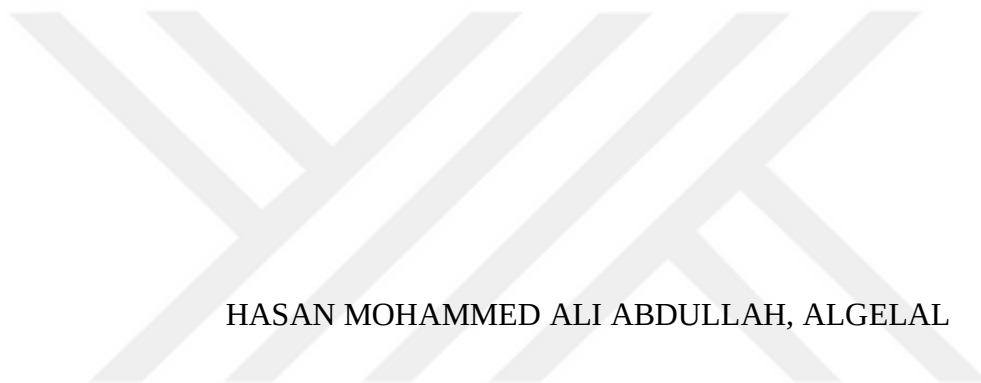


COATING OF TITANIUM ( $\text{TiAl}_6\text{V}_4$ ) ALLOY BY ELECTROSPUN POLY ( $\epsilon$ -  
CAPROLACTONE) (PCL)

H. ALGELAL

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES  
OF  
ATILIM UNIVERSITY



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COATING OF TITANIUM ( $\text{TiAl}_6\text{V}_4$ ) ALLOY BY ELECTROSPUN POLY ( $\epsilon$ -  
CAPROLACTONE) (PCL)

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BY

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Approval of the Graduate School of Natural and Applied Sciences, Atılım University.

---

Prof. Dr. Ali KARA

I certify that this thesis satisfies all the requirements as a thesis for the degree of **Master of Science in Atılım University**.

---

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This is to certify that we have read the thesis “COATING OF TITANIUM ( $\text{TiAl}_6\text{V}_4$ ) ALLOY BY ELECTROSPUN POLY ( $\epsilon$ -CAPROLACTONE) (PCL) “submitted by “HASAN MOHAMMED ALI ABDULLAH ALGELAL” and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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## ABSTRACT

### COATING OF TITANIUM (TiAl<sub>6</sub>V<sub>4</sub>) ALLOY BY ELECTROSPUN POLY (ε-CAPROLACTONE) (PCL)

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May 2020, 88 pages

The goal of this study is to fabricate a biomaterial implant composed of Titanium alloy TiAl<sub>6</sub>V<sub>4</sub> coated with poly (ε-caprolactone) (PCL) using electrospinning mechanism. Moreover, the effect of surface-treatment for the titanium alloy on the coating is also studied, whereas coating thickness is determined using a micrometer. Characterization of specimens' morphology is executed using Scanning Electron Microscopy (SEM). The wettability of the surface is performed using the contact angle (CA) and the optical micrographs of the Titanium alloy microstructure are carried out using optical microscopy. The detection of composition and elements in the substrates Energy dispersive spectroscopy (EDS) is also performed. For more quantitative analysis of surface morphology and to evaluate the roughness at the surface of implants, AFM and roughness measurements are used. To determine the adhesion of the PCL to the TiAl<sub>6</sub>V<sub>4</sub>, adhesion test is conducted. EDS shows that the obtained specimens are free from any other elements after being treated. The optical microscopy is used to observe the changes in the microstructure through optical micrographs, after pre-treating the alloys. Through SEM, the change in the surface morphology after grinding, polishing, and etching is also recorded. The roughness measurements indicate the mean values of roughness quantitatively, which are gradients from 0.005 micron in 3 micron polishing TiAl<sub>6</sub>V<sub>4</sub> sample to 0.56 micron in the 120 grinding TiAl<sub>6</sub>V<sub>4</sub> sample.

After measurement, the thickness of the coating is determined as 0.01 mm. The contact angle measurement shows that the best sample in hydrophilicity is the etched alloy after coating it with PCL, which is 58.63 °. The adhesion test also proves that the best two samples for coating adhesion are the etched and 1200 grinding: more than 99% of the coating do not stick out of the coating after the removal of the tape.

Keywords: Electrospinning, TiAl<sub>6</sub>V<sub>4</sub> alloy, Poly (ε-caprolactone)

## ÖZ

### COATING OF TITANIUM (TiAl<sub>6</sub>V<sub>4</sub>) ALLOY BY ELECTROSPUN POLY (ε-CAPROLACTONE) (PCL)

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Çalışmanın amacı, elektroğirme mekanizması kullanılarak poli (ε-kaprolakton) (PCL) ile kaplanmış titanyum alaşımı TiAl<sub>6</sub>V<sub>4</sub>'ten oluşan bir biyomateryal implant üretmektir. Ayrıca, titanyum alaşımı için yüzey işleminin kaplama üzerindeki etkisi de incelenirken, kaplama kalınlığı bir mikrometre kullanılarak belirlenmiştir. Örneklerin morfolojik karakterizasyonu Taramalı Elektron Mikroskopisi (SEM) kullanılarak gerçekleştirilmiştir. Yüzey ıslanabilirliği, temas açısı (CA) kullanılarak tayin edilmiştir ve titanyum alaşımlı mikroyapının optik mikrografları, optik mikroskopi kullanılarak elde edilmiştir. Substratlarda kompozisyon ve elementlerin tayini Enerji dağılımlı spektroskopisi (EDS) ile yapılmıştır. Yüzey morfolojisinin daha detaylı nicel analizi ve implantların yüzeyindeki pürüzlülüğü değerlendirmek için AFM ve pürüzlülük ölçümleri kullanılmıştır. PCL'nin TiAl<sub>6</sub>V<sub>4</sub>'e yapışmasını belirlemek için yapışma testi yapılmıştır. EDS ile sonuçlarına göre elde edilen örneklerin işlendikten sonra diğer elementlerden arınmış olduğu görülmüştür. Optik mikroskopi, alaşımların ön işleminden geçirilmesinden sonra optik mikrograflar vasıtasıyla mikro yapıdaki değişiklikleri gözlemlemek için kullanılmıştır. SEM ile taşlama, parlatma ve dağlamadan sonra yüzey morfolojisindeki değişim de kaydedilmiştir. Pürüzlülük ölçümleri, 3 mikron parlatma TiAl<sub>6</sub>V<sub>4</sub> numunesinde 0.005 mikrondan, 120 öğütme TiAl<sub>6</sub>V<sub>4</sub> numunesinde 0.56 mikrona kadar olan ortalama pürüzlülük değerlerini kantitatif olarak göstermiştir. Ölçümlerden sonra, kaplamanın kalınlığı 0.01 mm olarak belirlenmiştir. Temas açısı ölçümleri sonucunda en iyi hidrofilikliğe sahip numunenin 58.63° temas açısı ile PCL ile kaplanmış kazınmış alaşım olduğu görüşmüştür. Ayrıca yapışma testi, kaplama yapışması için en iyi iki adayın kazınmış ve 1200 öğütme numuneleri olduğunu göstermiştir: kaplamanın %99'undan fazlası, bandın çıkarılmasından sonra kaplamadan çıkmaz.

Anahtar kelimeler: Electrospinning, TiAl<sub>6</sub>V<sub>4</sub> alloy, Poly (ε-caprolactone)



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## TABLE OF CONTENTS

|                                                                                 |     |
|---------------------------------------------------------------------------------|-----|
| ABSTRACT .....                                                                  | iii |
| ÖZ .....                                                                        | iv  |
| ACKNOWLEDGMENTS.....                                                            | vi  |
| TABLE OF CONTENTS.....                                                          | vii |
| LIST OF TABLES.....                                                             | x   |
| LIST OF FIGURES .....                                                           | xii |
| 1. INTRODUCTION .....                                                           | 1   |
| 2. LITERATURE SURVEY .....                                                      | 5   |
| 2.1 Implants .....                                                              | 5   |
| 2.2 Titanium.....                                                               | 6   |
| 2.2.1 TiAl <sub>6</sub> V <sub>4</sub> .....                                    | 11  |
| 2.2.1.1 Responsible properties for the Biocompatibility of Titanium Alloys..... | 12  |
| 2.2.1.1.1 Mechanical Properties.....                                            | 13  |
| 2.2.1.1.2 Biological properties.....                                            | 14  |
| 2.2.1.2 Biomedical Applications of TiAl <sub>6</sub> V <sub>4</sub> .....       | 14  |
| 2.2.1.2.1 Hard Tissue Replacements .....                                        | 15  |
| 2.2.1.2.2 Applications of Titanium in Cardiac and Cardiovascular.....           | 16  |
| 2.2.1.2.3 Other Applications.....                                               | 18  |
| 2.2.1.3 Reasons for Coating or Surface Modification .....                       | 18  |
| 2.2.1.3.1 Surface modification techniques.....                                  | 19  |
| 2.2.1.3.2 Coating materials .....                                               | 19  |
| 2.3 Poly (ε-caprolactone) (PCL).....                                            | 21  |
| 2.3.1 PCL properties.....                                                       | 22  |
| 2.3.2 Biomedical Applications .....                                             | 26  |
| 2. 4 Electrospinning.....                                                       | 26  |
| 2.4.1 Parameters Affecting the Process .....                                    | 28  |
| 2.4.1 Process Parameters.....                                                   | 28  |
| 2.4.1.1 Applied Voltage.....                                                    | 28  |
| 2.4.1.2 Flow Rate .....                                                         | 28  |

|                                                                      |    |
|----------------------------------------------------------------------|----|
| 2.4.1.3 Needle-Collector Distance .....                              | 29 |
| 2.4.2 Solution Parameters .....                                      | 29 |
| 2.4.2.1 The Concentration .....                                      | 29 |
| 2.4.2.2 Viscosity.....                                               | 30 |
| 2.4.2.3 Polymer Molecular Weight .....                               | 30 |
| 2.4.2.4 Solution Conductivity .....                                  | 30 |
| 2.4.2.5 Role of Solvent .....                                        | 31 |
| 2.4.2.6 The Environmental Parameters.....                            | 31 |
| 3. EXPERIMENTAL STUDY .....                                          | 32 |
| 3.1. Materials .....                                                 | 32 |
| 3.2. Pretreatment Part .....                                         | 32 |
| 3.2.1 Cutting Stage .....                                            | 32 |
| 3.2.2 Grinding Stage .....                                           | 33 |
| 3.2.3 Polishing Stage .....                                          | 33 |
| 3.2.4 Etching Stage .....                                            | 33 |
| 3.3 Coating with PCL polymer .....                                   | 36 |
| 3.3.1 Preparation of the Solution.....                               | 36 |
| 3.3.2 Operation of Electrospinning.....                              | 36 |
| 3.4 Characterisations .....                                          | 36 |
| 3.4.1 Surface Analysis with Scanning Electron Microscopy (SEM).....  | 36 |
| 3.4.2 Optical Microscopy.....                                        | 36 |
| 3.4.3 Energy Dispersive Spectroscopy (EDS).....                      | 37 |
| 3.4.4 Roughness Measurement (RA).....                                | 37 |
| 3.4.5 AFM Atomic Force Microscopy Analysis .....                     | 37 |
| 3.4.6 Thickness Measurements.....                                    | 37 |
| 3.4.7 Contact Angle Measurements.....                                | 37 |
| 3.4.8 Adhesion Test .....                                            | 38 |
| 3.4.9 Immersion Test .....                                           | 39 |
| 4. RESULTS AND DISCUSSION.....                                       | 41 |
| 4.1 Characterisations of the Titanium Alloy before Coating.....      | 41 |
| 4.1.1 Scanning Electron Microscope SEM Examinations. ....            | 41 |
| 4.1.2 Energy Dispersive Spectrometry EDS Test.....                   | 41 |
| 4.1.3 Optical Microscope .....                                       | 52 |
| 4.1.4 Atomic Force Microscopy (AFM) and Roughness Measurements ..... | 54 |
| 4.2 Characterizations the Samples after Coating with PCL .....       | 66 |

|                                           |    |
|-------------------------------------------|----|
| 4.2.1 Thickness Measurements .....        | 66 |
| 4.2.2 CA-Contact Angle Measurements ..... | 69 |
| 4.2.3 Adhesion Test .....                 | 73 |
| 5. CONCLUSIONS .....                      | 78 |
| REFERENCES .....                          | 80 |



## LIST OF TABLES

|                                                                                                                                                                                          |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Table 2. 1 Human tensile properties of cortical bones [3] .....                                                                                                                          | 8  |
| Table 2.2 Compressive properties of cortical bones for the human [3] .....                                                                                                               | 9  |
| Table 2. 3 Compressive properties of cancellous bones for the human [3] .....                                                                                                            | 10 |
| Table 2.4. Properties of 1 to 5 grades [23] .....                                                                                                                                        | 11 |
| Table 2.5 Mechanical properties of titanium and its alloys [3] .....                                                                                                                     | 13 |
| Table 2.6. Measures of hardness for titanium and its alloys [3] .....                                                                                                                    | 14 |
| Table 2. 7. Methods of surface modification methods for titanium and its alloys [3] .....                                                                                                | 20 |
| Table 2. 8. PCL physical properties at room conditions [41] .....                                                                                                                        | 22 |
| Table 2. 9. The general properties, mechanical properties, thermal properties, processing properties, electrical properties and absorption permeability of PCL [according to ASTM] ..... | 23 |
| Table 3. 1 The standard composition of $TiAl_6V_4$ .....                                                                                                                                 | 32 |
| Table 3. 2 The pretreatment processes performed before coating the specimens .....                                                                                                       | 34 |
| Table 3. 3 A diagram showing the practical steps of the thesis .....                                                                                                                     | 35 |
| Table 3. 4 The Situations of wetting angle [69] .....                                                                                                                                    | 38 |
| Table 3. 5 Classification of the adhesion levels [ASTM D3359] .....                                                                                                                      | 39 |
| Table 3. 6 The ions of simulated body fluid .....                                                                                                                                        | 39 |
| Table 3. 7 Amounts of reagents that have been used for preparing SBF [72] .....                                                                                                          | 40 |
| Table 3. 8 A diagram showing the immersion test steps. ....                                                                                                                              | 40 |
| Table 4. 1 Percentage of elements in sample grinded with P120 grid paper .....                                                                                                           | 43 |
| Table 4. 2 Percentage of elements in sample grinded with P320 grid paper .....                                                                                                           | 44 |
| Table 4. 3 Percentage of elements in sample grinded with P500 grid paper .....                                                                                                           | 45 |
| Table 4. 4 Percentage of elements in sample grinded with P800 grid paper .....                                                                                                           | 46 |
| Table 4. 5 Percentage of elements in sample grinded with P1200 grid paper .....                                                                                                          | 47 |
| Table 4. 6 EDS analysis of sample polished with 9 $\mu$ m diamond paste. ....                                                                                                            | 48 |
| Table 4. 7 EDS analysis of sample polished with 3 $\mu$ m diamond paste. ....                                                                                                            | 49 |
| Table 4. 8 EDS analysis of sample polished with 1 $\mu$ m diamond paste. ....                                                                                                            | 50 |
| Table 4. 9 Percentage of elements in sample polished with OP-S .....                                                                                                                     | 51 |

|                                                                                                                             |    |
|-----------------------------------------------------------------------------------------------------------------------------|----|
| Table 4. 10 Percentage of elements in sample etched with 100ml distilled water, 80 ml HNO <sub>3</sub> , and 10 ml HF ..... | 52 |
| Table 4. 11 the Surfaces roughness of the samples .....                                                                     | 55 |
| Table 4. 12 The thickness of the samples before and after the coating .....                                                 | 68 |
| Table 4. 13 The amount of average contact angle for the samples .....                                                       | 70 |
| Table 4. 14 A Comparison between the surface roughness and contact angle .....                                              | 71 |
| Table 4. 15 The adhesion test results.....                                                                                  | 74 |



## LIST OF FIGURES

|                                                                                                                                                                             |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2. 1 Pure metals and their biocompatibility [14] .....                                                                                                               | 6  |
| Figure 2. 2 Pure titanium covered by oxide film [3] .....                                                                                                                   | 8  |
| Figure 2.3 Places of hard tissue in the body[3] .....                                                                                                                       | 15 |
| Figure 2.4: Artificial hip joint.[3] .....                                                                                                                                  | 16 |
| Figure 2.5. The artificial heart valve.[3] .....                                                                                                                            | 17 |
| Figure 2. 6. The artificial vascular stents.[3].....                                                                                                                        | 17 |
| Figure 2. 7 Bone plate and Bone screw[32] .....                                                                                                                             | 18 |
| Figure 2. 8 electrospinning device parts [46] .....                                                                                                                         | 27 |
| Figure 3. 1 Example of how contrast can arise [68] .....                                                                                                                    | 34 |
| Figure 4. 1 SEM micrographs of TiAl <sub>6</sub> V <sub>4</sub> samples .....                                                                                               | 42 |
| Figure 4. 2 EDS analysis of sample grinded with P120 grid paper .....                                                                                                       | 43 |
| Figure 4. 3 EDS analysis of sample grinded with P320 grid paper .....                                                                                                       | 44 |
| Figure 4. 4 EDS analysis of sample grinded with P500 grid paper .....                                                                                                       | 45 |
| Figure 4. 5 EDS analysis of sample grinded with P800 grid paper .....                                                                                                       | 46 |
| Figure 4. 6 EDS analysis of sample grinded with P1200 grid paper .....                                                                                                      | 47 |
| Figure 4. 7 EDS analysis of sample polished with 9 $\mu$ m diamond paste. ....                                                                                              | 48 |
| Figure 4. 8 EDS analysis of sample polished with 3 $\mu$ m diamond paste. ....                                                                                              | 49 |
| Figure 4. 9 EDS analysis of sample polished with 1 $\mu$ m diamond paste. ....                                                                                              | 50 |
| Figure 4. 10 EDS analysis of sample polished with OP-S solution.....                                                                                                        | 51 |
| Figure 4. 11 EDS analysis of sample etched with 100ml distilled water, 80 ml HNO <sub>3</sub> ,<br>and 10 ml solution.....                                                  | 52 |
| Figure 4. 12 optical micrographs of the TiAl <sub>6</sub> V <sub>4</sub> samples .....                                                                                      | 53 |
| Figure 4. 13 Profile measurement of the sample grinded with P120 grid paper, showing<br>the optical micrograph of the position of measurement and the roughness profile.... | 56 |
| Figure 4. 14 Profile measurement of the sample grinded with P320 grid paper, showing<br>the optical micrograph of the position of measurement and the roughness profile.... | 57 |
| Figure 4. 15 Profile measurement of the sample grinded with P500 grid paper, showing<br>the optical micrograph of the position of measurement and the roughness profile.... | 58 |

|                                                                                                                                                                                                                                 |    |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4. 16 Profile measurement of the sample grinded with P800 grid paper, showing the optical micrograph of the position of measurement and the roughness profile....                                                        | 59 |
| Figure 4. 17 Profile measurement of the sample grinded with P1200 grid paper, showing the optical micrograph of the position of measurement and the roughness profile. ....                                                     | 60 |
| Figure 4. 18 Profile measurement of the sample polished with 9 $\mu$ m diamond paste, showing the optical micrograph of the position of measurement and the roughness profile. ....                                             | 61 |
| Figure 4. 19 Profile measurement of the sample polished with 3 $\mu$ m diamond paste, showing the optical micrograph of the position of measurement and the roughness profile. ....                                             | 62 |
| Figure 4. 20 Profile measurement of the sample polished with 1 $\mu$ m diamond paste, showing the optical micrograph of the position of measurement and the roughness profile. ....                                             | 63 |
| Figure 4. 21 Profile measurement of the sample polished with OP-S solution, showing the optical micrograph of the position of measurement and the roughness profile....                                                         | 64 |
| Figure 4. 22 Profile measurement of the sample etched with 100ml distilled water, 80 ml HNO <sub>3</sub> , and 10 ml HF solution, showing the optical micrograph of the position of measurement and the roughness profile. .... | 65 |
| Figure 4. 23 AFM images of titanium alloy after treatment .....                                                                                                                                                                 | 67 |
| Figure 4. 24 the differences in the contact angle between the samples .....                                                                                                                                                     | 70 |
| Figure 4. 25 The shape of the water droplet on the specimens .....                                                                                                                                                              | 72 |
| Figure 4. 26 A diagram explain the relation between surface roughness of the alloy and the contact angle.....                                                                                                                   | 73 |
| Figure 4. 27 Comparison of adhesion strength for the samples of PCL/ TiAl <sub>6</sub> V <sub>4</sub> .....                                                                                                                     | 75 |
| Figure 4. 28 (A) Acceptable roughness (B) Lowe micro-roughness (C) large micro-roughness.....                                                                                                                                   | 76 |
| Figure 4. 29 The samples after steak of the tape .....                                                                                                                                                                          | 77 |

## **CHAPTER 1**

### **1. INTRODUCTION**

Implant is a tool placed under the human skin, subdermal or transdermal, which helps to relieve the body's bones and joints. They are utilised in the treatment of bone fractures, scoliosis, osteoarthritis, chronic pain, and spinal stenosis. Screws, pins, plates, and rods are used for fractured bones during the healing process. Implants should initiate the desired host response under ideal conditions to avoid any unwanted reaction from nearby or distant tissues. The reaction between the implant and the tissue around the implant can lead to complexity.

