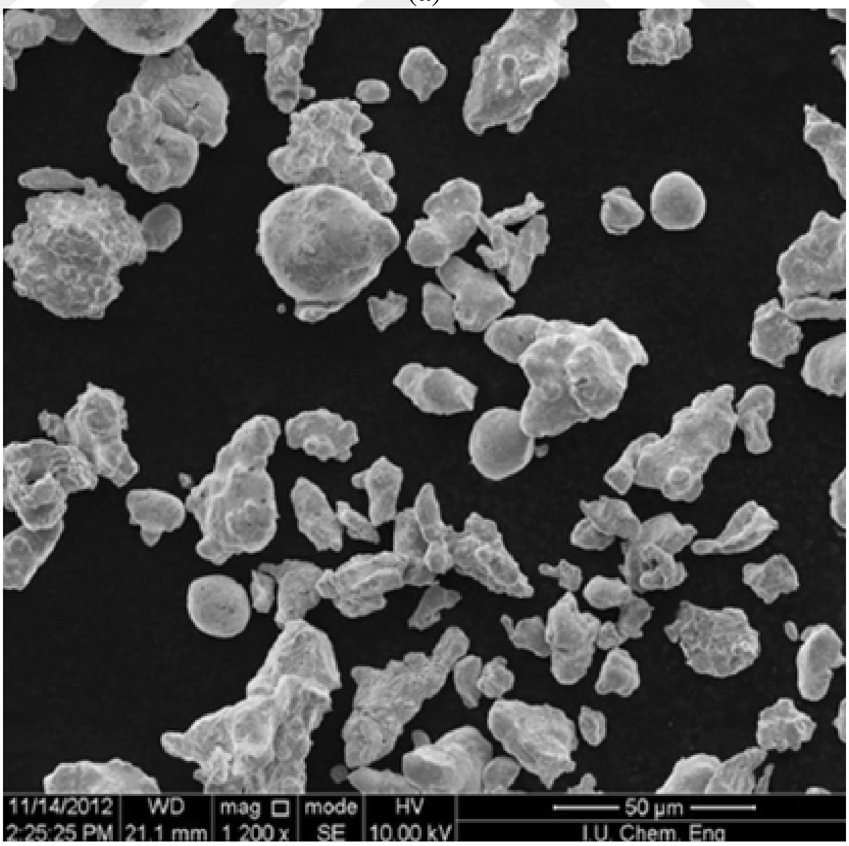
(a)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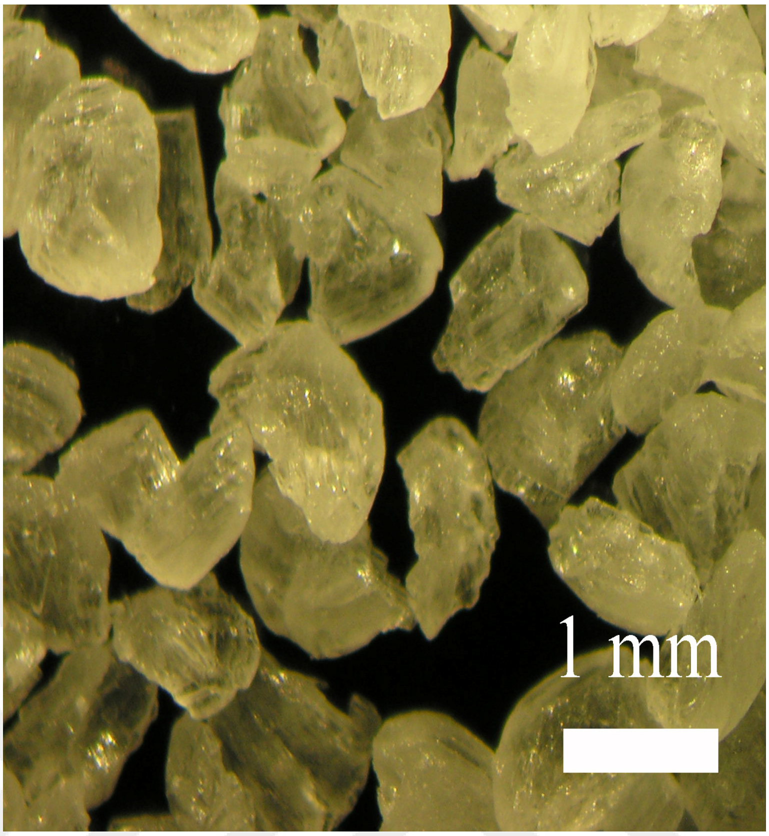
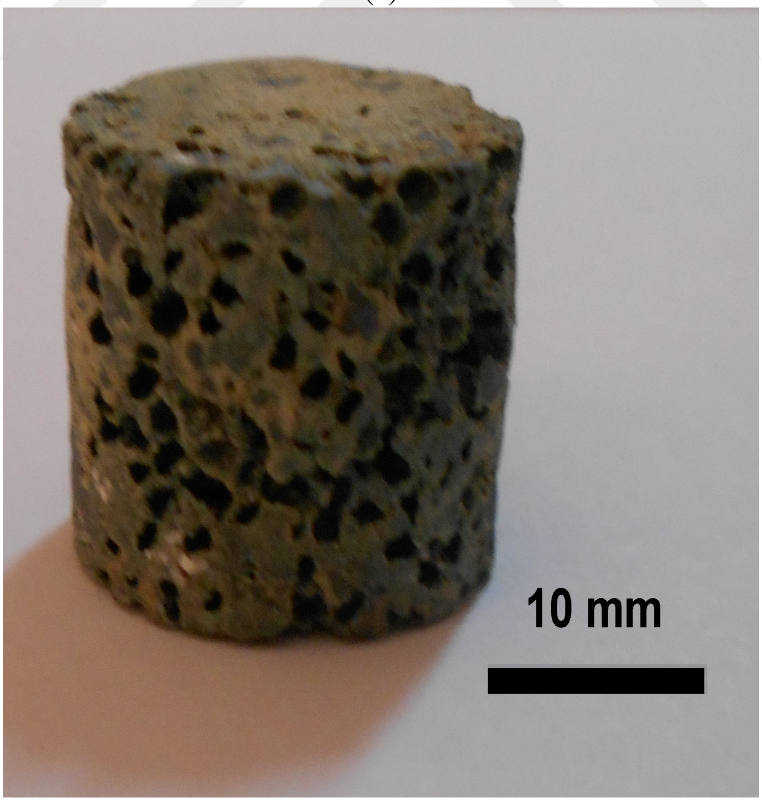