For the rebuilding of failed hard tissue, metallic implants are extremely significant. Metallic biomaterials cannot be substituted by polymers or ceramics at present, because toughness and mechanical strength are the most significant safety requirements for a biomaterial under conditions of load bearing. Metallic biomaterials, such as Co-Cr alloys, stainless steels, pure titanium and its alloys are widely utilised for their superior mechanical properties[1].

Fabricating implants by Ti-alloy is a promising technique for improving the osteoinduction of implants[2]. Titanium, once known as a rare metal, is considered as one of the most significant metals in industry these days. Titanium and titanium alloys are commonly utilised in biomedical equipments and components, essentially as hard tissue substitutes as well as in cardiovascular and cardiac applications [3].

Interest in the manufacture of titanium alloys is because of the characteristics which titanium has that include distinguished strength to weight ratio, machinability, formability, low modulus, good fatigue strength, excellent corrosion resistance, and biocompatibility[4]. Titanium and titanium alloys are relatively good corrosion resistance and are inert due to thin surface oxide. However, titanium and its alloys

cannot accommodate all clinical requests , hence there is a need for surface modification[3].

The most desired metallic material for biomedical implementation is TiAl<sub>6</sub>V<sub>4</sub>. However, the alloy has a potential toxic effect due to the release of aluminum and vanadium[5] and is the most commonly utilised among titanium alloys[6] Because of its excellent properties, titanium and its alloys are widely used in artificial bones, dental implants and joints as hard tissue[3].

PCL is a synthetic polymer extracted from crude oil's chemical synthesis. PCL is distinguished by special properties such as biodegradability, a transition temperature of  $-60^{\circ}\text{C}$ , and low melting point  $60^{\circ}\text{C}$ , neutral charge, the capability to degrade in bacteria-media, and hydrophobicity [7].PCL has been electrospun for biomedical and food applications because of its good biocompatibility with very low toxicity.[8] PCL utilisations have been restricted because of many disadvantages, like poor mechanical properties, low degradation rate and poor hydrophilicity. PCL is regularly mixed with nanoparticles or some polymers to overcome these disadvantages [9]. Nevertheless, direct polymer electrospun nanofibers on the metallic surfaces cause adhesion problems at the metallic interface and polymer.[10] This poor adhesion of the metallic polymer may cause problems in implants in the long term. One of the solutions to increase the adhesion of polymeric nanofibers is to change the roughness of the metal surface or treat the surface with chemicals to etch the surface and this will be carried out in this study.

Different techniques utilised for fabrication scaffolds of polymer nanofibers like self-assembling peptide reactions, Vapor-phase polymerization, phase separation, Extraction, Drawing, Tinplating, Bacterial cellulose, and electrospinning will be demonstrated[11].

In the literature, there are different methods to manufacture fibrous structures for scaffold-tissue engineering; but the established techniques are three - self-assembly, phase separation and electrospinning, which is the most common [12].

In the same context, electrospinning is the most widely and multilaterally studied method for fabrication scaffolds of polymer nanofibers[11].

Electrospinning is an electric charge driven method fabricating polymer nanofibers from a melt or liquid polymer solution fed through a capillary tube, into an area of high electric voltage [11]. Electrospinning is a low-cost process used to form melts with high surface area to volume ratio.

The electric field is generated by connecting a source of high voltage power to the capillary tip in the kilovolt range. As the electric charge overcomes the liquid surface tension a Taylor cone is formed by the cooling of melts or evaporation of some solvent to form nanofibers on the target.

Many processing parameters can regulate microstructure and nanofiber sizes like the voltage, solution conductivity, orifice size, solution viscosity, feed rate and the distance from capillary to collector.

Electrospinning has seen an enormous increase in commercial attention and research due to its cost viability and ease of use., the high control level of fiber diameter, wide materials selection. Arrangement and microstructure due to the process set up is simple.

Electrospinning has positive advantages such as wide versatility allowing control over microstructure, arrangement, and fiber diameter; also, the wide range of materials selection in addition to its cost-effectiveness and easiness in setting up. However, it has some disadvantages like microstructure arrangement or 2-Dimensional pore, poor cell infiltration into the core of the scaffolds, and toxic solvents are often used[11].

The surface of implants from a medium convenient for adhesion of bacteria and reproduction finally leads to a biofilm that totally prevents access to the drug action resistant and immune system. The weak interaction between implant and tissue causes the reduction in fixing time of the bone.

Titanium causes inflammatory responses and allergic reactions in vivo because of the metallic debris for the surface particle resulting from wear.  $\text{TiAl}_6\text{V}_4$  releasing ions of vanadium and aluminum in the soft and hard tissues cause inflammation, biopsies, cytotoxicity and adverse tissue reactions for patients [13]. Although titanium and titanium alloys are inert materials, the human body encapsulates the implant by fibrous

tissue after implementation. Therefore, that titanium implant needs to be coated by a biocompatible and bioactive layer.[3]

The aim of this study is to increase the osteointegration with the bone to prevent the fracture, implant loosening and unnecessary costs. The overall objective is to reduce patient's pain by coating the titanium surface with a bioactive material to prevent inflammatory responses, cytotoxicity, biopsies, adverse tissue reactions and allergic reactions in vivo.

Also coating a nanofiber polymer provides a big surface-area-to-volume ratio by utilising electrospinning techniques and this provides space for bone attachment and subsequently increases cellular proliferation.

Organic coatings are widely used to enhance the thromboresistance, dielectric strength, lubricity, corrosion resistance, antimicrobial action and wear properties[10]. The polymer is considered a low-cost solution that can change the negative effects caused by titanium implants.

PCL's hydrophobic nature causes lack of cell attachment, poor wettability, low mechanical properties and biological reactions. Coating it to the titanium alloys may solve these problems as well as decrease the cost as the polymer is inexpensive. Moreover, it is environment friendly and of heavier weight; and is biodegradable because it has an advantage over metal implants by decreasing the transfer of stress to the damaged tissue [10]. The electrospun nanofibers on the metallic surfaces cause adhesion problems, the solution can be the change in the roughness of the metal surface.

In this study,  $\text{TiAl}_6\text{V}_4$  alloy is pretreated with different surface modification methods and is coated with Poly ( $\epsilon$ -Caprolactone) (PCL). The pretreatment effect of  $\text{TiAl}_6\text{V}_4$  surface on coating adhesion of Poly ( $\epsilon$ -caprolactone) is examined. Also, the effect of the surface adjustment on the wettability of the coated sample is studied. Besides, the benefit of coating on bone conductivity as well as the bioactivity of the implant surface is observed.

## CHAPTER 2

### 2. LITERATURE SURVEY

#### 2.1 Implants

An implant is a medical tool with the purpose to substitute a missing bone or joint. It is mostly used to support a damaged bone for knee and hip joint. The known side effects of this substitution are: weakening of the bone called osteoporosis, injury and inflammation in the bone joints usually resulting a loss in the tissue function or can cause severe pain [14].

One of the most significant things for design and choice of materials is the medical response of the body to the material. Because high number of reactions would occur once the implant is placed with the host tissue. These interactions assign the biological compatibility of an implant, which also decide the implant's effectiveness. [15] There are several reasons leading to failure of the implants i.e. corrosion resistance, low wear and high modulus compared to the high modulus of bone.

In the literature, elements like TA, TI, MO, NB, ZR, W, SN and AU are classified as biocompatible, whereas V, AL, CR, etc. are identified as dangerous elements for the human body [1]. In figure 2.1, detailed information about the base metals and their compatibility is depicted. Consequently, the safe and biocompatible elements are preferred when designing biomedical materials [14].

Generally, if an implant has a larger modulus than the bone to be replaced, stress shielding is used to prevent the transfer of necessary stress to the adjusted bone. This also generates bone resorption between the death of bone cells and the implant [16]. Co-Cr based alloys; TI and its alloys; and 316L stainless steel are among the most commonly used metallic materials for implants [14].

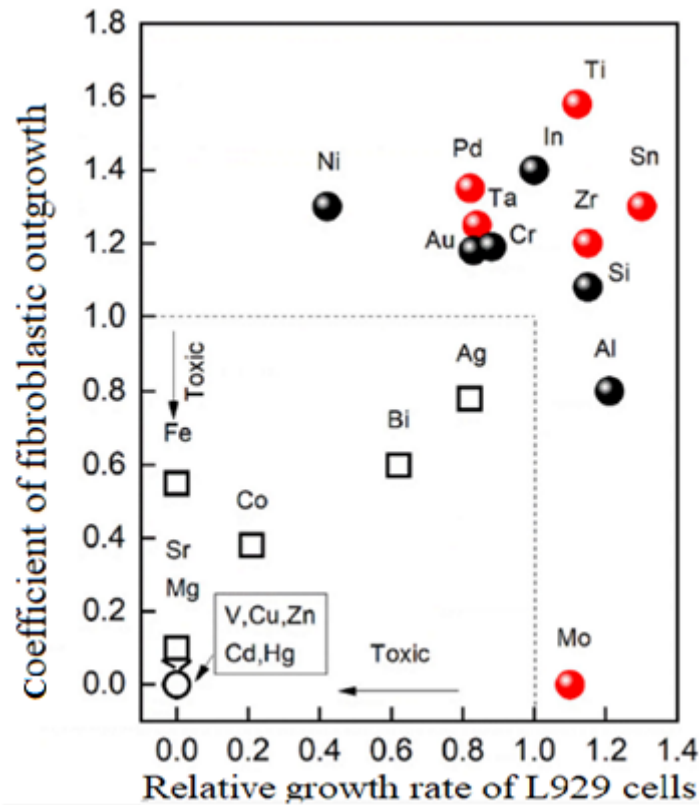


Figure 2. 1 Pure metals and their biocompatibility [14]

## 2.2 Titanium

Titanium (Ti) is widely used as a biomaterial in dental fixations and bone implants due to its biocompatibility, low density, good corrosion resistance, and high fatigue resistance in physiological environments and inert material [17]. The bio inert oxide-covering layer that can rapidly develop on the top of Ti implants in a physiological state is responsible for its biocompatibility and improvement in the bone response to the implants (Figure 2.2) [18]. Nevertheless, this bio oxide layer causes weak osteo-inductivity due to its porous and thin texture; low wear resistance and low hardness, particularly in applications like prostheses that bear impact, constant friction and wear [19].

Titanium oxide film can degrade and dissolve when exposed to the heavy mechanical loading. By putting the unprotected metal on corrosive, somatic fluids cannot regenerate the oxide film. It will cause leakage of metal ions and occasional clinical problems [20].

The surface of implants from a medium suitable for adhesion of bacteria and reproduction finally lead to the biofilm that can completely prevents access to the drug action resistance and immune system. The weak interaction between the implant and tissue contributes to the reduction in fixture time of the bone and can cause fracture and implant loosening which may lead to implant failure[18]. Subsequent to this condition, it can increase not only the patient's pain but also expenses for the treatment [21]. Taking into account the direct contact and subsequent biological reactions that take place between implants and tissues, surface modification is an effective substitution to provide the necessary reactions via the functionalization of the surface implants[18].

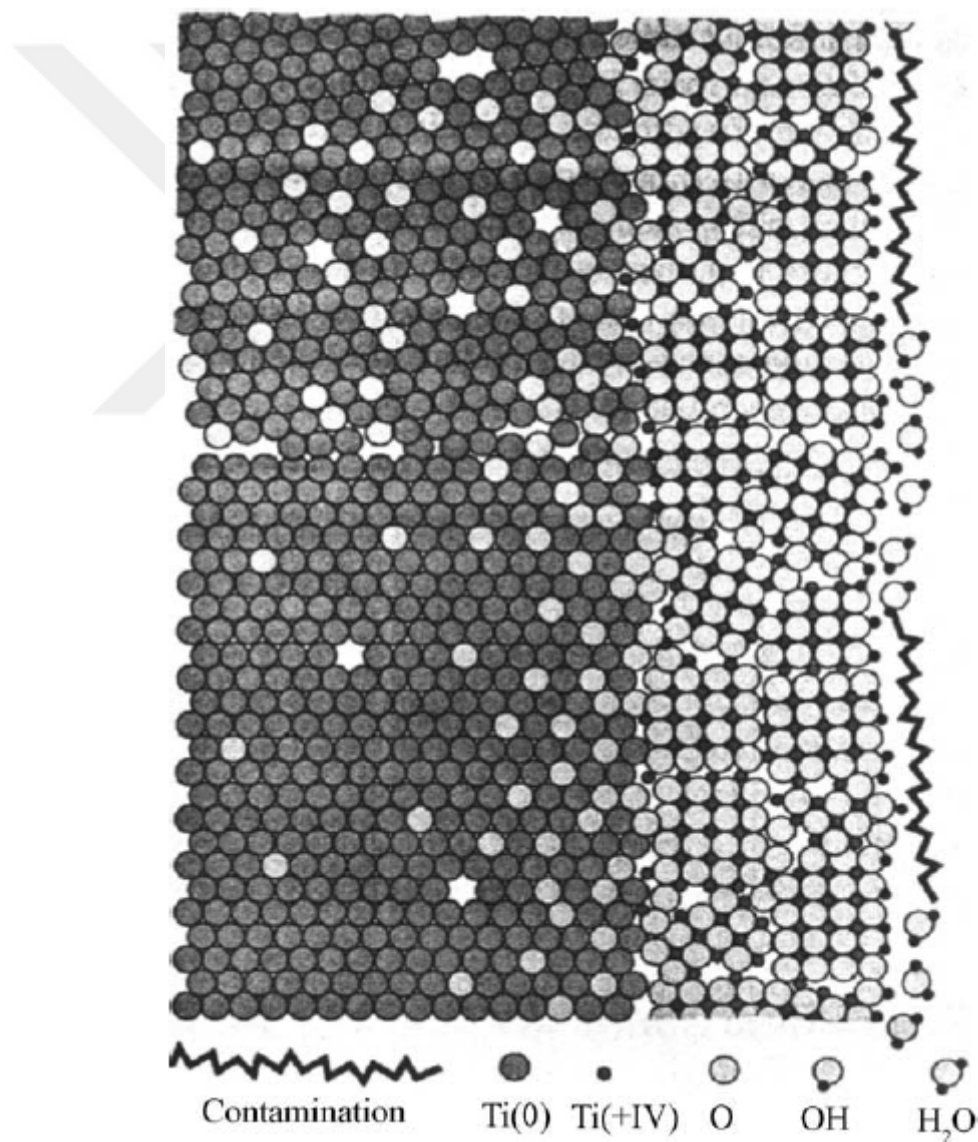


Figure 2. 2 Pure titanium covered by oxide film [3]

Apparently, by comparing the data in Table 2.1- 2.3, the elastic moduli of Ti alloys are found to be similar in the bone. The density of Co–Cr-based alloys, 316L stainless steel and Ti alloys is 8.3–9.2 g-cm<sup>3</sup> , 7.9 g-cm<sup>3</sup> and 4.4–4.5 g-cm<sup>3</sup> , respectively [22]. It can be noticed that the density of Ti alloys is lesser than 316L stainless steel and Co–Cr-based alloys, and also found similar to those of bones. Thus, titanium alloys are considered an excellent choice when compared to other mineral implants.

The tensile properties of the humans' cortical bone are shown in **Table 2.1** and a list of the compressive properties of humans' cortical bone and cancellous bone is presented in **Table 2.2 and 2.3**.

Table 2. 1 Human tensile properties of cortical bones [3]

| <b>Bone</b> | <b>Age</b> | <b>E [GPa]</b> | <b>density<br/><math>\rho</math> [g cm<sup>-3</sup>]</b> | <b>ultimate<br/>tensile<br/>strain<br/><math>\epsilon</math> max [%]</b> | <b>ultimate<br/>tensile<br/>strength<br/><math>\sigma</math> UTS [MPa]</b> |
|-------------|------------|----------------|----------------------------------------------------------|--------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Fibula      | 41.5       | 19.2           | 1.91                                                     | 2.10                                                                     | 100                                                                        |
| Fibula      | 71         | 15.2           | 1.73                                                     | 1.19                                                                     | 80                                                                         |
| Femur       | 41.5       | 14.9           | 1.91                                                     | 1.32                                                                     | 102                                                                        |
| Femur       | 71         | 13.6           | 1.85                                                     | 1.07                                                                     | 68                                                                         |
| Femur*      | 15-89      | 15.2           | 1.9                                                      | 2                                                                        | 141                                                                        |
| Femur**     | 15-89      | 15             | 1.8                                                      | 1.8                                                                      | 134                                                                        |
| Femur       | 20-89      | 16.8           | -                                                        | 2.83                                                                     | 132                                                                        |
| Humerus*    | 15-89      | 15.6           | 1.77                                                     | 2.2                                                                      | 149                                                                        |
| Humerus_**  | 15-89      | 16.1           | 1.72                                                     | 1.9                                                                      | 151                                                                        |
| Tibia       | 41.5       | 18.9           | 1.96                                                     | 1.76                                                                     | 106                                                                        |
| Tibia       | 71         | 16.2           | 1.83                                                     | 1.56                                                                     | 84                                                                         |
| Tibia       | 20-89      | 23.8           | -                                                        | 3.09                                                                     | 156                                                                        |

(\*) for male and \*\* for female.

Table 2.2 Compressive properties of cortical bones for the human [3]

| <b>Tissue source</b>                                | <b>Age</b> | <b>elastic<br/>modulus<br/>E [GPa]</b> | <b>ultimate<br/>tensile<br/>strength<br/><math>\sigma_{UTS}</math> [MPa]</b> | <b>hardness<br/>H<br/>[MPa]</b> |
|-----------------------------------------------------|------------|----------------------------------------|------------------------------------------------------------------------------|---------------------------------|
| Tibia<br>interstitial<br>Lamellae<br>(longitudinal) | 57/61      | 25.8                                   | -                                                                            | 736                             |
| Tibia osteons<br>(longitudinal)                     | 75/61      | 22.5                                   | -                                                                            | 614                             |
| Tibia                                               | 30-89      | 28                                     | 195                                                                          | -                               |
| Femur                                               | 20-89      | 17.6                                   | 194                                                                          | -                               |

For most medical applications, TiAl<sub>6</sub>V<sub>4</sub> alloy is preferred over pure titanium for orthopedic and dental implants due to its strong solubility that significantly varies with temperature and makes much easier the manufacturing of high strength products.

Presently, there are four CP-TI classes and one titanium alloy fabricated for applications of dental implants. According to their strength, ASTM classified first four grades as pure, whilst the fifth (TiAl<sub>6</sub>V<sub>4</sub>) is categorized as strongest, shown in **Table 2. 4.**

Table 2. 3 Compressive properties of cancellous bones for the human [3]

| <b>Tissue source</b>     | <b>Age</b> | <b>elastic modulus<br/>E [GPa]</b> | <b>density<br/><math>\rho</math> [g cm<sup>-3</sup>]</b> | <b>ultimate tensile strength<br/><math>\sigma_{UTS}</math> [MPa]</b> | <b>ultimate tensile strain<br/><math>\epsilon_{max}</math> [%]</b> |
|--------------------------|------------|------------------------------------|----------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------|
| Lumbar spine             | 71-84      | 0.02                               | 0.19                                                     | 1.55                                                                 | -                                                                  |
| Lumbar spine             | 15-87      | 0.07                               | 0.24                                                     | 2.45                                                                 | -                                                                  |
| Femur                    | 58-83      | 0.39                               | 0.5                                                      | 7.36                                                                 | -                                                                  |
| Proximal tibia           | 59-82      | 0.45                               | 0.29                                                     | 5.33                                                                 | -                                                                  |
| Vertebra (horizontal)    | 15-87      | 0.02                               | -                                                        | 0.9                                                                  | 8.50                                                               |
| Vertebra (vertical)      | 15-87      | 0.07                               | -                                                        | 2.5                                                                  | 7.4                                                                |
| Tibia                    | 16-83      | 0.64                               | 0.45                                                     | 8.8                                                                  | 2.2                                                                |
| Tibia head (female)      | 14-89      | 0.02                               | 0.22                                                     | 2.2                                                                  | 6.9                                                                |
| Tibia head (male)        | 14-89      | 0.03                               | 0.22                                                     | 3.9                                                                  | 8.3                                                                |
| Lumbar vertebra (female) | 14-89      | 0.04                               | 0.2                                                      | 2.7                                                                  | 6.10                                                               |
| Lumbar vertebra (male)   | 14-89      | 0.06                               | 0.2                                                      | 4.6                                                                  | 6.7                                                                |

Table 2.4. Properties of 1 to 5 grades [23]

| Property                        | ASTM Grade |         |         |         |         |
|---------------------------------|------------|---------|---------|---------|---------|
|                                 | 1          | 2       | 3       | 4       | 5       |
| Elongation (%)                  | 24         | 20      | 18      | 15      | 10      |
| Yield strength (MPa)            | 170        | 275     | 380     | 483     | 795     |
| Elastic Modulus (GPa)           | 103-107    | 103-107 | 103-107 | 103-107 | 114-120 |
| Ultimate Tensile Strength (MPa) | 240        | 345     | 450     | 550     | 860     |

### 2.2.1 TiAl<sub>6</sub>V<sub>4</sub>

TiAl<sub>6</sub>V<sub>4</sub> is one of the most widely used alloys and has long been the primary medical titanium. In fabricated orthopedic prosthesis implants and dental restoration, TiAl<sub>6</sub>V<sub>4</sub> is preferred because of its good mechanical properties, corrosion resistance and biocompatibility [24-27]. It is also in use for orthopedics, in the annealed condition , and in traumatology implants[25]

TiAl<sub>6</sub>V<sub>4</sub> dissolves in physiological saline and releases V and Al into the body that causes Alzheimer's disease, peripheral neuropathy, and osteomalacia by changing the activity of enzymes related to the inflammatory response. Moreover, titanium and its alloys don't make a chemical bond with the bones so it needs to be coated to promote osseointegration [26,27].

The preparation of the metal surface before the coating has a significant effect on adhesion of the coating [28].

Low integration of the tissue to the implants decreases the fixture time of the bones and can further lead to implant loosening, malunion or implant failure [28]. Furthermore, direct contact can cause biological reactions between tissues and implants. The surface modification is an effective way to increase the adhesion of the coating through the modification of the surface [28].

The proper interconnection of material with the bones is a first and foremost requirement to stop failure, hence surface adjustment is used to promote biological function and Osseo integration [10]. The surface characteristics of the implant material, like chemistry, roughness and morphology highly affects tissue integration and cellular reactions. Therefore, it is evident that the surface characteristics play a significant role in choosing the material of the implant[10].

In addition to effective coating, it is vital that there is an acceptable adhesion with the metal, therefore the metal's nature and the surface preparation must be taken into consideration before coating [28]. Many titanium surface modification techniques have been published in over the past few years [29]. One way of developing and modifying the titanium osteoconductive properties is its conversion by taking into account bioactive substances.

The polymer coating is environment-friendly and cheap to apply. Moreover, the polymer coating can change the negative effects caused by titanium implants, heavier weight compared to normal bone and stress protection effects. The biodegradable synthetic polymers received more appreciation than metal implants due to their tendency against high stress, consequently it help tissues to heal more quickly. In addition, the nanotechnology polymer coating can supply larger surface area to volume proportion by using electrospinning techniques, [30].

#### **2.2.1.1 Responsible properties for the Biocompatibility of Titanium Alloys**

Strong corrosion-resistance, low electronic conductivity rate, physiological Ph values of the thermodynamic state, oxide isoelectric rate of 5-6, and low ion making propensity in aqueous state are required for the implants Furthermore, the negative film-covered surface should be positively charged a little in physiological Ph. and titanium has a dielectric constant similar to that of water. [23]

### 2.2.1.1.1 Mechanical Properties

**Table 2.5** summarises the mechanical properties of Ti and its alloys. In orthopedics, titanium is very promising because of its low elastic modulus and high specific strength [31]. Titanium has low abrasion and wear resistance due to its low hardness, as shown in **Table 2.6**. [3]

Table 2.5 Mechanical properties of titanium and its alloys [3]

| Alloy designation                                           | Microstructure              | YS (MPa)* | E (GPa)* | UTS (MPa)* |
|-------------------------------------------------------------|-----------------------------|-----------|----------|------------|
| Ti-35Nb-5Ta-7Zr-0.4O<br>(TNZTO)                             | Metastable b                | 976       | 66       | 1010       |
| Ti-35Nb-5Ta-7Zr<br>(TNZT)                                   | Metastable b                | 530       | 55       | 590        |
| Ti-15Mo-3Nb-0.3O<br>(21SRx)                                 | Metastable b +<br>silicides | 1020      | 82       | 1020       |
| Ti-13Nb-13Zr                                                | a0/b                        | 900       | 79       | 1030       |
| Ti-Zr                                                       | Cast a0/b                   | N/A       | N/A      | 900        |
| Ti-0/20Zr-0/20Sn-<br>4/8Nb-2/4Ta <sup>+</sup><br>(Pd, N, O) | a/b                         | 726-990   | N/A      | 750-1200   |
| Ti-15Mo-5Zr-3Al                                             | Aged b + a                  | 1215      | 100      | 1310       |
|                                                             | Metastable b                | 771       | 82       | 812        |
| Ti-12Mo-6Zr-2Fe<br>(TMZF)                                   | Metastable b                | 1000-1060 | 74-85    | 1060-1100  |
| Ti-5Al-2.5Fe                                                | a/b                         | 914       | 110      | 1033       |
| Ti-6Al-7Nb<br>(protasul-100)                                | a/b                         | 921       | 105      | 1024       |
| Ti-6Al-4V                                                   | a/bk                        | 850-900   | 110      | 960-970    |
| cpTi                                                        | a                           | 692       | 105      | 785        |
| Bone                                                        | Viscoelastic<br>composite   | -         | 10-40    | 90-140     |

\*YS (MPa) is yield strength, E (GPa) is elastic modulus and UTS (MPa) is Ultimate strength

Table 2.6. Measures of hardness for titanium and its alloys [3]

| <b>Grad designation and Type</b> | <b>Metallurgical condition</b> | <b>Typical hardness (Rockwell)</b> |
|----------------------------------|--------------------------------|------------------------------------|
| Ti-35Nb-7Zr-5Ta (b)              | 1300 °F                        | 35 HRC                             |
| Ti-12Mo-6Zr-2Fe (b)              | 1400° F                        | 33 HRC                             |
| Ti-15Mo-2.8Nb-0.2Si (b)          | 1475 °F                        | 24 HRC                             |
| Ti-15Mo (b)                      | 1475 °F                        | 24 HRC                             |
| Ti-6Al-7Nb (a/b)                 | 1300 °F                        | 32 HRC                             |
| Ti-6Al-4V (a/b)                  | 1300 °F                        | 36 HRC                             |
| Ti-3Al-2.5V (a/b)                | 1300 °F                        | 24 HRC                             |
| Ti cp-4 (a)                      | 1300 °F                        | 100 HRB                            |
| Ti cp-3 (a)                      | 1300 °F                        | 90 HRB                             |
| Ti cp-2 (a)                      | 1300 °F                        | 80 HRB                             |
| Ti cp-1 (a)                      | 1300 °F                        | 70 HRB                             |

#### 2.2.1.1.2 Biological properties

Titanium and its alloys have strong corrosion resistance and are inert due to the therein surface oxide. In a biological system, usually they are able to avoid corrosion as titanium absorbs proteins easily from biological liquids. For example, certain proteins including laminin V, collagenase, complement proteins, albumin, glycosaminoglycans, fibrinogen, and fibronectin are set to absorb to the titanium surface. This surface can also support the growth and differentiation of cells[3].

#### 2.2.1.2 Biomedical Applications of TiAl<sub>6</sub>V<sub>4</sub>

Titanium alloys have gained a lot of attention in biomedical applications; TiAl<sub>6</sub>V<sub>4</sub> has always been preferred for biomedical applications. It has been extensively used for implant systems in order to replace damaged hard tissues, for instance, industrial knee joints, industrial hip joints, screws for break repairing, bone plates, cardiac valves, industrial hearts, and pacemakers[23].

#### 2.2.1.2.1 Hard Tissue Replacements

Hard tissue gets frequently damaged due to ageing, impact, or any other cause. It is a common exercise to replace damaged hard tissues with artificial alternatives, depending on the place of the implants and the functions to perform. **Fig 2.3** illustrates the hard tissues in the human's body.

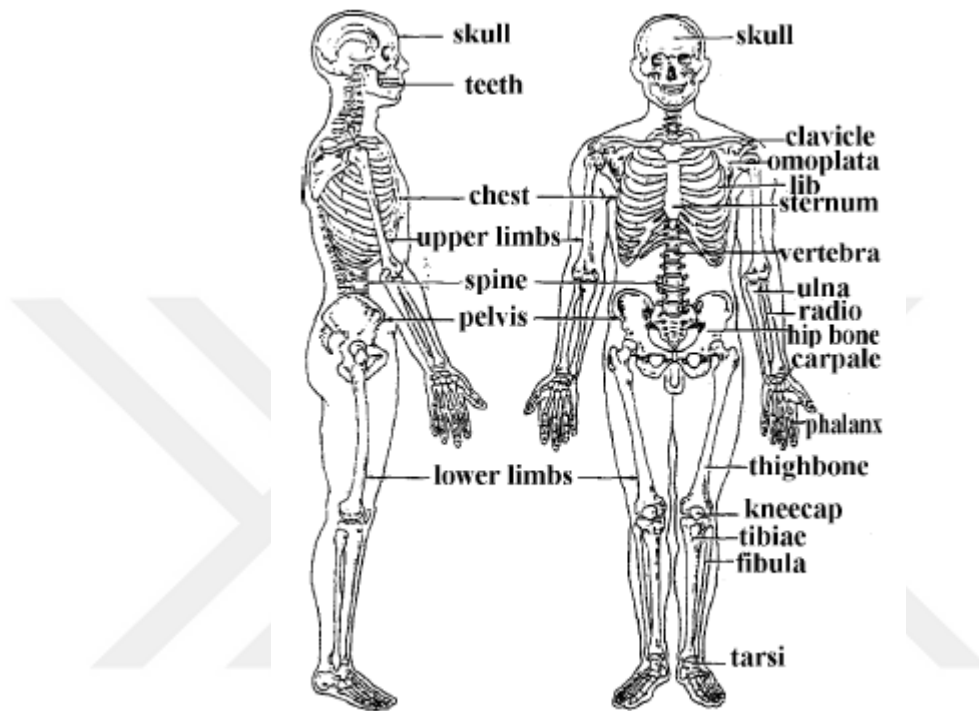


Figure 2.3 Places of hard tissue in the body[3]

Titanium and its alloys are considered one of the most attractive material in dental devices like crowns, implants, overdentures, components of dental implant operations, and bridges. Pure titanium is utilised commercially in the implants of teeth.

One of the most popular uses of TI and its alloys is synthetic hip joints that contain stem and synthetic bearings (cup and femoral head), as shown in **Fig 2.4**.

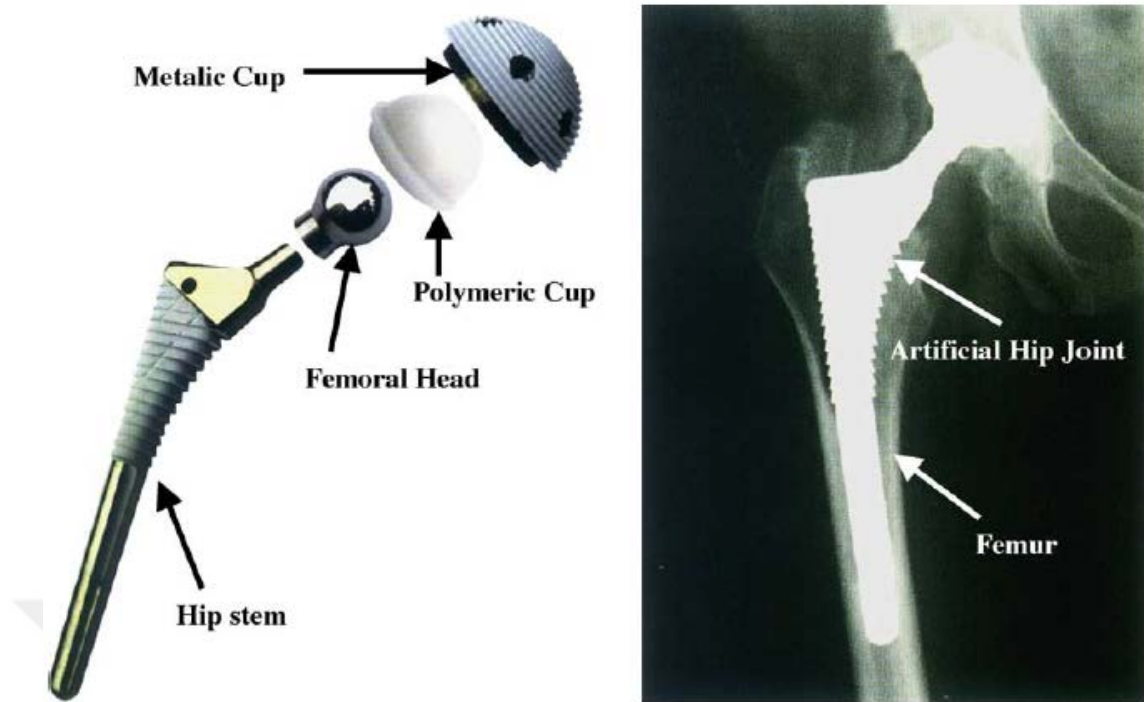


Figure 2.4: Artificial hip joint.[3]

Titanium and its alloys are also commonly used in artificial knee joints which consist of the patella, tibial component, and femoral component [3].

#### 2.2.1.2.2 Applications of Titanium in Cardiac and Cardiovascular

Due to their specific properties, titanium and its alloys are popular in cardiovascular implants as well. Examples of early use includes circulatory tools, safety cases in pacemakers, and artificial heart valves in various forms. The popular design for the heart valve—the ring and pillar—are made of titanium and/or titanium alloys, whereas the disc is made of pyrolytic carbon (**Figure 2.5**). A sewing ring made of knitted Teflon cloth is placed around the ring while the sutures set the prosthesis to the heart[3]. In addition, titanium and its alloys (Stents) are utilized in the treatment of cardiovascular diseases. The nickel-titanium alloy is mostly preferred due to its particular shape as shown in (**Figure 2.6**).



Figure 2.5. The artificial heart value.[3]



Figure 2. 6. The artificial vascular stents.[3]

#### 2.2.1.2.3 Other Applications

Titanium and its alloys are an exciting materials in implants of osteosynthesis due to their special properties that meet the needs of osteosynthesis applications. Typical osteosynthesis implants involve bone plates, screws, maxillofacial implants etc., (Figure 2.7).

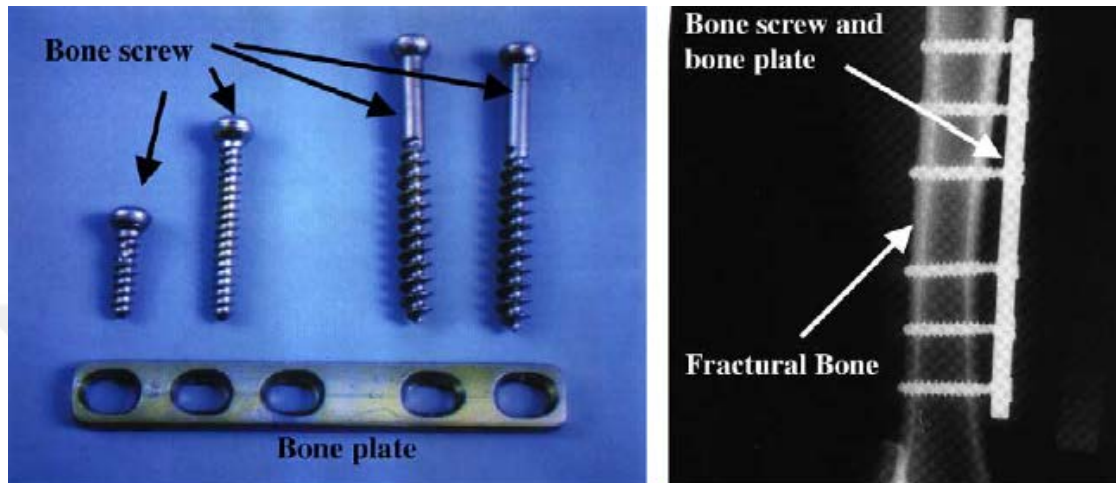


Figure 2. 7 Bone plate and Bone screw[32]

#### 2.2.1.3 Reasons for Coating or Surface Modification

In implants made up of titanium, the natural industrialisation procedure commonly leads to an oxidized, polluted surface layer that is often compacted, plastically deformed, non-uniform and pad defined. It is certain that these natural surfaces are not appropriate for biomedical applications and some surface handling is needed. Another mentionable cause for surface modification on titanium medical devices is that appointed surface properties different from those in the bulk are often desired; for instance, good bone formability is required to achieve biological integration. In devices that have contact with blood like artificial heart valves, blood compatibility is critical. In other usages, strong wear and corrosion resistance is also desired.