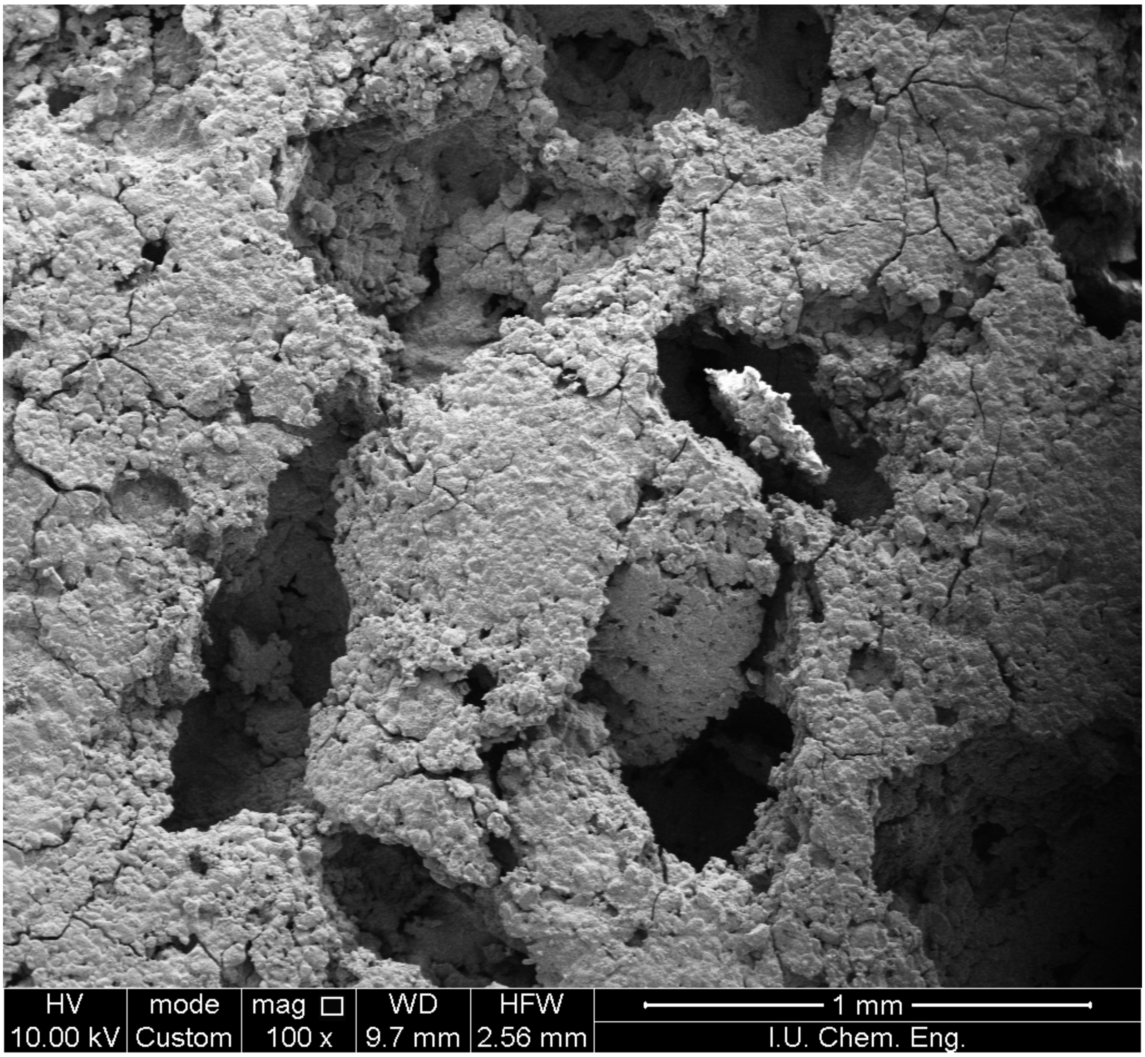
(c)



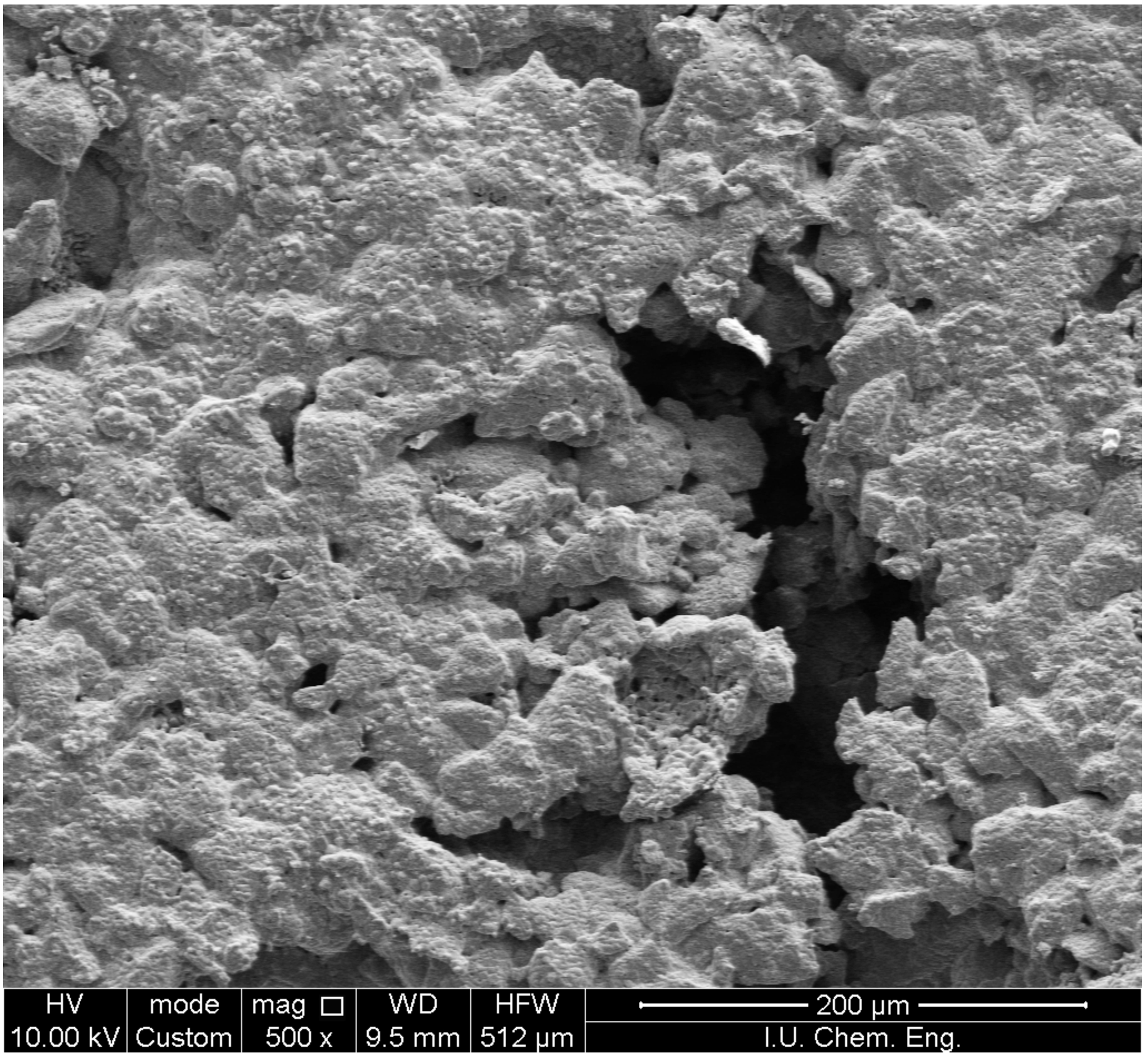
(d)