#### **2.2.1.3.1 Surface modification techniques**

Over the last decade, surface roughness has increased in order to improve the mechanical interlocking, to increase bondable surface area, and to improve the tribological properties of the alloy[33]. According to various clinical needs, a difference in surface modification planner is proposed, depicted in **Table 2. 7**.

The surface characteristics of the implant materials such as roughness, chemistry and morphology have a tremendous effect on tissues integration and cellular interactions. Therefore, surface properties are the key element in determining the biocompatibility of the implant material, osseointegration, and bioactivity

Titanium implants have bad mechanical interlocking and low bonding ability with the bone tissue and do not promote osteogenesis - this is very important to prevent implant failure. Hence, to improve the biological function and the osseointegration of TI implants, surface modification is utilized [10]. The coating process is widely used in material-processing applications to improve tribological properties, biocompatibility, bioactivity, and bone conductivity.

#### **2.2.1.3.2 Coating materials**

Coating with bioactive material is one of the many possible ways for improving and modifying the osteo-inductive quality of TI. However, there are many disadvantages of this process as well that includes bad degradation of the popular coating materials and a decrease in the available bone growth space, like hydroxyapatite.

In literature, it has been identified that highly porous coating layers with big surface area to volume ratio can solve the problems of cellular proliferation and bone attachment. However, the brittle structure of bio-ceramic materials makes it a complicated process in porous structures that can create colonisation and cellular spreading[10].

Table2. 7. Methods of surface modification methods for titanium and its alloys [3]

| Methods of surface modification                                                                                                                              | Objective                                                                                                     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------|
| <b>Mechanical methods</b><br>- grinding<br>- blasting<br>- machining<br>- polishing                                                                          | Improve bonding adhesion                                                                                      |
| <b>Chemical methods</b><br>- acidic treatment<br>- hydrogen peroxide<br>- alkaline treatment                                                                 | Improve biocompatibility<br>Bioactivity<br>Bone conductivity                                                  |
| <b>Sol-gel</b>                                                                                                                                               | Improve biocompatibility<br>Bioactivity<br>Bone conductivity                                                  |
| <b>Anodic oxidation</b>                                                                                                                                      | Improve biocompatibility<br>Bioactivity<br>Bone conductivity and corrosion resistance                         |
| <b>Chemical vapor deposition (CVD)</b>                                                                                                                       | Improve blood compatibility, corrosion resistance, and wear resistance                                        |
| <b>Physical methods</b><br>- thermal spray<br>- flame spray<br>- plasma spray<br>- high velocity oxygen fuel (HVOF)<br>- detonation gun spray coatings(DGUN) | Improve corrosion resistance biological properties, and wear resistance                                       |
| <b>Biochemical methods</b>                                                                                                                                   | Induce tissue response and specific cell by means of proteins, growth or surface immobilised peptides factors |
| - physical vapor deposition (PVD)<br>- ion plating<br>- evaporation<br>- sputtering                                                                          | Improve blood compatibility, corrosion resistance and wear resistance                                         |
| <b>Glow discharge plasma treatment</b>                                                                                                                       | Clean, oxide, remove native oxide layer, nitride surface                                                      |
| <b>Ion deposition and implantation</b><br>- PIII<br>- beam line ion implantation                                                                             | Improve corrosion resistance, biocompatibility and wear resistance, modify surface composition                |

### 2.3 Poly ( $\epsilon$ -caprolactone) (PCL)

During the past decades, the industrial polymer ( $\epsilon$ -caprolactone) (PCL) has received lot of attention in various tissue-engineering applications. PCL is a hydrophobic ball-like polymer, and its melting point ranges from 55-60 °C and glass transition temperature is -62 ° C. It is dissolved by a group of various organic solvents within the framework of room temperature such as gasoline, toluene, cyclohexanone, chloroform, dichloromethane etc.,[34].

Because of the solubility of the polymer and the compatibility of its mixture, it is extensively used in biomedical applications for being biologically absorbable and compatible with life. Moreover, the cost of industrial polymer is low as its rate of deterioration ranges from 2-5 years which is regarded as slow degradation. It has a set of mechanical properties that make it suitable for a variety of applications due to its hydrophobic and semi-crystalline nature[35].

There are lots of properties that have led to PCL being widely used in scaffold manufacturing techniques including sticky and rheological properties as a result of its low cost, FDA, low melting point, and very good compatibility. PCL and its co-polymers have been used in a wide range of fields in various manufacturing techniques including bird separation, electrospinning, robust free fabrication, fine particles, and gravity yarn. However, it also has limitations, such as poor performance in cell bonding and uncontrolled biological interactions with substances and hydrophobia. There are a variety of different ways to eliminate this problem, including mixing with other polymers and surface modification[36]. Additionally, using the electrospinning technique PCL can be manufactured as a microfiber with remarkable properties, such as surface area and high porosity, which are essential in biomedical applications. PCL electrospun fibers also serve as a temporary bases for differentiation, diffusion and elevation of adhesion to various types of cultured cells. [11,37]

PCL alone has been widely used in tissue engineering applications or as a mixture with other synthetic and natural polymers as a scaffold. Hoda Behrami and others showed the benefit of PCL nanofibrous scaffolds loaded with USS (unrestricted somatic stem cells) to achieve good results of the healing process of skin defects in rat models[38]. Furthermore, Bonvallet et al. reported that PCL collagen scaffolds' layer-by-layer technique supplies a suitable environment for the proliferation and survival of fibroblasts [39].

### 2.3.1 PCL properties

PCL is a semi-crystalline polymer with a melting point between 59°C and 64°C, and a glass transition temperature is -60 °C. The average number of molecular weights—rated by the molecular weight (Mn)—of PCL specimens may differ from 10,000 to 42,500. It is insoluble in diethyl ether, petroleum ether, and alcohol; and is soluble in 2-nitropropane, benzene, dichloromethane, cyclohexanone, carbon tetrachloride, toluene, and chloroform at room temperature. It has low solubility in 2-butanone, acetone, dimethylformamide, acetonitrile and ethyl acetate – its physical properties are listed in Table 2.8 ,[40 41]. The other properties including general, mechanical, thermal, processing, electrical, and absorption permeability are provided by ASTM and shown in Table 2.9. PCL has viscoelastic and rheological properties that make it possible to be fabricated from a wide amount of scaffold technologies. PCL and its copolymers have gained this advantage by being successfully utilised in gravity spinning, electrospinning, solid freeform fabrication, micro particles, and phase separation. However, it also has some disadvantages: its hydrophobic nature causes lack of cell attachment, poor wettability, and the biological reactions with the material are uncontrolled.

PCL degradation is slow that makes it appropriate for long term delivery as compared to polyglycolic acid and other polymers. Moreover, it spans a period of more than one year[40].

Table2. 8. PCL physical properties at room conditions [41]

|                                                           |                                |
|-----------------------------------------------------------|--------------------------------|
| 1% secant modulus                                         | 50000 psi                      |
| Elongation                                                | ~ 750%                         |
| Yield stress                                              | 1600 psi                       |
| Tensile strength                                          | 3500 psi                       |
| Glass transition temperature (1 Hz) partially crystalline | 213 k                          |
| Amorphous                                                 | 202° k                         |
| Melting point                                             | 63° C                          |
| Volume resistivity (23° C, 50% RH)                        | 4.76 X 10 <sup>11</sup> ohm/cm |

Table2. 9. The general properties, mechanical properties, thermal properties, processing properties, electrical properties and absorption permeability of PCL  
[according to ASTM]

| <b>Composition overview</b>                                             |                                  |
|-------------------------------------------------------------------------|----------------------------------|
| Formula (C <sub>6</sub> H <sub>10</sub> O <sub>2</sub> ) <sub>n</sub> . |                                  |
| Base.                                                                   | Polymer                          |
| Polymer class.                                                          | Thermoplastic : semi-crystalline |
| Filler (by weight) %.                                                   | 0%                               |
| Composition detail.                                                     | Polymer 100%                     |

| <b>Bio data.</b>                         |     |
|------------------------------------------|-----|
| R <sub>0</sub> HS (EU) compliant grades? | yes |

| <b>Mechanical properties.</b> |                                                         |
|-------------------------------|---------------------------------------------------------|
| Compressive modulus.          | 0.05630 X 10 <sup>6</sup> -0.0640 X 10 <sup>6</sup> psi |
| Flexural modulus.             | 0.0753 X 10 <sup>6</sup> -0.064 X 10 <sup>6</sup>       |
| Young's modulus.              | 0.05630 X 10 <sup>6</sup> -0.0640 X 10 <sup>6</sup> psi |
| Poisson's ratio.              | 0.480-0.50                                              |
| Tensile strength.             | 5.860-6.150 Ksi                                         |
| Yield strength.               | 3.060-5.580 Ksi                                         |
| Elongation.                   | 679 – 948 % strain                                      |
| Compressive strength.         | 3.060-5.550 Ksi                                         |
| Hardness – Rockwell R.        | 46.20-38.80                                             |
| Hardness – Rockwell M.        | 30.30 – 55                                              |
| Hardness –Vickers.            | 6.320-11.50 HV                                          |
| Hardness – shore A.           | 95-100                                                  |
| Hardness – shore D.           | 53-57                                                   |
| Fracture toughness.           | 1.830-1.860 Ksi.in <sup>0.5</sup>                       |

|                                    |                 |
|------------------------------------|-----------------|
| Fatigue strength at $10^7$ cycles. | 1.520-2.540 Ksi |
|------------------------------------|-----------------|

|                                  |                                      |
|----------------------------------|--------------------------------------|
| <b>Impact properties.</b>        |                                      |
| Impact strength, notched. 23° C. | 23.10 – 26.30 ft.lbf/in <sup>2</sup> |

|                                       |                                               |
|---------------------------------------|-----------------------------------------------|
| <b>Thermal properties.</b>            |                                               |
| Glass temperature.                    | -97.60 - -74.20 ° F                           |
| Melting point.                        | 127 – 144 ° F                                 |
| Maximum service temperature.          | 104 – 122 ° F                                 |
| Heat deflection temperature. 0.45MPa. | 86 – 104 ° F                                  |
| Minimum service temperature.          | -76 - -58 ° F                                 |
| Specific heat capacity.               | 0.3390 – 0.3580 BTU/lb. ° F                   |
| Thermal conductivity.                 | 0.09820 – 0.1040 BTU.ft/h.ft <sup>2</sup> ° F |
| Thermal expansion coefficient.        | 87.80 – 95.60 microstrain/ ° F                |

|                              |                   |
|------------------------------|-------------------|
| <b>Processing properties</b> |                   |
| Molding pressure range.      | 7.250 – 7.540 Ksi |
| Mold temperature.            | 60.10 – 86.40 ° F |
| Melt temperature.            | 223 271 ° F       |
| Linear mold shrinkage.       | 0.150 – 0.70 %    |

|                                               |                                     |
|-----------------------------------------------|-------------------------------------|
| <b>Electrical properties</b>                  |                                     |
| Dielectric strength * dielectric breakdown.   | 412 – 429 V/mil.                    |
| Dissipation factor * dielectric loss tangent. | $5.850e^{-4}$ – 0.007520.           |
| Dielectric constant – relative permittivity.  | 4.28 -4.30.                         |
| Electrical resistivity.                       | $6.3e^{18}$ – $6.36e^{20}$ uohm.cm. |

|                                |               |
|--------------------------------|---------------|
| <b>Absorption permeability</b> |               |
| Water absorption for 24 hours  | 0.33 – 0.35 % |

|                                    |                   |
|------------------------------------|-------------------|
| <b>Durability.</b>                 |                   |
| Fluids and sunlight, UV radiation. | Good.             |
| Flammability.                      | Highly flammable. |

|                                                              |                                                              |
|--------------------------------------------------------------|--------------------------------------------------------------|
| <b>Material production primary: water and CO<sub>2</sub></b> |                                                              |
| Water usage.                                                 | $1.17 \text{ e}^4 - 1.29 \text{ e}^4 \text{ in}^3/\text{lb}$ |
| Sox creation.                                                | $0.08010 - 0.08850 \text{ lb/lb}$                            |
| NOx creation. L8                                             | $0.02670 - 0.02950 \text{ lb/lb}$                            |
| Primary production CO <sub>2</sub> footprint.                | $6.010 - 6.640 \text{ lb/lb}$                                |
| Embodied energy, primary production.                         | $1.41 \text{ e}^4 - 1.56 \text{ e}^4 \text{ kcal/lb}$        |

|                                     |                                                        |
|-------------------------------------|--------------------------------------------------------|
| <b>Material processing: energy.</b> |                                                        |
| Polymer machining energy.           | $213 - 236 \text{ kcal/lb.}$                           |
| Polymer extrusion energy.           | $726 - 800 \text{ kcal/lb.}$                           |
| Polymer molding energy.             | $1.68 \text{ e}^3 - 1.85 \text{ e}^3 \text{ kcal/lb.}$ |

|                                                       |                                  |
|-------------------------------------------------------|----------------------------------|
| <b>Material processing( CO<sub>2</sub> footprint)</b> |                                  |
| Polymer machining CO <sub>2</sub> .                   | $0.1580 - 0.1740 \text{ lb/lb.}$ |
| Polymer extrusion CO <sub>2</sub> .                   | $0.5360 - 0.5910 \text{ lb/lb.}$ |
| Polymer molding CO <sub>2</sub> .                     | $1.240 - 0.1740 \text{ lb/lb.}$  |

|                                                                        |                               |
|------------------------------------------------------------------------|-------------------------------|
| <b>Material recycling: CO<sub>2</sub>, energy and recycle fraction</b> |                               |
| A renewable resource                                                   | $\chi$                        |
| Biodegrade                                                             | $\sqrt{\phantom{x}}$          |
| Landfill                                                               | $\sqrt{\phantom{x}}$          |
| Combust for energy recovery                                            | $\sqrt{\phantom{x}}$          |
| Down cycle                                                             | $\sqrt{\phantom{x}}$          |
| Recycle                                                                | $\sqrt{\phantom{x}}$          |
| Combustion CO <sub>2</sub>                                             | $2.260 - 3.370 \text{ lb/lb}$ |

|                                     |                                           |
|-------------------------------------|-------------------------------------------|
| Heat of combustion                  | $3.04\text{e}^3 - 3.2\text{e}^3$ kcal/lb  |
| Recycle fraction in current supply  | 0.1%                                      |
| CO <sub>2</sub> footprint recycling | 1.320 – 1.330 lb/lb                       |
| Embodied energy recycling           | $4.75\text{e}^3 - 4.79\text{e}^3$ kcal/lb |

### 2.3.2 Biomedical Applications

PCL is decomposed by hydrolysis of its ester bonds in physiological environments (for instance in the human body), thus received a great deal of interest for its use as biomaterial implant. In particular, it is effective for the manufacturing of long-term implantation devices due to its degradation which is even slower than polylactide[42]. PCL is utilised in the human body in different applications, for instance suture, a device of drug delivery or adhesion barrier. Following the recent introduction of a PCL-based microsphere dermal filler, it is also utilised in the rapidly growing field of human aesthetics.

PCL-based products are able to correct facial ageing signs like contour laxity and volume loss that are able to produce immediate as well as long-lasting natural effects [43]. It is also used in dentistry in the filling of the root canal and for purposes of re-treatment [44].

## 2. 4 Electrospinning

Electrospinning is a simple way to produce polymers, nano and microfibers from a wide amount of materials including ceramics, polymers, and composites for the applications of tissue engineering[7]. Electrospinning has gained much recognition in the last ten years for the fabrication of nanofiber, because of its flexibility, ease of use, and the possibility to fabricate fibers in nanoscale and/or in micro. Fabrication of electrospun fibers can be done with different materials and can either be directed or randomly organised in order to obtain a desired biological response and mechanical properties. Moreover, there are various ways to adjust the electrospinning composition so as to merge various properties and various materials, especially drugs and DNA/RNA[45]. Recently, the technique of electrospinning has received notable attention as it permits continuous production of fibers with a diameter from submicron

to nanometers with high surface area to volume ratio, which is around a thousandth of the width of a human hair.

In many applications, electrospinning has been used mainly for fiber-based sensors, catalytic nanofibers, tissue engineering scaffolds, and filtration membranes. Electrospinning is a cheap and easy technique consisting of a collector, pump, and a high voltage supply. Through the electrospinning procedure, the polymer solution is carried at the end of the needle tip capillary by surface tension. Applied high voltage electrostatic power is charged with the polymer solution that can contract the surface tension. Ultimately, the electrostatic repulsion overcomes the tension of the surface and thereby a jet of charged liquids is carried by a solution droplet from the tip of the conical shape, known as the Taylor cone. In addition, the jet actualises the evaporation of the solvent and the polymer fibers are collected by this powerful technique. It is conceivable to stretch a huge number of different natural and manufactured polymers into fibers of several kilometers in length.

Electrospinning is one of the simplest techniques that allows the production of several nanofibers to be utilised in different applications, whilst the parameters that influence the process must be considered. The different components of the electrospinning device are explained in Figure 2.8.

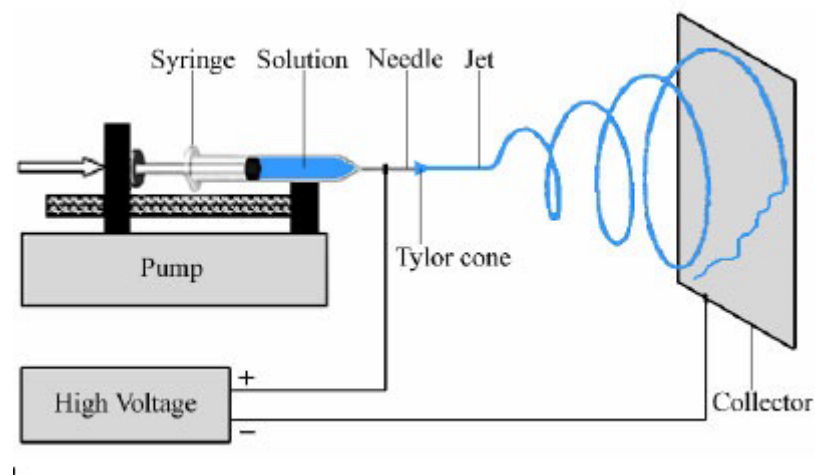


Figure 2. 8 electrospinning device parts [46]

### **2.4.1 Parameters Affecting the Process**

There are several factors in the electrospinning process that play a significant role in morphology. Based upon structure and properties of the product, these factors are categorised as solution parameters, environmental parameters, and process parameters. The solution parameters include the molecular weight of the polymer, concentration, solution conductivity, and viscosity. The environmental parameters consist of temperature and relative humidity. Lastly, the process parameters are the flowrate and the distance between the collector and needle.

#### **2.4.1 Process Parameters**

There are many parameters affecting on the coating characteristics like fiber's diameter and morphology of the fibers and other features

##### **2.4.1.1 Applied Voltage**

Applied voltage is considered crucial for the electrospinning procedure due to its effect on the formation of nanofiber. To start a charged jet, the applied voltage must reach the specific threshold voltage, whereas this threshold differs from polymer to polymer.