Figure 4.1: Images of a) Ti, b) Cu, c) carbamide powders and d) the specimen

Figure 4.2 shows the SEM images of a) the sintered sample (cracked surface) and b) cell-wall of the sintered specimen at higher (100X) magnification. As seen from the Figure 4.2, there is a suitable sintering. Micro-pores were mostly eliminated. Copper (Cu) addition was also enhaced the sinterability of samples (Ti-5%Cu).



(a)



(b)

Figure 4.2: SEM pictures of a) crack surface, b) cell-wall of the specimen

4.2. ELECTROCHEMICAL CORROSION STUDY

4.2.1. OCP

Open-circuit potential (OCP) ca be used to evaluate corrosion behaviour in electrochemical corrosion studies. Higher OCP indicates that the metal is nobler and in equilibrium in this solution (electrolyte). High F^- (which may comes from toothpaste) and low pH (high acidity) were decreased the OCP levels of the alloys, as expected. Titanium-copper alloys were nobler (shows high potential) than pure titanium. Corrosion performance of the specimens was better than the pure-titanium (green curve).

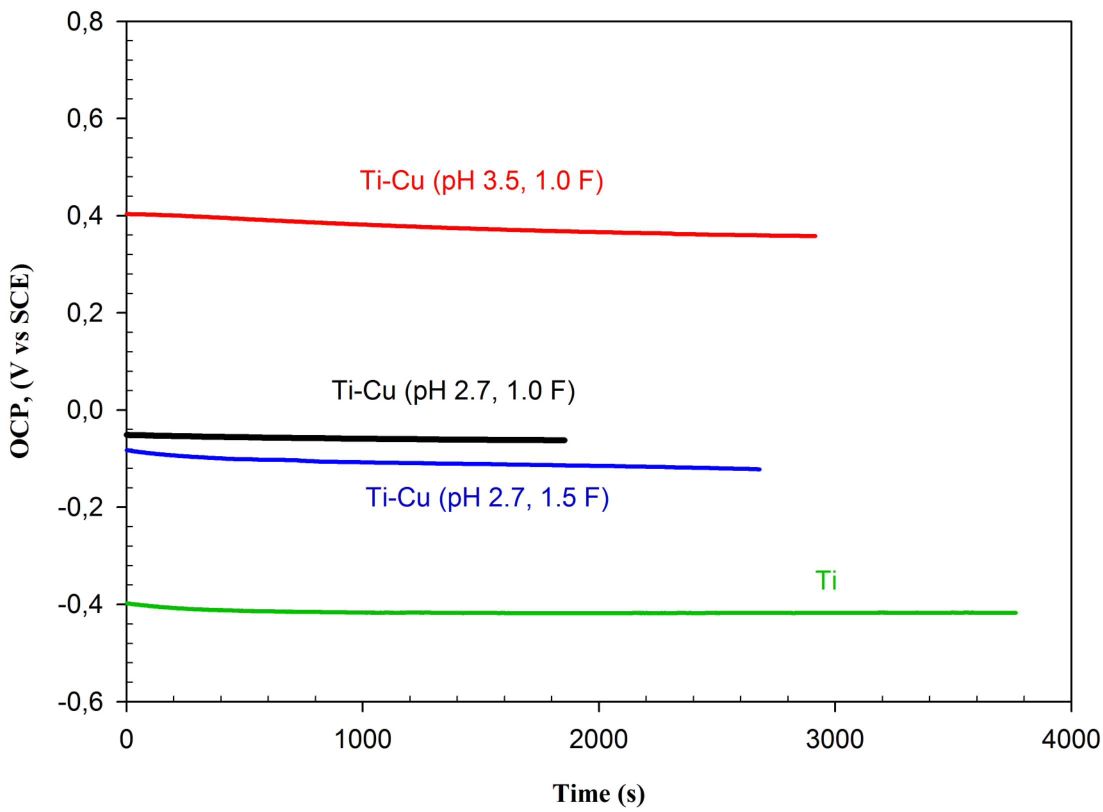


Figure 4.3: OCP curves of the specimens

4.2.2. Tafel Curves

In corrosion (electrochemical based) experimental studies, Tafel test, which is the most popular test, can be used to examine the corrosion rate and performance. High F^- (which may comes from toothpaste) and low pH (acidic conditions) were increased the corrosion rate. Corrosion performance of the samples was better than pure-titanium (green curve).

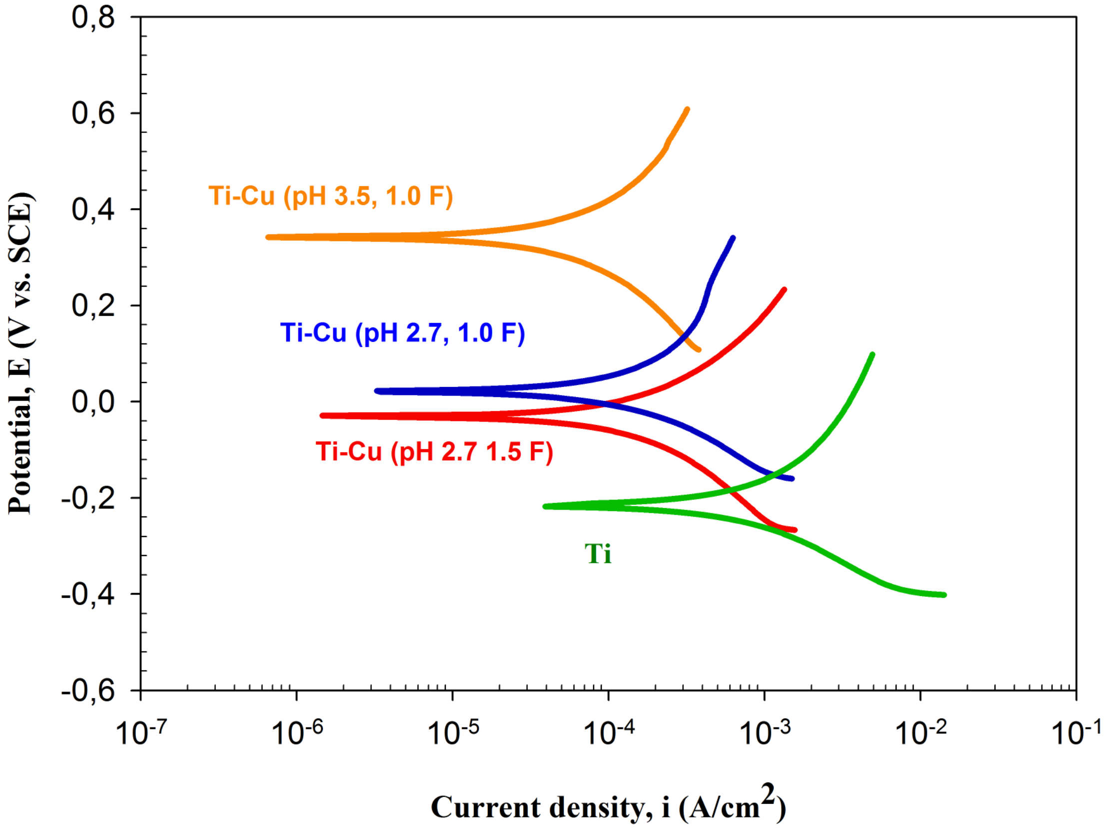


Figure 4.4: Tafel test results of the specimens

4.2.3. Cyclic Polarization

The cyclic polarization test was performed for examination and evaluation of pitting or crevice corrosion formation. Localised corrosion is very dangerous for titanium or cobalt based prosthesis. Hysteresis (closed loop) between forward (up) and reverse (down) polarizations indicates the pitting corrosion. Corrosion (localized) performance of the samples was better than pure-titanium (blue curve). Pure-titanium has a larger loop (pitting tendency).