The relation between the fiber diameter and the voltage factor can also have an effect on the performance of electrospinning. From previous studies, it is revealed that the large fiber's diameter is due to the higher voltages [47], which is directly related to the applied voltage. It can cause stretching of the polymer solution due to the charge repulsion inside the jet[48]. Some researchers argued that there is only a slight effect of the voltage on the fiber diameter of polyethylene oxide (PEO) [49]. The diameter of the fibers can also be reduced using high voltage[50], which is attributed to the extension of the polymer fluid in relation to the repulsion of charge in the jet[51]. However, the degree of significance varies with other parameters like concentration and distance[52].

##### **2.4.1.2 Flow Rate**

To keep the Taylor cone fixed during the electrospinning process, the flow rate of the solution must remain at a specific level. Generally, low feeding rate is considered favorable to guarantee sufficient time for the fluid to evaporate resulting in the smaller

diameter[53]. Nonetheless, if the flow rate is too high, fibers with thick diameters will be formed because fibers cannot dry before reaching the collector[54]. Another study argued that the higher flow rate leads to an increase in the solvent evaporation which can further lead to an increase in pore diameter [55].

#### **2.4.1.3 Needle-Collector Distance**

The factors like collector gap and needle have been reviewed in terms of their influence on the diameters and morphology of the fibers and to allow fibers to dry before being gathered by the collector with a minimum distance. In addition, a beaded morphology is observed if the distance is either too small or too large [45]. Subsequently, a basic separation distance is needed to create a uniform and smooth electrospun fibers; moreover, the separation can determine whether the resultant process is electrospinning or electrospraying.

#### **2.4.2 Solution Parameters**

##### **2.4.2.1 The Concentration**

The process of electrospinning is mainly subjected to the uniaxial expansion of the charged jet, which is greatly influenced by the polymeric solution concentration. More importantly, the concentration should be ideal for obtaining the chain texture. Up to this point, the concentration should be very high or very low, as the solution is diluted. Then the fiber will break into droplets before reaching the collector because of the influence of the surface tension, resulting in electro spraying instead of electrospinning[56]. Also, the polymer fragments can cause beaded nanofibers or beads. Increasing the concentration of the polymeric solution to the ideal level results in an increase in the chain texture. This helps to overcome the surface tension that is generated during the formation of uniform electrospun nanofibers. Although, exceeding the concentration over its critical value will prevent the solution flowing, it can eventually lead to beaded nanofibers[57]. It is also mentionable that the diameter and the length of the fibers are relative to the concentration within the ideal range [51].

#### **2.4.2.2 Viscosity**

Solution viscosity is a very significant factor due to its effect on the morphology and fiber size. The concentration is strongly affected by the viscosity of the polymer solution. In general, the viscosity increases relative to the concentration. When it is the case, very high viscosity leads to strong ejection from the solution of jets while low viscosity .surface tension is the dominant factor for the process of electrospinning and producing beaded fibers.[58] So, the ideal viscosity is desired so as to produce continuous fibers. In terms of solution parameters, polymer concentration, polymer molecular weight, and viscosity should correlate with each other.

#### **2.4.2.3 Polymer Molecular Weight**

The molecular weight of the polymer has a significant effect on the morphogenesis of the electrospun fibers due to its direct influence - with electrical and rheological properties of the electrospinning solution like conductivity, viscosity, dielectric strength and surface tension being the same as the polymer concentration [59]. With a fixed concentration, the continuous fiber cannot be formed with low molecular weight polymers. It can lead to the formation of beads instead of smooth fibers. Also, with high molecular weight, polymers are hard to produce from the spindle tip to a high viscosity and are liable to form micro-strips[58].

#### **2.4.2.4 Solution Conductivity**

The conductivity of the solution not only affects the Taylor cone formation, but also helps to regulate the fiber diameter. It depends upon the solvent type and the existence of charged ions in the solution and the polymer. To charge the surface of the droplet, the solution must be conductive or there must not be electrospinning. Making the conductivity of the solution ideal increases the surface charge of the droplet that helps to create a Taylor cone. In addition, it will reduce the diameter of the fiber[60]. Exceeding the conductivity critical level will obstruct the Taylor cone formation and the presence of an electric field will expose the fiber jet of the highly conductive solution to a higher tensile strength, resulting in an adequate extension which will further lead to the formation of beads. Previous studies stated that greater tensile forces results from a small diameter of fibers[48]. Moreover, in the strong electric field it was

discovered that the jet of highly conductive solution was extremely unstable that resulted in a wide distribution of the fiber diameter. The solution conductivity and the solution can be modified and the nanofibers can be obtained with a smaller diameter by adding sufficient ionic salts to the solution like  $\text{NaH}_2\text{PO}_4$ ,  $\text{KH}_2\text{PO}_4$  and  $\text{NaCl}$  [61].

#### **2.4.2.5 Role of Solvent**

The solvent is another determining factor that enormously affects the creation of beadless and smooth electrospun fibers. In order to choose the appropriate solvent, two basic things should be taken into consideration: the chosen solvent must fully dissolve the polymer; and the reasonable boiling point should be taken into consideration. It is necessary to avoid highly volatile or less volatile solvent as less volatile solvent restricts drying through the jet flight, furthermore solvent deposition containing fibers will form beaded nanofibers. Likewise, highly volatile solvents cause jet drying at the needle tip because of their high evaporation points and low boiling[62]. Moreover, when two solvents are dissolving a polymer, one of them acts as a non-solvent resulting in a phase separation because of their different evaporation levels. This leads further to the production of highly porous electrospun fibers [63].

#### **2.4.2.6 The Environmental Parameters**

In addition to the solution parameters and electrospinning, environmental factors like temperature and relative humidity have also gained considerable attention. It is believed that these factors affect the morphology and diameter of the electrospun fibers[62,63]. Overflowing wetness causes small pores to appear on the fibers to surface, pore merging as well as formation of beads [66]. Furthermore, the electrospinning process has been done under vacuum that created high electrical fields and hence larger fiber diameter are generated [49]. As far as the temperature is concerned, two conflicting effects appear in terms of diameter scaling for the process of electrospun fibers. First, decrease in the viscosity of the solution. Secondly, increase in the evaporation rate of the solvent. Even though these effects are somewhat conflicting in nature, they both have the same effect on the fiber in the form of reduction in its diameter [67].

## CHAPTER 3

### 3. EXPERIMENTAL STUDY

#### 3.1. Materials

Poly (ε-caprolactone) (PCL, linear, MW=80,000 g/mol). Chloroform and methanol are used as the solvents of PCL, purchased from Sigma-Aldrich (St. Louis, USA, MO). TiAl<sub>6</sub>V<sub>4</sub> is used in a cylindrical rod. The standard composition of alloy is illustrated in Table 3.1, whereas the practical steps are illustrated in Figure 3.2.

Table 3. 1 The standard composition of TiAl<sub>6</sub>V<sub>4</sub>

| Chemical composition | Percentage of chemical composition |
|----------------------|------------------------------------|
| Titanium             | ~90%                               |
| Aluminum             | ~6%                                |
| Vanadium             | ~4%                                |

#### 3.2. Pretreatment Part

In this study, ten types of specimens (PCL/TiAl<sub>6</sub>V<sub>4</sub> 120p grinded, PCL/ TiAl<sub>6</sub>V<sub>4</sub> 320p grinded, PCL/TiAl<sub>6</sub>V<sub>4</sub> 500p grinded, PCL/TiAl<sub>6</sub>V<sub>4</sub> 800p grinded, PCL/ TiAl<sub>6</sub>V<sub>4</sub> 1200p grinded, PCL/ TiAl<sub>6</sub>V<sub>4</sub> nine micron polished, PCL/ TiAl<sub>6</sub>V<sub>4</sub> three micron polished, PCL/ TiAl<sub>6</sub>V<sub>4</sub> one micron polished, PCL/ TiAl<sub>6</sub>V<sub>4</sub> OP-S polished, PCL/ TiAl<sub>6</sub>V<sub>4</sub> etched ) are prepared. The pretreatment steps are illustrated in Table 3.2.

##### 3.2.1 Cutting Stage

TiAl<sub>6</sub>V<sub>4</sub> specimens are transformed to a cylinder (10 mm x 10 mm x 2 mm) using a Struers Secotom-10 precision cutting machine, equipped with a diamond cut-off wheel from the same company. Afterwards, it was washed with distilled water, cleaned with ethanol, and air-dried.

### **3.2.2 Grinding Stage**

TiAl<sub>6</sub>V<sub>4</sub> samples are grinded mechanically with silicon carbide sheets having following specifications: p120 grit for specimen one; p120 and p320 grit for specimen two; p120, p320, and p500 grit for specimen three; p120, p320, p500, and p800 grit for specimen four; and p120, p320, p500, p800, p1200 grit for specimens five, six, seven, eight, nine and ten. Then all the samples are washed with distilled water, cleaned with ethanol, and air-dried.

### **3.2.3 Polishing Stage**

TiAl<sub>6</sub>V<sub>4</sub> specimens are polished with nine micron for specimen 6, nine micron and three micron for specimen 7, nine micron and three micron and one micron for specimens 8, 9 and 10. Then specimens 9 and 10 are handled with OP-S- polishing. Finally, all samples are washed with distilled water, cleaned with ethanol, and air-dried.

### **3.2.4 Etching Stage**

The etching is an operation to expose the microstructure of the metal by the chosen chemical. It also removes the highly deformed thin layer, which is developed during the operations of grinding and polishing. In alloys that have more than one phase, etching makes contrast between regions through differences in reflectivity or topography. This also indicates that contrast can appear in various mechanisms. The stability of the region, crystallographic orientation, and the present phase influence the rate of etching.

The specimen ten is etched carefully using 100ml distilled water, 80 ml HNO<sub>3</sub> and 10 ml HF by a cotton bud sweep on the surface for a few times to prevent over-etching. Then, the specimen is washed in alcohol and dried immediately

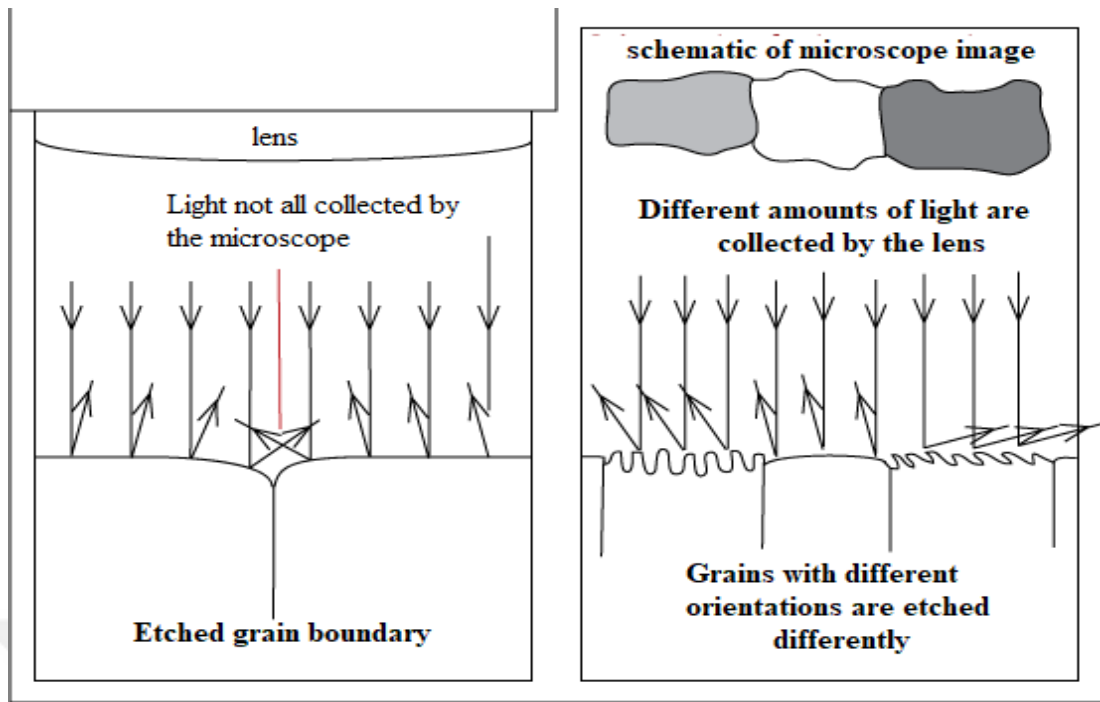


Figure 3. 1 Example of how contrast can arise [68]

Table 3. 2 The pretreatment process performed before coating the specimens

| Specimen<br>no | grinding |      |      |      |       | polishing          |                    |                    |      | ETCH |
|----------------|----------|------|------|------|-------|--------------------|--------------------|--------------------|------|------|
|                | p120     | p320 | p500 | p800 | p1200 | 9<br>$\mu\text{m}$ | 3<br>$\mu\text{m}$ | 1<br>$\mu\text{m}$ | OP-S |      |
| 1              | *        |      |      |      |       |                    |                    |                    |      |      |
| 2              | *        | *    |      |      |       |                    |                    |                    |      |      |
| 3              | *        | *    | *    |      |       |                    |                    |                    |      |      |
| 4              | *        | *    | *    | *    |       |                    |                    |                    |      |      |
| 5              | *        | *    | *    | *    | *     |                    |                    |                    |      |      |
| 6              | *        | *    | *    | *    | *     | *                  |                    |                    |      |      |
| 7              | *        | *    | *    | *    | *     | *                  | *                  |                    |      |      |
| 8              | *        | *    | *    | *    | *     | *                  | *                  | *                  |      |      |
| 9              | *        | *    | *    | *    | *     | *                  | *                  | *                  | *    |      |
| 10             | *        | *    | *    | *    | *     | *                  | *                  | *                  | *    | *    |

(\*) The process have been done

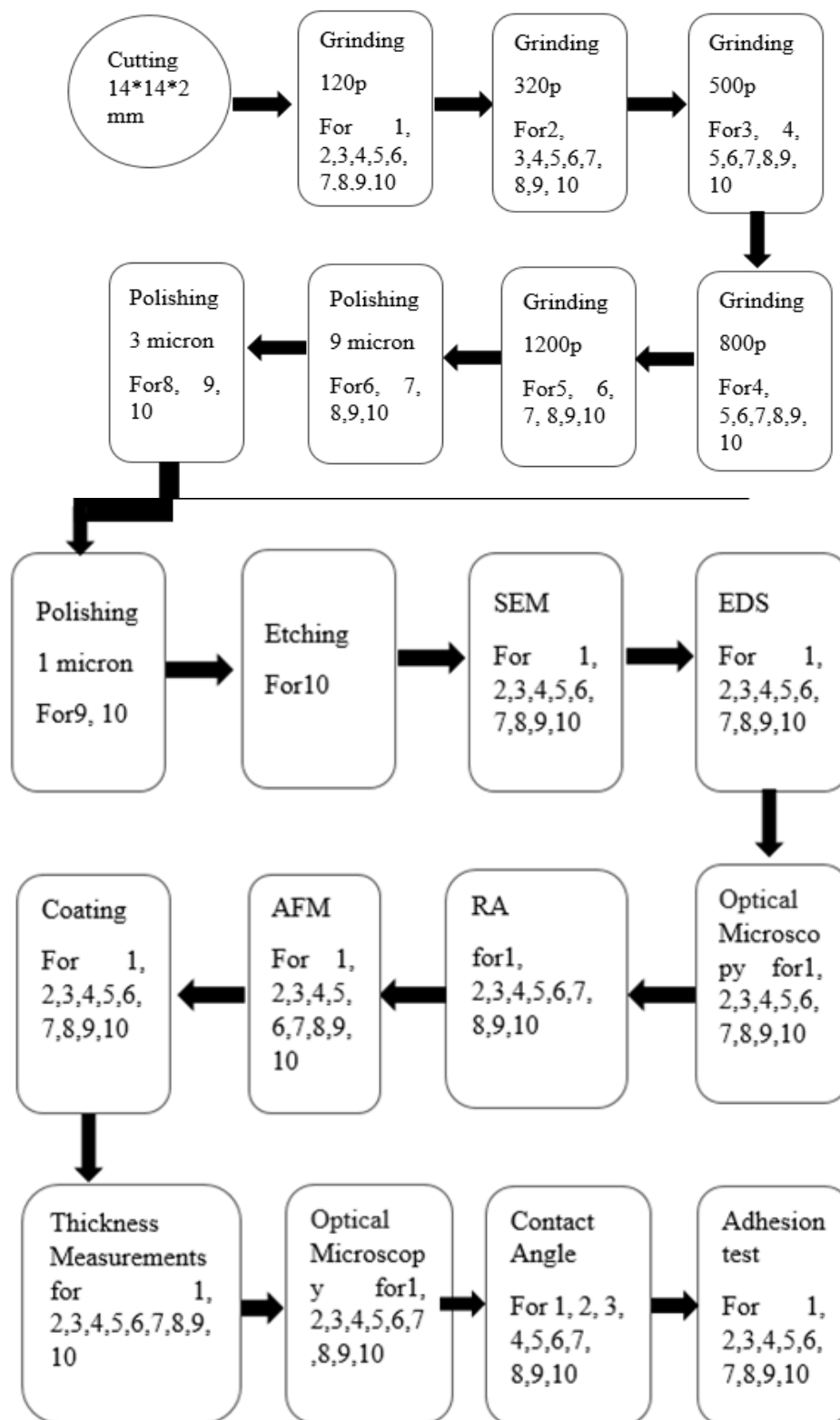


Table 3. 3 A diagram showing the practical steps of the thesis

### **3.3 Coating with PCL polymer**

The titanium alloys are coated with PCL by electrospinning process

#### **3.3.1 Preparation of the Solution**

The parameters are kept the same to that of the previous study conducted at the same laboratory [7]. The PCL was dissolved (15wt%) in the mixture prepared from chloroform/methanol (75/25 v/v) at 30 °C, and mixed for two hours.

#### **3.3.2 Operation of Electrospinning**

The electrospinning device having a single horizontal needle injector with a plastic syringe (capacity of 5ml) is used to reserve the solution. The space between the collector and the needle is specified as 13 cm. The TiAl<sub>6</sub>V<sub>4</sub> samples are put on the collector by two-sided sticky tape to coat them by coating scaffolds. Then, the liquid is fed through the concentrically arranged needle at the end, blunted to form a stable jet. Syringe pumps control the flow of the solution through the needle. The PCL scaffolds are electrospun for three hours because the titanium alloy need more time to attain the required thickness at 24 °C temperature.

### **3.4 Characterisations**

Different characterizations are performed for examine the samples before and after coating

#### **3.4.1 Surface Analysis with Scanning Electron Microscopy (SEM)**

For morphology characterisation of TiAl<sub>6</sub>V<sub>4</sub> and surface properties, SEM Carl Zeiss EVO LS15 (Oberkochen, Germany) is used with operation parameters of EHT (10-15 kV) accelerating voltage and WD (7.5-8.5 mm) working distance. Different magnifications are used for the observation, such as 250X, 500X, 1KX, 2.5KX, and 5KX. The measures are obtained using ImageJ Launcher software program.

#### **3.4.2 Optical Microscopy**

The surfaces of pretreated TiAl<sub>6</sub>V<sub>4</sub> samples are examined with optical microscope, operated under bright field illumination and at magnifications of 50x, 100x, 200x, 500x and 1000x.

### **3.4.3 Energy Dispersive Spectroscopy (EDS)**

For detecting the chemical composition of the substrates, ‘energy dispersive X-ray spectroscopy’ (EDS) technique is employed. For EDS analysis, Bruker Quantax XFlash 5010 (Billerica, MA, USA) is attached to the SEM, operating at 10 kV accelerating voltage.

### **3.4.4 Roughness Measurement (RA)**

For more quantitative analysis of surface morphology and to evaluate the roughness at the surface of implants, AFM and Ra measurements (the arithmetical deviation of the profiles) are obtained using Alicona device (BRUKER).

### **3.4.5 AFM Atomic Force Microscopy Analysis**

For obtaining three-dimensional images for the sample's surface and to determine the average roughness values, AFM analysis is used.

### **3.4.6 Thickness Measurements**

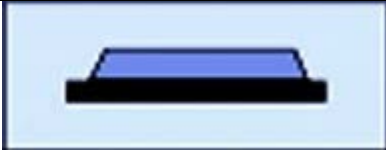
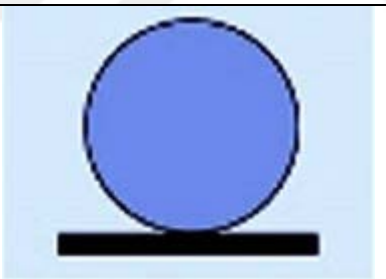
The electrospun thickness of PCL is measured by a caliper. It is also used to measure the increase in the thickness of  $\text{TiAl}_6\text{V}_4$  samples after coating.

### **3.4.7 Contact Angle Measurements**

The wettability and surface tension of the electrospun PCL/  $\text{TiAl}_6\text{V}_4$  is determined using CA contact angle goniometry - Phoenix (Suwon, South Korea) achieved by measuring the contact angle of two particular ultra-pure water points for every sample.

The CA values are measured using photographs of water drops on the top of PCL/  $\text{TiAl}_6\text{V}_4$  specimens. The same is utilised to describe the effective and fundamental surface properties of the samples and the quality of its surface to observe the roughness effect of alloy on the sample. Different situations of wetting angle are illustrated in Table 3.4.

Table 3. 4 The Situations of wetting angle [69]

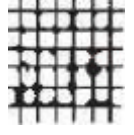
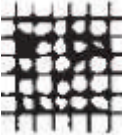
|                |                                                                                      |                    |
|----------------|--------------------------------------------------------------------------------------|--------------------|
| $\alpha = 0$   |    | spreading          |
| $\alpha < 90$  |    | Good wetting       |
| $\alpha = 90$  |    | Incomplete wetting |
| $\alpha > 90$  |   | Incomplete wetting |
| $\alpha > 180$ |  | Non wetting        |

### 3.4.8 Adhesion Test

Adhesion of the PCL to the  $\text{TiAl}_6\text{V}_4$  is determined using the crosshatch and tape pull test in accordance with the ASTM D3359 standard[70]. One test is performed for every sample by cutting the coat with a  $30^\circ$  angle cutting edge using a sharp razor blade and one-inch (25-mm) wide semi-transparent tape[71]. It is performed over three horizontal and three vertical lines, making squares of 3\*3 mm. The tape is extracted

from a side parallel to the sample after 2 min. Depending on Table 3.5, the adhesion is evaluated.

Table 3. 5 Classification of the adhesion levels [ASTM D3359]

|                       |      |                                                                                   |                                                                                   |                                                                                    |                                                                                     |                     |
|-----------------------|------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|---------------------|
| for example<br>6 cuts | None |  |  |  |  | More<br>than<br>65% |
| classification        | 5    | 4                                                                                 | 3                                                                                 | 2                                                                                  | 1                                                                                   | 0                   |

### 3.4.9 Immersion Test

First, the simulated body fluid (SBF) is prepared which has ion concentration similar to the concentrations in the blood with the bioactivity of synthetic materials resulting in the formation of apatite on substrates. The ions of SBF that has been used are in Table 3. 6.

Table 3. 6 The ions of simulated body fluid.

| Ion          | Concentration /m M |
|--------------|--------------------|
| $K^+$        | 5                  |
| $Na^+$       | 142                |
| $Mg^{2+}$    | 1.5                |
| $Ca^{2+}$    | 2.5                |
| $Cl^-$       | 103                |
| $HCO_3^-$    | 10                 |
| $Hpo_4^{2-}$ | 1                  |
| $So_4^{2-}$  | 0.5                |

At the first stage, HEPES is disbanded in 100 mL of 0.2M-NaOH aqueous. Then, 700 mL of ultra-pure water is used from a polypropylene beaker at 36.5 °C, and the reagents are put in the water and dissolved as in Table 3.7.

Table 3. 7 Amounts of reagents that have been used for preparing SBF [72]

| reagents                                           | Amounts   |
|----------------------------------------------------|-----------|
| NaCl                                               | 5.403 g   |
| NaHCO <sub>3</sub>                                 | 0.504 g   |
| Na <sub>2</sub> CO <sub>3</sub>                    | 0.426 g   |
| KCl                                                | 0.225 g   |
| K <sub>2</sub> HPO <sub>4</sub> .3H <sub>2</sub> O | 0.230 g   |
| MgCl <sub>2</sub> . 6H <sub>2</sub> O              | 0.311 g   |
| 0.2 M --NaOH                                       | 100 mLg   |
| HEPES <sup>b</sup>                                 | 17.892 gg |
| CaCl <sub>2</sub>                                  | 0.293 g   |
| Na <sub>2</sub> SO <sub>4</sub>                    | 0.072 g   |
| 1.0 M--NaOH                                        | 15 mL     |

After SBF preparation, the four samples (1200 grinded, etched, coated one and an untreated one) are placed in 250 mL SBF at  $37.5 \pm 0.2$  °C. After that, the samples are characterised by SEM and EDS. The steps of the immersion test are illustrated in Table 3.8.

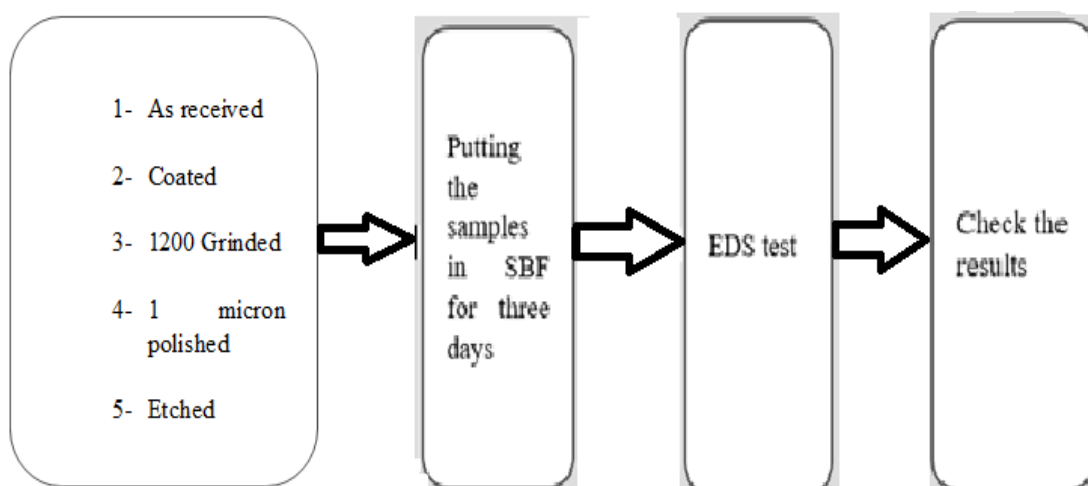


Table 3. 8 A diagram showing the immersion test steps.

## CHAPTER 4

### 4. RESULTS AND DISCUSSION

#### 4.1 Characterisations of the Titanium Alloy before Coating

The characterization of the Ti-alloy before coating is investigated in this section.

##### 4.1.1 Scanning Electron Microscope SEM Examinations.

The real topography of titanium alloy samples after treatment are shown in Figure 4.1. The changes observed in different images are a result of grinding, polishing, etching operation, and the characteristic dales of different geometry. The figures also indicate that the major smears or the grinding cracks are created on the grinded samples during the process. While the smears start to become less apparent or even disappear in the polished samples are a result of loose abrasive operations. This demonstrated the surface morphology of different pretreatment for  $\text{TiAl}_6\text{V}_4$ . moreover, the change in the microstructure for the etched sample after modifying it with the chemical solution ( 100ml distilled water, 80 ml  $\text{HNO}_3$  and 10 ml HF) can be noticed clearly[68,69].

##### 4.1.2 Energy Dispersive Spectrometry EDS Test

The elements on the surface of titanium alloy are determined by using EDS to confirm the composition of the alloy i.e., 90%/6%/4% wt. This also help to confirm the absence of any other elements that have been attached to them during treatment [70,71].

Figures 4.1 to 4.10 show the percentages of elements on the surface of the specimens, whereas Tables 4.1 to 4.10 indicate that the samples are free from any other elements. It should be noted that the measurement obtained are within the detection limits of the EDS technique. For most cases, EDS cannot detect trace elements, i.e. elements smaller than 1 wt.%.

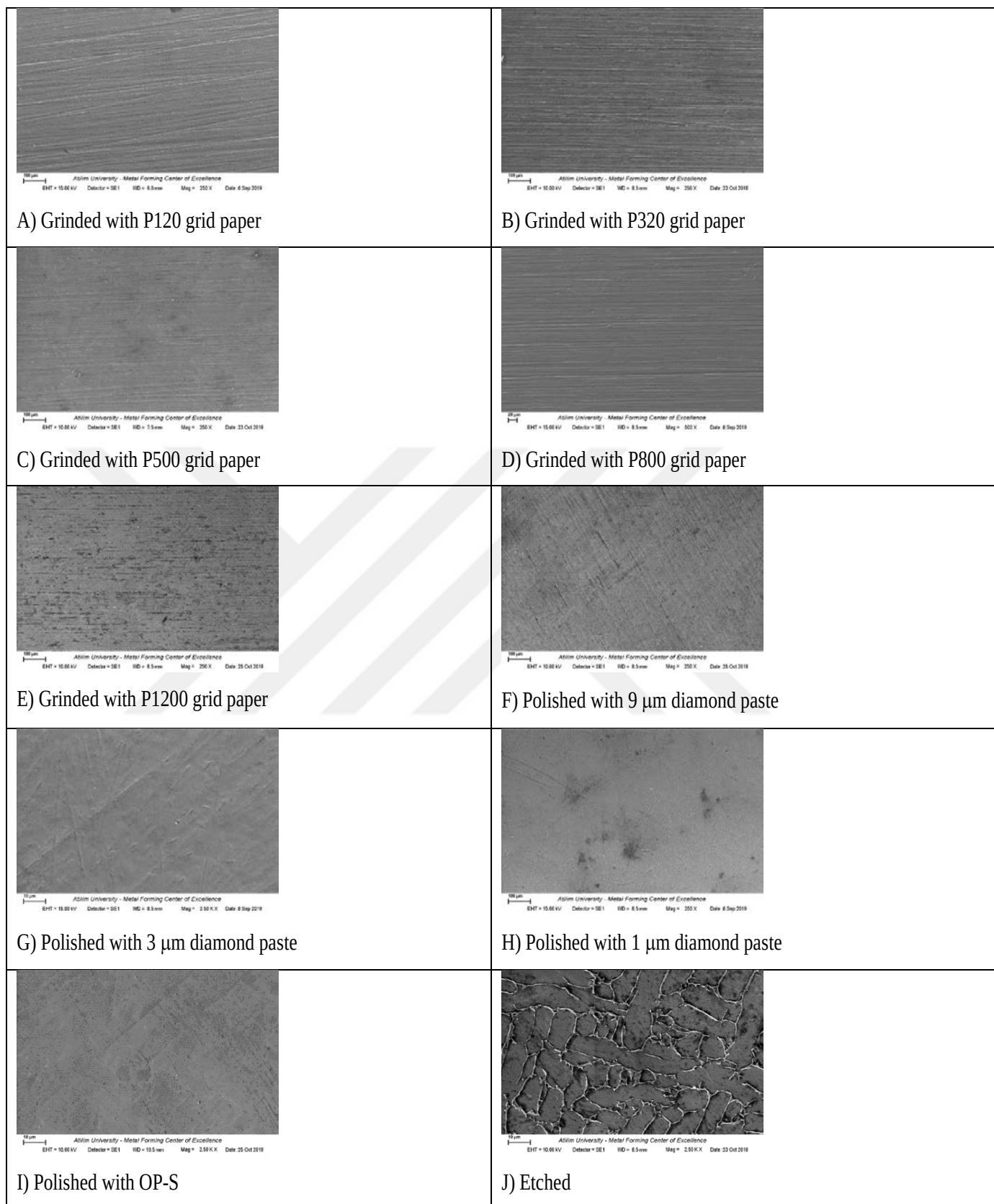


Figure 4. 1 SEM micrographs of  $\text{TiAl}_6\text{V}_4$  samples

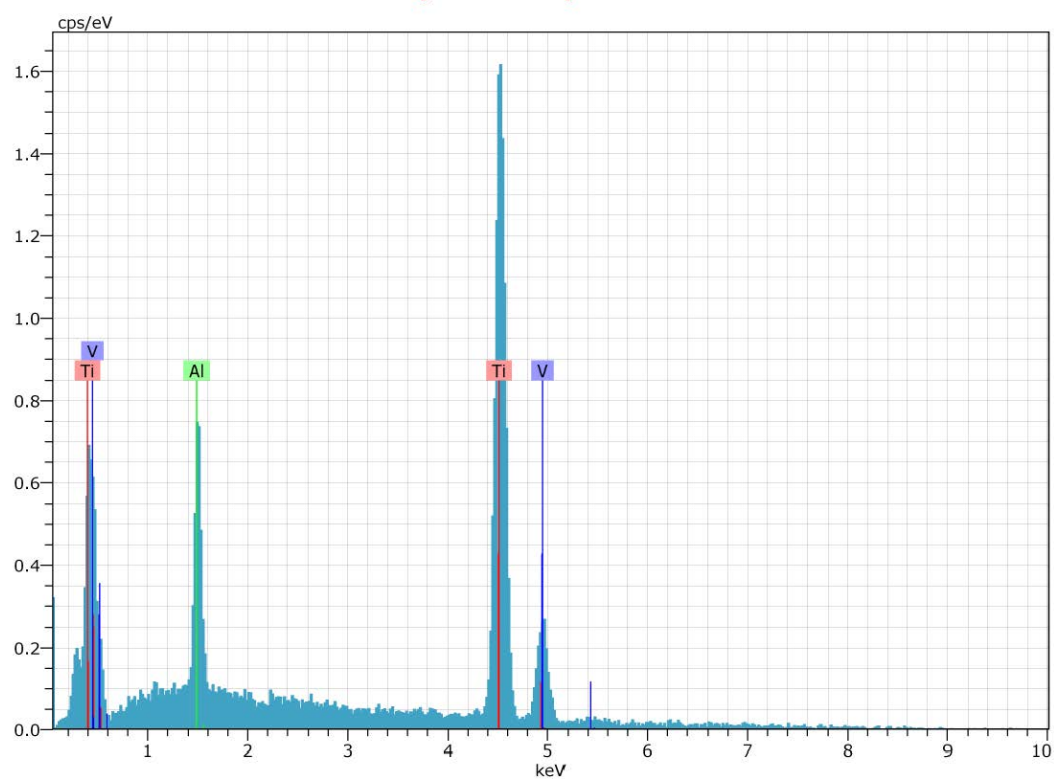


Figure 4. 2 EDS analysis of sample grinded with P120 grid paper

Table 4. 1 Percentage of elements in sample grinded with P120 grid paper

| Elements | Atomic Number | series   | Unn. C (wt %) | Norm. C (wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 82.17         | 89.43          | 86.32          | 6.8       |
| V        | 23            | K-series | 5.04          | 5.49           | 4.98           | 3.4       |
| Al       | 13            | K-series | 4.67          | 5.08           | 8.70           | 0.3       |

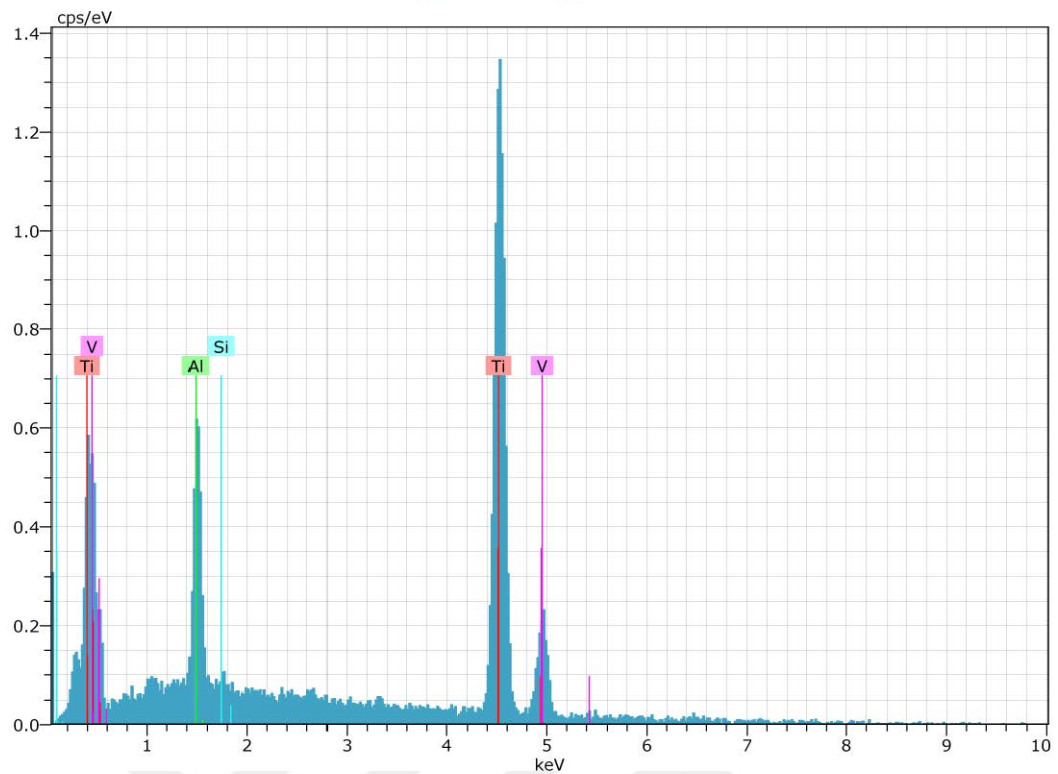


Figure 4. 3 EDS analysis of sample grinded with P320 grid paper

Table 4. 2 Percentage of elements in sample grinded with P320 grid paper

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 85.27         | 88.83          | 85.29          | 7.3       |
| V        | 23            | K-series | 5.15          | 5.37           | 4.84           | 3.5       |
| Al       | 13            | K-series | 5.32          | 5.54           | 9.44           | 0.3       |
| Si       | 14            | K-series | 0.25          | 0.26           | 0.42           | 0.1       |