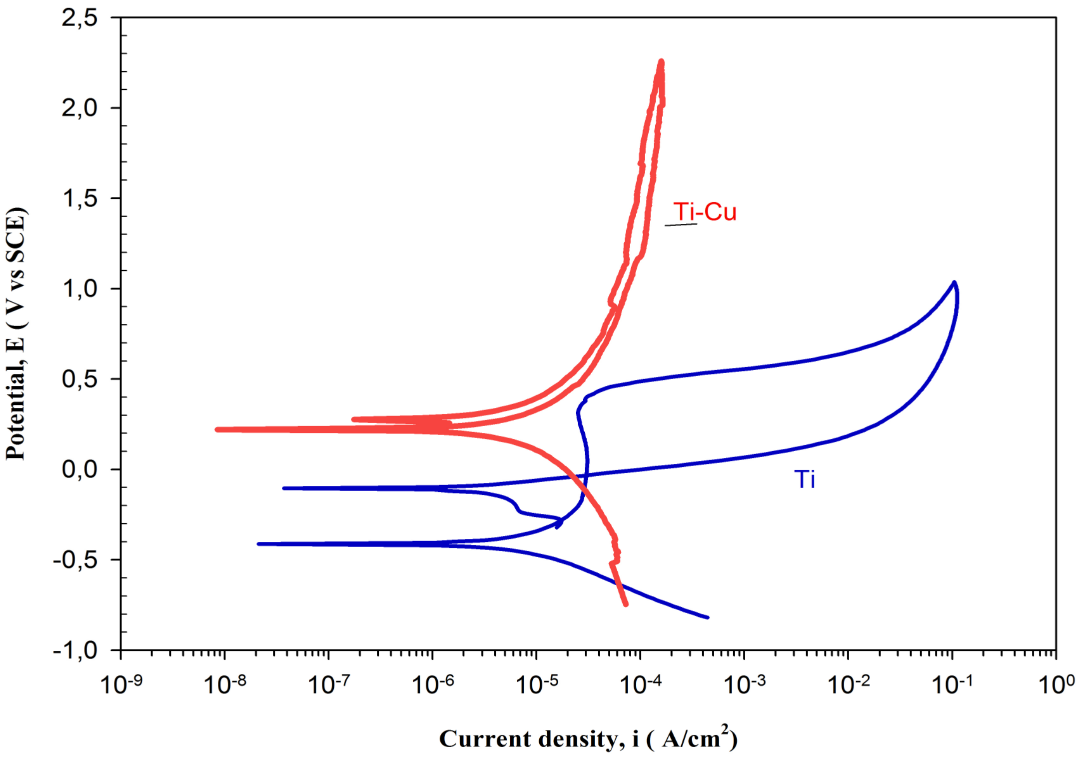


Figure 4.5: Cyclic polarization test results

4.3. STATIC IMMERSION TESTS

General impact of the duration time (up to 4 weeks) of the immersion in SBF solution on the weight change (loss) of the samples was tested by the gravimetrical method. Ti ion release was also measured by the ICP-MS. As seen from the Figure 4.6, Ti metal ion release and weight loss values were increased with duration, as expected. Weight loss was about 1 % for 4 weeks of immersion time. As the L50 (toxicity) value of the Ti metal is higher than the current Ti ion release level, the titanium-copper alloy sample is not cytotoxic (safe or non-toxic) for the living body.