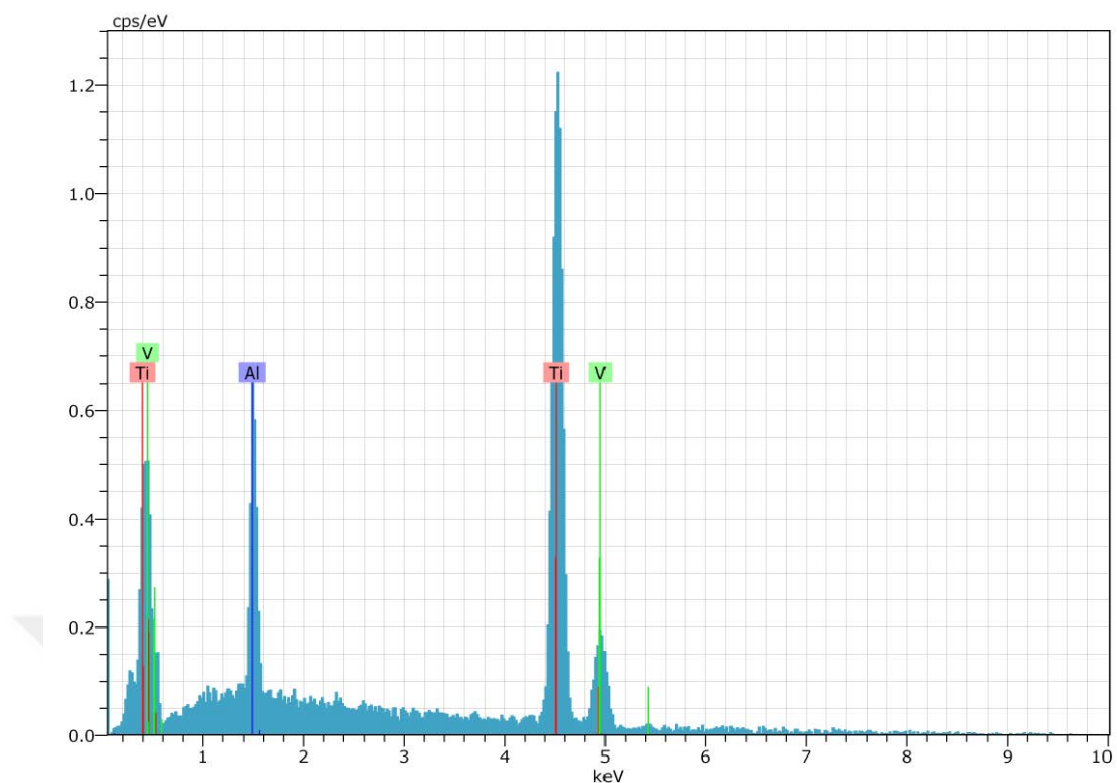


Figure 4. 4 EDS analysis of sample grinded with P500 grid paper

Table 4. 3 Percentage of elements in sample grinded with P500 grid paper

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 82.96         | 90.70          | 87.11          | 7.0       |
| V        | 23            | K-series | 3.37          | 3.68           | 9.57           | 0.3       |
| Al       | 13            | K-series | 5.13          | 5.61           | 3.32           | 2.3       |

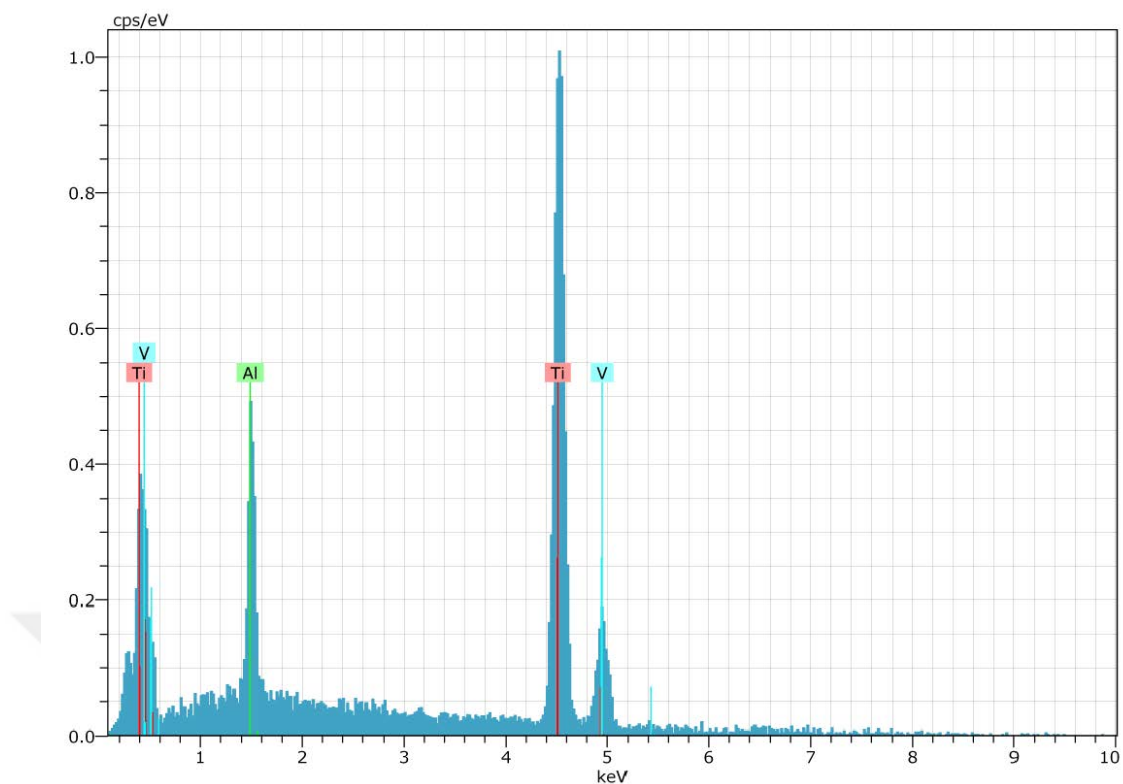


Figure 4. 5 EDS analysis of sample grinded with P800 grid paper

Table 4. 4 Percentage of elements in sample grinded with P800 grid paper

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 83.88         | 88.20          | 85.00          | 7.9       |
| V        | 23            | K-series | 6.12          | 6.43           | 5.82           | 4.1       |
| Al       | 13            | K-series | 5.10          | 5.36           | 9.17           | 0.3       |

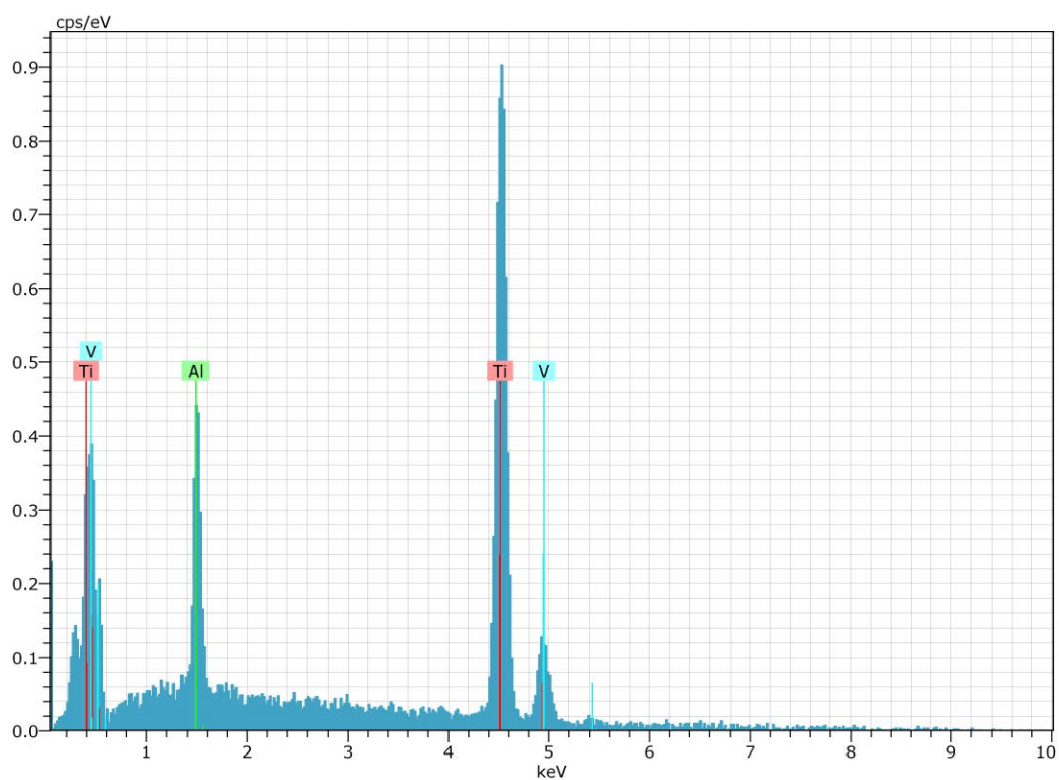


Figure 4. 6 EDS analysis of sample grinded with P1200 grid paper

Table 4. 5 Percentage of elements in sample grinded with P1200 grid paper

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 79.44         | 90.24          | 86.58          | 7.4       |
| Al       | 13            | K-series | 5.08          | 5.77           | 9.82           | 0.3       |
| V        | 23            | K-series | 3.51          | 3.99           | 3.60           | 2.4       |

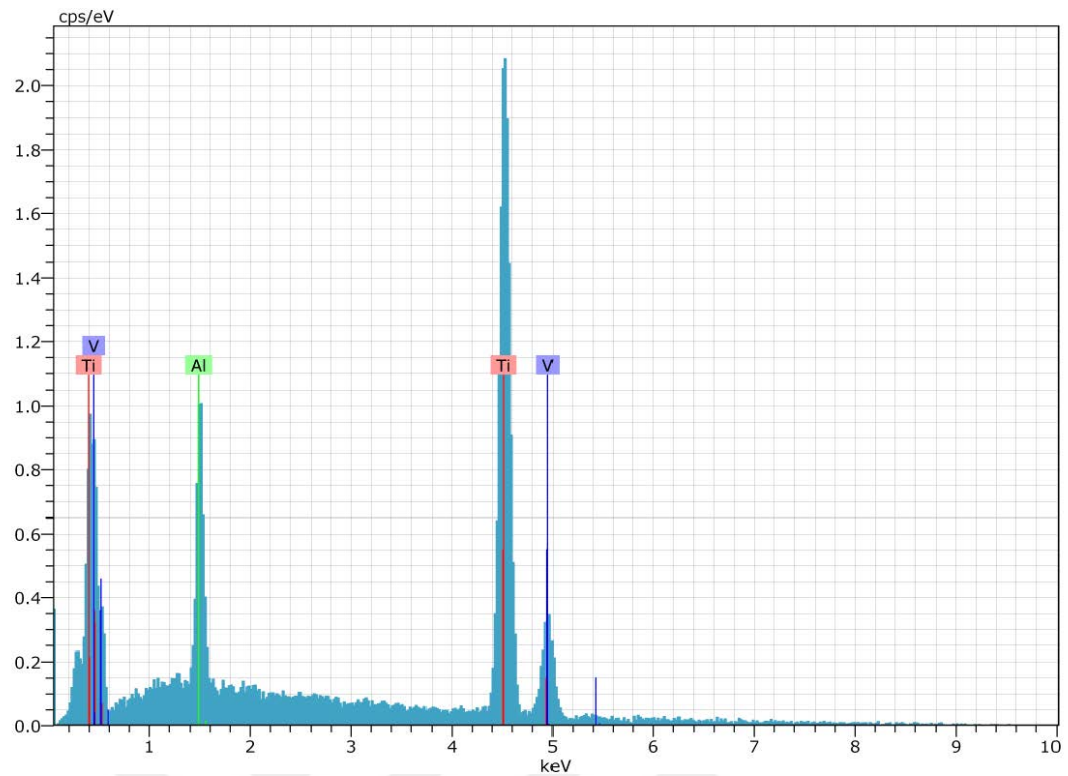


Figure 4. 7 EDS analysis of sample polished with 9  $\mu\text{m}$  diamond paste.

Table 4. 6 EDS analysis of sample polished with 9  $\mu\text{m}$  diamond paste.

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 84.13         | 90.16          | 86.68          | 6.0       |
| V        | 23            | K-series | 4.02          | 4.31           | 3.89           | 0.3       |
| Al       | 13            | K-series | 5.13          | 5.53           | 9.43           | 2.7       |

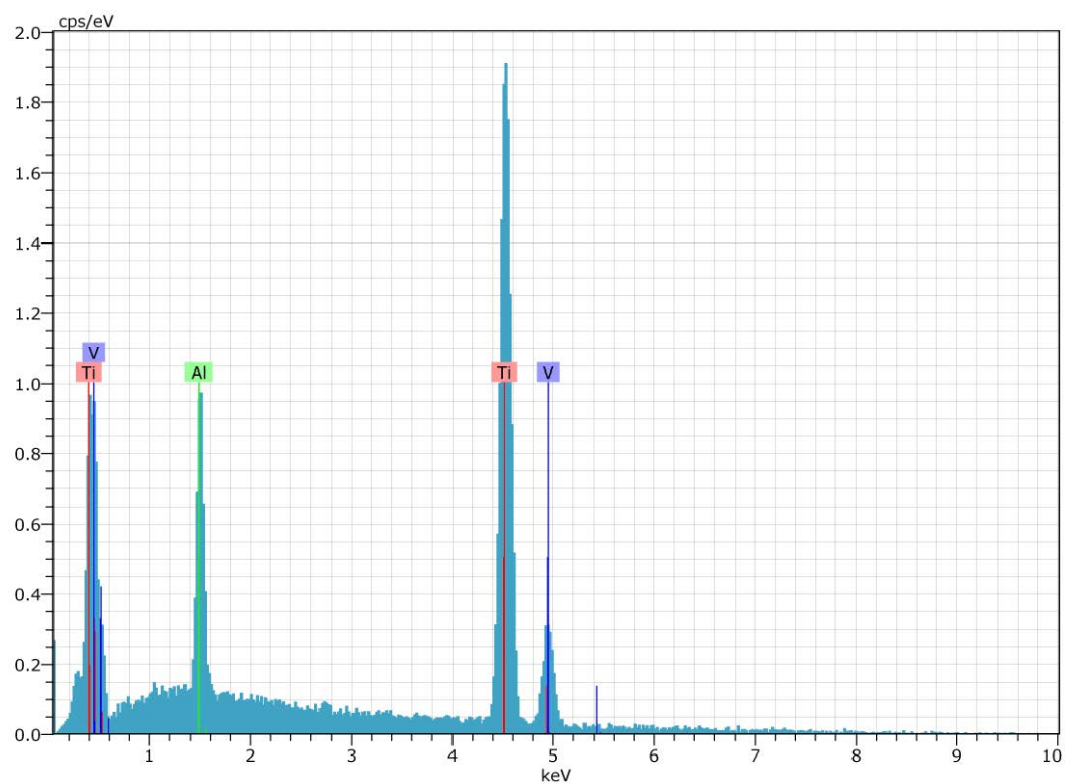


Figure 4. 8 EDS analysis of sample polished with 3  $\mu\text{m}$  diamond paste.

Table 4. 7 EDS analysis of sample polished with 3  $\mu\text{m}$  diamond paste.

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 86.52         | 89.98          | 86.20          | 6.4       |
| Al       | 13            | K-series | 5.75          | 5.98           | 10.16          | 0.3       |
| V        | 23            | K-series | 3.86          | 4.04           | 3.64           | 2.6       |

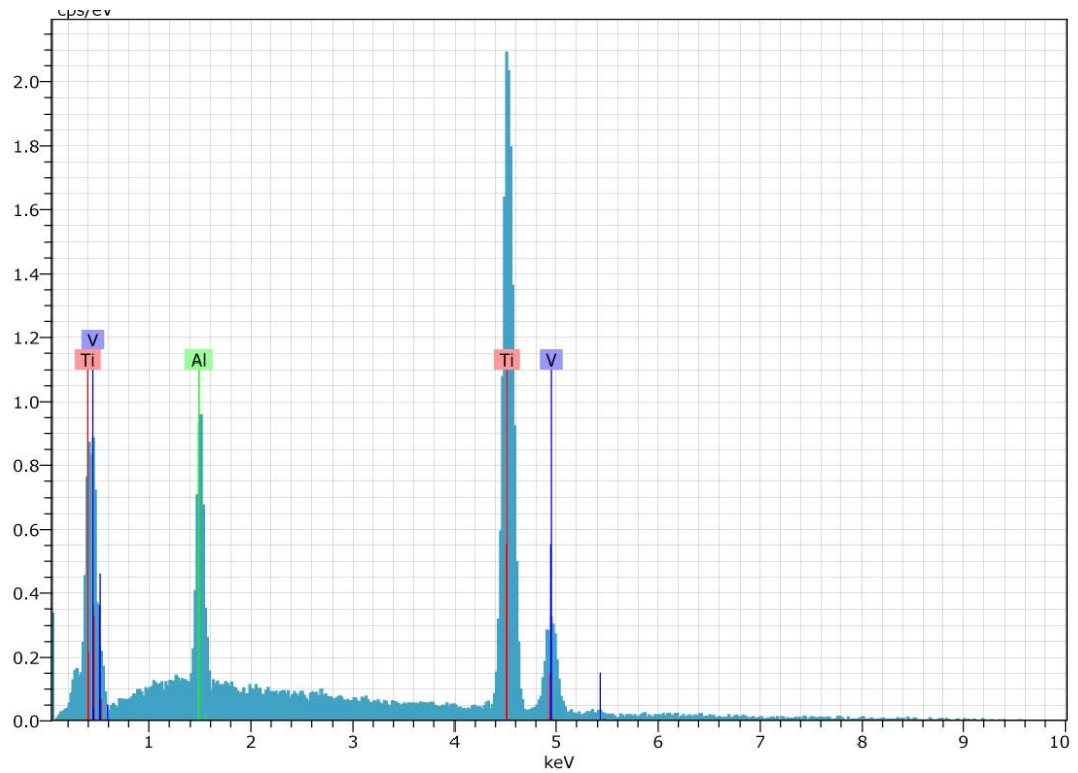


Figure 4. 9 EDS analysis of sample polished with 1  $\mu\text{m}$  diamond paste.

Table 4. 8 EDS analysis of sample polished with 1  $\mu\text{m}$  diamond paste.