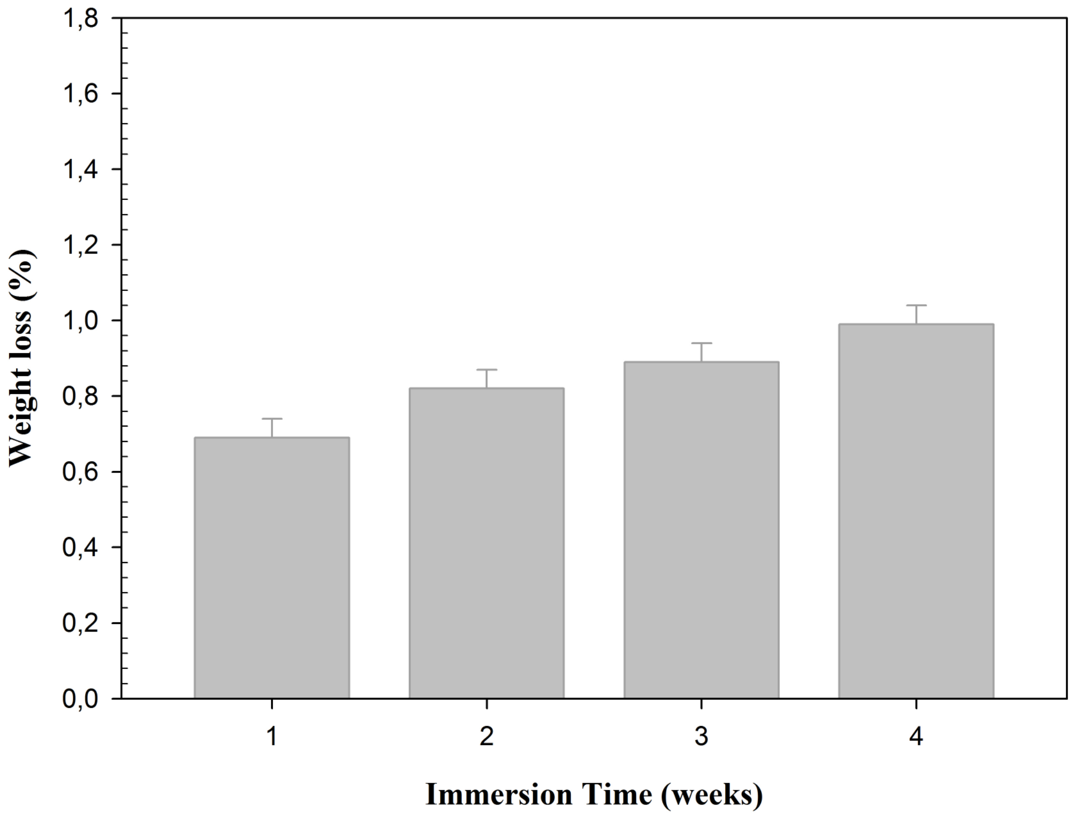


Figure 4.6: Weight loss-immersion time relation in the specimens

4.4. SURFACE TREATMENT

In general, formation of the apatite-based surface layer (similar to chemical composition of natural bone) is very important and necessary for osseointegration between the implant and the surrounding bony tissue. In general, TiO_2, Nb_2O_5, SiO_2, Ta_2O_5 and ZrO_2 can form bone-like apatite film on their surface.

In this thesis, it is clear that the bio-active bone-like coating was obtained after surface treatment and subsequent gel formation. Ti-OH groups are reason for bone-like apatite coating.

Surface activation by high temperature heat treatment produces an active surface layer (sodium-titanium based oxide) and this layer accelerates precipitation of apatite-based film.

Electrostatic interaction of the activated implant surface with Ca and P ions in the body fluids leads to biomineralization of the bone-like apatite.

Thus, activated surface (after sodium hydroxide treatment) chemically bonded to the calcium (Ca) ions, which comes from the solution, by using its negative charge.

EDS analysis was confirmed the bone-like apatite film (Ca and P rich phase) formation on the surface of the specimens. Precipitate phase was also contained O and C, which indicates that this phase is a carbonate containing hydroxyapatite.

4.5. RAPID PROTOTYPING

Rapid prototyping (additive manufacturing or 3-dimensional printing) method was used in order to produce dental implant (srew type) prototypes. Dental implant prototypes were produced by a 3-dimensional printing device. 3-dimensional printing (rapid prototyping) device was stereolithography type. Photopolymer resin was used as raw material. Figure 4.7 shows the root (or srew) type dental implant prototypes produced by 3-D printing method (stereolithography based).

Figure 4.7: Dental implant prototypes

5. DISCUSSION

Antibacterial highly porous Ti-5%Cu based alloy foams, with low elastic modulus, for orthopaedical or dental implant usage were manufactured by PM based space holder-sintering route. The alloys (Ti-5%Cu) were manufactured with a beta-titanium microstructure.

The water-leaching method for space holder (carbamide) removal is very attractive because water is cheap, non-toxic. There are no any environmental disadvantages in this process.

Sintering temperature of the alloy (compared to the commercial and traditional Ti alloys was decreased with copper alloying. This was attributed and related to the liquid (eutectic) phase formation provided by Cu-Ti reaction.

Machining (drilling, cutting or turning) properties of the alloys were increased by copper alloying.

Average diameter and morphology of the macro pores was similar to the size and shape of the pore forming agent (urea). The average size of these pores (macro) was about 550 µm. This value is proper for prosthesis.

The specimens consist of open (interconnected) macro-porous (cellular) structure. The surface of the samples consists of a thin rutile-based oxide layer (TiO_2).

Low pH and high F^- values of the solution lead to porous oxide formation with high corrosion rates. High F^- and low pH were increased the corrosion rate.

Alkali (sodium hydroxide) treatment developed bioactivity. It is found that, high F^{--} concentrations and low pH values were decreased the corrosion potential value of the alloy according to the corrosion tests.

High fluoride (F^-) ion$^-$ concentration and decreasing (low) pH values were lowered the electrochemical corrosion resistance value and enhanced the corrosion rate (current density) values of the alloy, as shown in the Tafel tests.

Corrosion performance of the samples was to be better than pure-titanium samples.

Elastisity modulus of the samples was suitable according to the compression tests. Elastisity of the samples was close to human bony tissue.

As a result, highly porous Ti-5%Cu based alloy foam with antibacterial behaviour can be used as a biomaterial in dental implant (root type or srew type) production.

6. CONCLUSIONS AND RECOMMENDATIONS

Antibacterial highly porous Ti-5 wt. % Cu based alloy foams, with low elastic modulus, for orthopaedical or dental implant (hard tissue) applications were manufactured by the powder metallurgy based space holder-sintering method. The alloys (Ti-5%Cu) were manufactured with a low elastic modulus beta-titanium microstructure. The powder metallurgy based space holder method was used because open (interconnected) porous structure can be produced, which is important for biomedical alloications. The water-leaching method for space holder (carbamide) removal is very attractive because water is cheap, non-toxic. There are no any environmental disadvantages in this process.

Sintering temperature of the alloy (compared to the traditional Ti alloys) was decreased with copper alloying. This was attributed to the liquid (eutectic) phase formation provided by Cu-Ti reaction. Machining (drilling, cutting or turning) properties of the Ti alloys were increased by copper alloying.

Mean diameter and morphology of the macro-pores was similar to the size and shape of the pore forming agent (urea). The average size of these pores (macro) was about 550 μm. This value is proper for biomedical implant (hard tissue) applications. The sintered specimens consist of open (interconnected) porous (cellular) microstructure. The surface of the specimens consists of a thin protective rutile-based oxide layer (TiO_2).

Alkali (sodium hydroxide) surface treatment provided bioactivity to the samples. It is found that, high F^{--} concentrations and low pH values were decreased the corrosion potential value of the alloy according to the electrochemical corrosion tests.

Low pH and high F^- values of the SBF solution lead to porous oxide formation at the surface with high electrochemical corrosion rates. High F^- and low pH values were increased the electrochemical corrosion rate of the alloys. High fluoride (F^-) ion$^-$ concentration and decreasing (low) pH values were lowered the electrochemical corrosion resistance value and increased the electrochemical corrosion rate (current density) values of the alloy, as shown in the Tafel tests. Electrochemical corrosion performance of the Ti alloy samples was to be better than pure-titanium (cp-Ti) samples in the SBF environment.

Elastisity modulus of the produced samples was suitable according to the compression tests. Elastisity of the samples was close to human bony tissue, which is good to prevent stress shielding effect between the implant and human bone.

As a result, highly porous Ti-5%Cu based alloy foam with open pores and antibacterial behaviour can be used as a biomedical material in dental implant (root type or srew type) manufacturing.

Future Recommendations:

In vivo (animal) tests should be carried out with collaboration of surgeons or with veterinary faculty (ethical permission must be taken).

Moore extensive mechanical characterization (tensile and compression tests) studies should be perform on the specimens.

Moore extensive electrochemical corrosion tests (at different test conditions) should be carried out in SBF environment.

Heat treatment (aging or precipitation hardening) should be carried out in order to improve the mechanical (yield and tensile strength) properties of the alloy.

Different alloying elements, such as Ta, Zr, Sn and Co, should be added in order to obtain different and superior properties.

Bio-mechanical analysis should be performed on the prototypes (dental, total-hip or total-knee implants).

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