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 87.44         | 89.99          | 86.57          | 6.4       |
| Al       | 13            | K-series | 5.30          | 5.46           | 9.31           | 0.3       |
| V        | 23            | K-series | 4.43          | 4.55           | 4.12           | 3.0       |

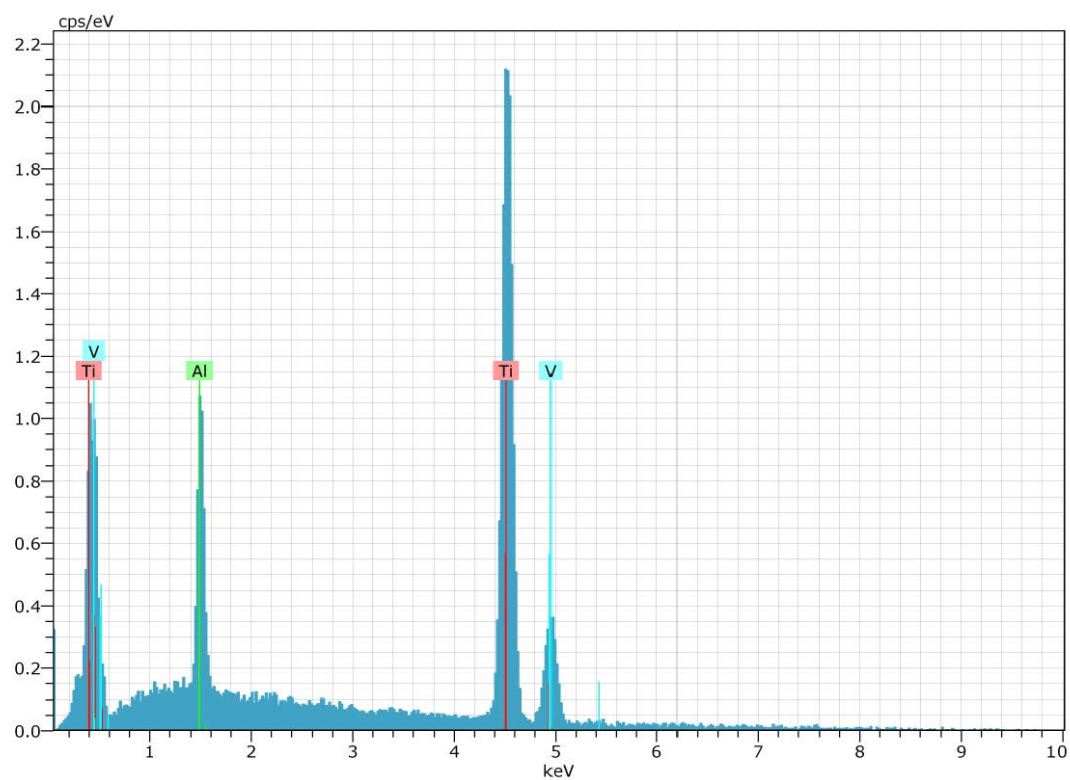


Figure 4. 10 EDS analysis of sample polished with OP-S solution

Table 4. 9 Percentage of elements in sample polished with OP-S

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 91.24         | 89.35          | 85.92          | 6.6       |
| Al       | 13            | K-series | 5.66          | 5.55           | 9.47           | 0.3       |
| V        | 23            | K-series | 5.21          | 5.10           | 4.61           | 3.5       |

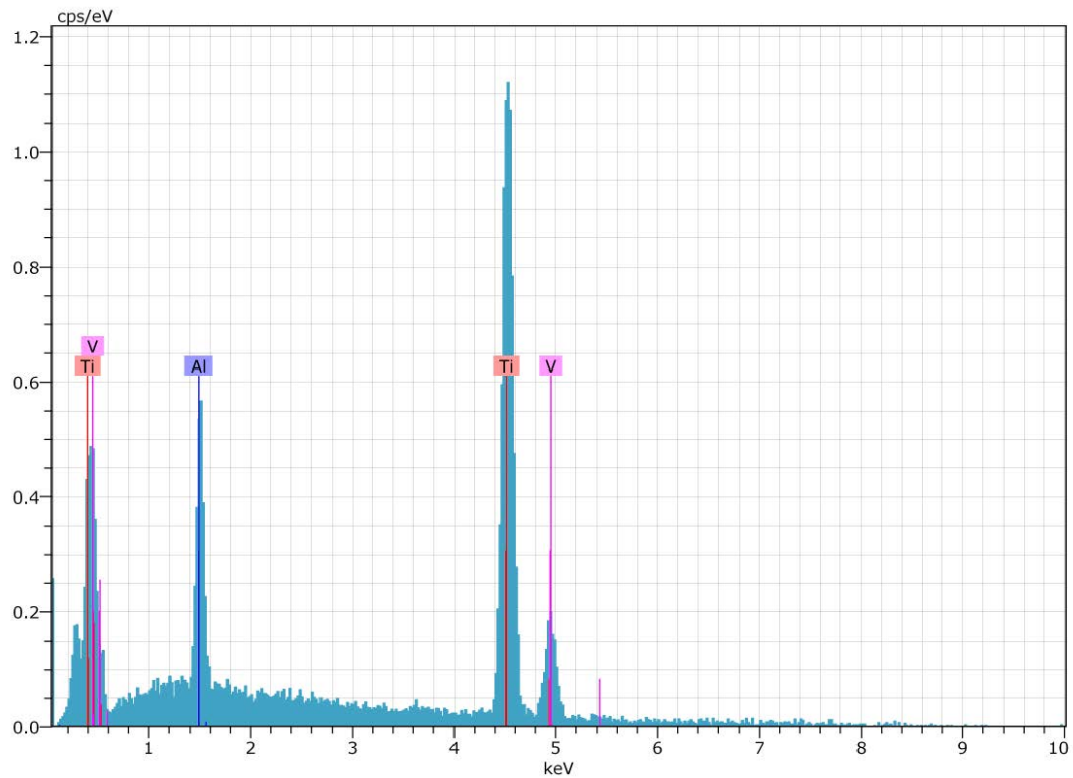


Figure 4. 11 EDS analysis of sample etched with 100ml distilled water, 80 ml HNO<sub>3</sub>, and 10 ml solution.

Table 4. 10 Percentage of elements in sample etched with 100ml distilled water, 80 ml HNO<sub>3</sub>, and 10 ml HF

| Elements | Atomic Number | series   | Unn. C (Wt %) | Norm. C (Wt %) | Atom. C (at %) | Error (%) |
|----------|---------------|----------|---------------|----------------|----------------|-----------|
| Ti       | 22            | K-series | 85.14         | 88.41          | 84.99          | 7.7       |
| V        | 23            | K-series | 5.72          | 5.94           | 5.37           | 3.9       |
| Al       | 13            | K-series | 5.44          | 5.65           | 9.64           | 0.3       |

#### 4.1.3 Optical Microscope

To get the satisfactory and comprehensive results, surface analysis is performed using optical microscope. The optical micrographs of titanium alloy microstructure after grinding, polishing, and etching are displayed in Figure 4.11. The micrograph in the figure exhibits in detail the changes in the surface microstructure after etching, which results from the effect of distilled water, HNO<sub>3</sub>, and HF.

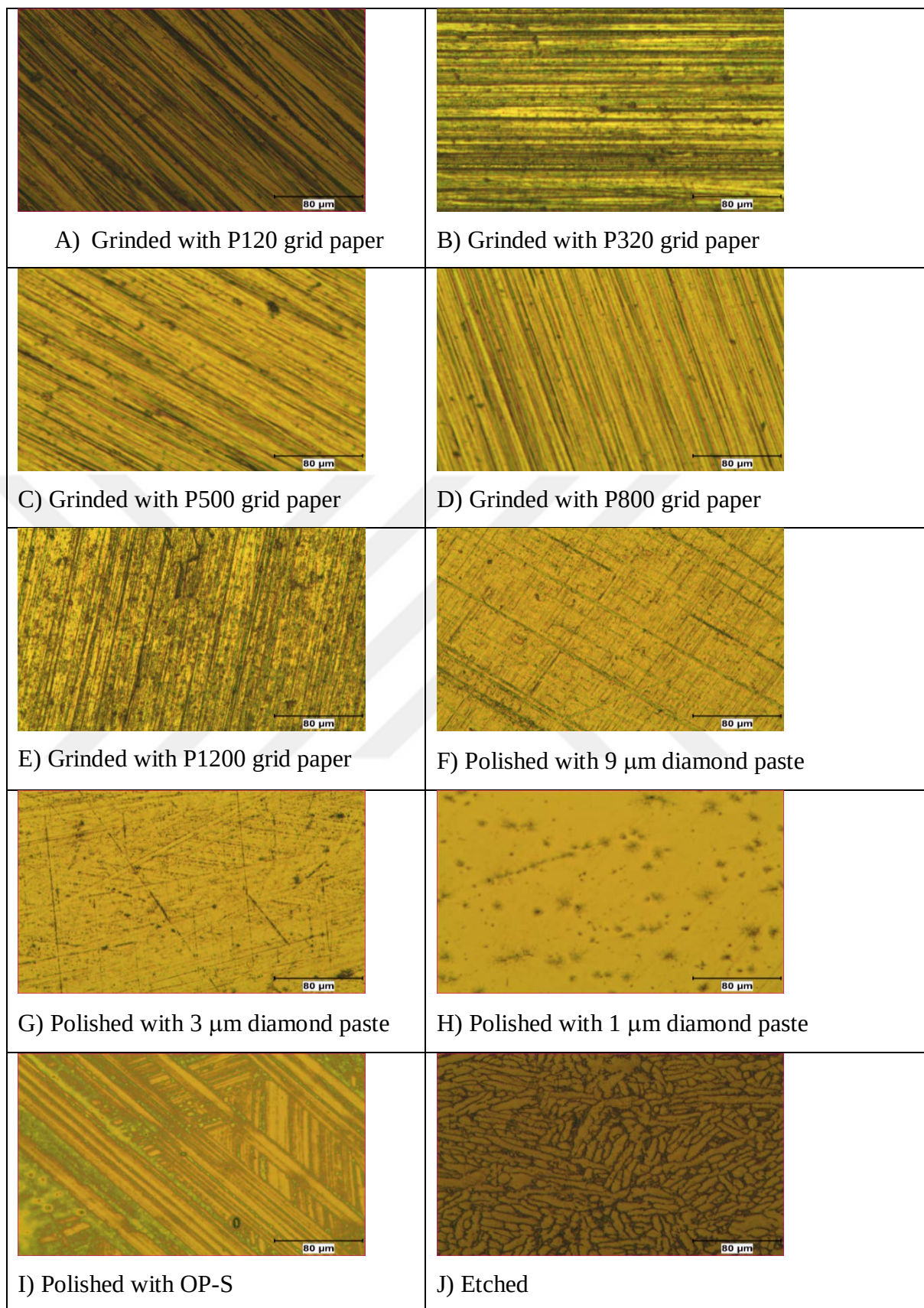


Figure 4. 12 optical micrographs of the  $\text{TiAl}_6\text{V}_4$  samples

#### 4.1.4 Atomic Force Microscopy (AFM) and Roughness Measurements

The mean values of roughness for the different pre-treated samples of titanium alloy are shown in Table 4.11. The results from AFM analysis on all the samples are displayed in the Figure 4.14 - 4.23. All parameters indicate the variation in surface texture or topography. It is evident from the Table 4.11 that the highest mean value of 0.56 is obtained for the sample 120 grinding  $\text{TiAl}_6\text{V}_4$

The roughness profile parameter ( $R_a$ ) for the second grinding stage is found to be 0.28, and this value is close to the roughness parameter from the first grinding stage for  $\text{TiAlSiZr}$  alloy which is 0.25. It can be stated that every sample has some similarity characteristics. This value decreased to 0.11 for  $\text{TiAl}_6\text{V}_4$  after the third stage as it was expected. For  $\text{TiAlSiZr}$  alloy, this value increased to 0.43, which is quite unexpected, mainly due to the chemical reactions taking place and damage in the machined surface.

At sample 800 grinding  $\text{TiAl}_6\text{V}_4$  increased merely by 2 micron. This increase is small and is considered normal because of the clogged up some of the active face of the grinding wheel[77].

The least value for  $\text{TiAl}_6\text{V}_4$  is obtained for the sample 3-micron polishing, which is 0.05. This value is closer to that of the  $\text{TiAlSiZr}$  alloy polishing, which is 0.03 [77].

The mean value for the samples 1200 grinding  $\text{TiAl}_6\text{V}_4$  and Etch  $\text{TiAl}_6\text{V}_4$  is 0.07. These samples are the best samples in adhesion, and maybe this roughness value is appropriate for miscibility with electrospun PCL.

The mean value for electrospun PCL is 3  $\mu\text{m}$  and this level of roughness is more than that of titanium alloy, which provides space for bone attachment and subsequently increases cellular proliferation[73,10].

After the first treatment with 120 p grinding, the surface exhibited parallel, distinct, and uniform distributed traces of machining. The maximum peak reaches two microns and the depth of valleys exceeded -2 micron. This is similar to the grinding of  $\text{TiAlSiZr}$  alloy, while in  $\text{TiAlSiZr}$  alloy the average height of peaks did not exceed 1.0 micron due to the different kind of alloys[77].

Table 4. 11 the Surfaces roughness of the samples

| Sample type                                         | Surfaces roughness (profiles arithmetical deviation ) |
|-----------------------------------------------------|-------------------------------------------------------|
| 120 grinding TiAl <sub>6</sub> V <sub>4</sub>       | 0.56                                                  |
| 320 grinding TiAl <sub>6</sub> V <sub>4</sub>       | 0.28                                                  |
| 500 grinding TiAl <sub>6</sub> V <sub>4</sub>       | 0.11                                                  |
| 800 grinding TiAl <sub>6</sub> V <sub>4</sub>       | 0.13                                                  |
| 1200 grinding TiAl <sub>6</sub> V <sub>4</sub>      | 0.07                                                  |
| 9 micron polishing TiAl <sub>6</sub> V <sub>4</sub> | 0.08                                                  |
| 3 micron polishing TiAl <sub>6</sub> V <sub>4</sub> | 0.05                                                  |
| 1 micron polishing TiAl <sub>6</sub> V <sub>4</sub> | 0.08                                                  |
| OP-S polishing TiAl <sub>6</sub> V <sub>4</sub>     | 0.13                                                  |
| Etch TiAl <sub>6</sub> V <sub>4</sub>               | 0.07                                                  |

After the second treatment with 320 p grinding, the sample exhibited more of parallel, distinct, and uniformly distributed traces of machining. The maximum peak did not exceed 1.5 microns and the depth of valleys remained less than -1.5 micron

After the third treatment, measures show high depression. The transition in the metal texture of the treated surface is also observed. The large, parallel machining effects consequence of preliminary grinding are removed. This is close to the second grinding operation for TiAlSiZr alloy; lesser depth of 0.5 micron and lesser peak of 0.7 micron is obtained for TiAl<sub>6</sub>V<sub>4</sub> alloy[77].

After the fourth treatment, measures exhibit that the peak do not exceed 0.5 microns and the depth of valleys do not exceed 0.5 microns.

After the fifth treatment with 1200 p grinding, measures show more fall in the high depression that the peak fell to about 0.2 microns and depth to about -0.3 micron

After three polishing operations 9, 3, and 1 micron are featured by less densely distributed valleys. The depth is less than 0.25 and the approximate peak is 0.3, and this is the same for TiAlSiZr alloy which is 0.25[77]. Except small anomalies noticed

in the sample of 1-micron, that caused one of the highest peaks are more than 1.5 micron.

Compare results with TiAlSiZr alloy proving that the pretreatment operations are performed in the right way.

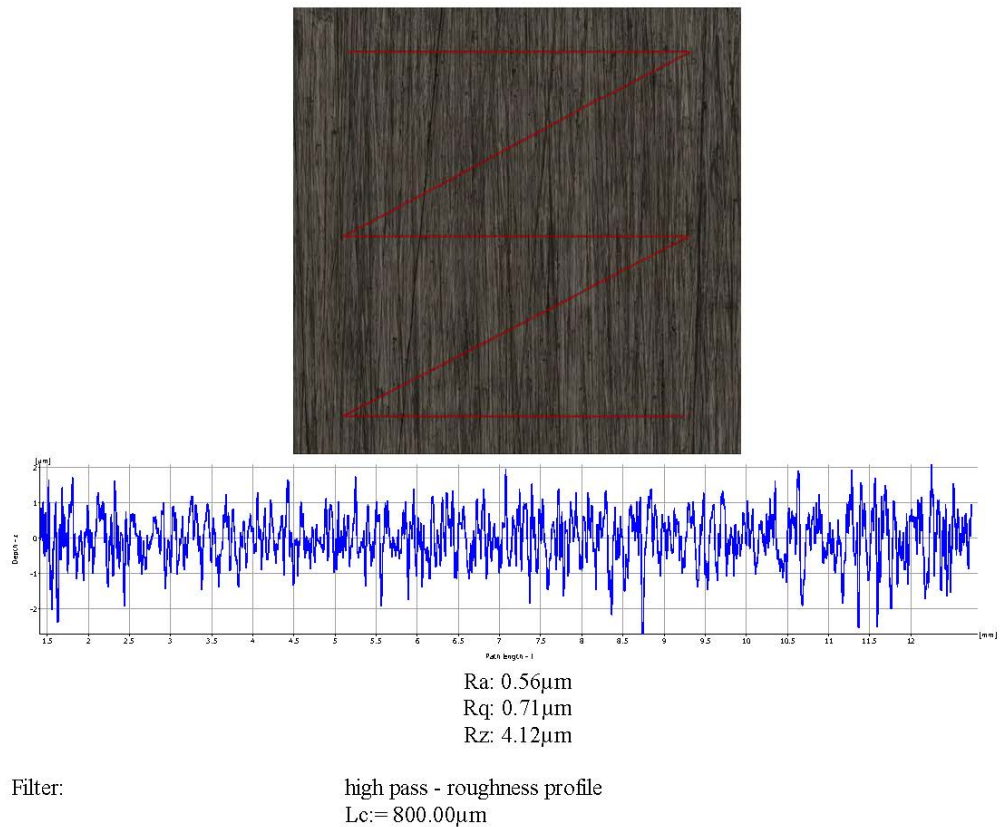


Figure 4. 13 Profile measurement of the sample grinded with P120 grid paper, showing the optical micrograph of the position of measurement and the roughness profile.

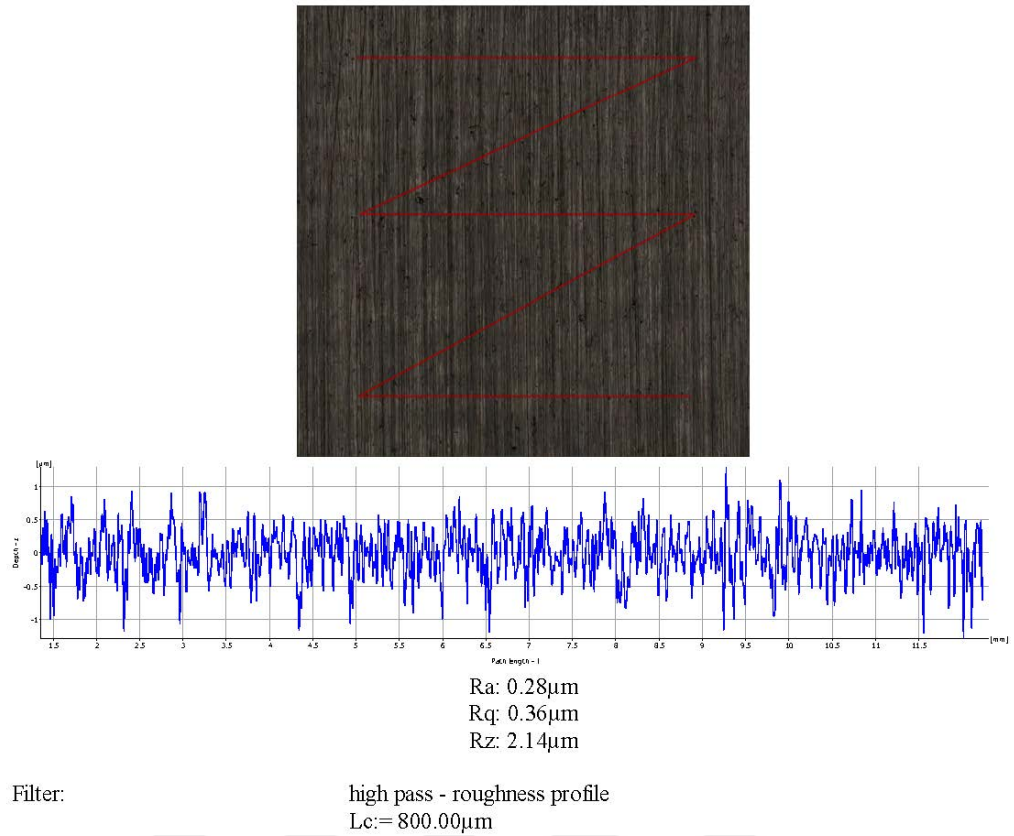


Figure 4. 14 Profile measurement of the sample grinded with P320 grid paper, showing the optical micrograph of the position of measurement and the roughness profile.

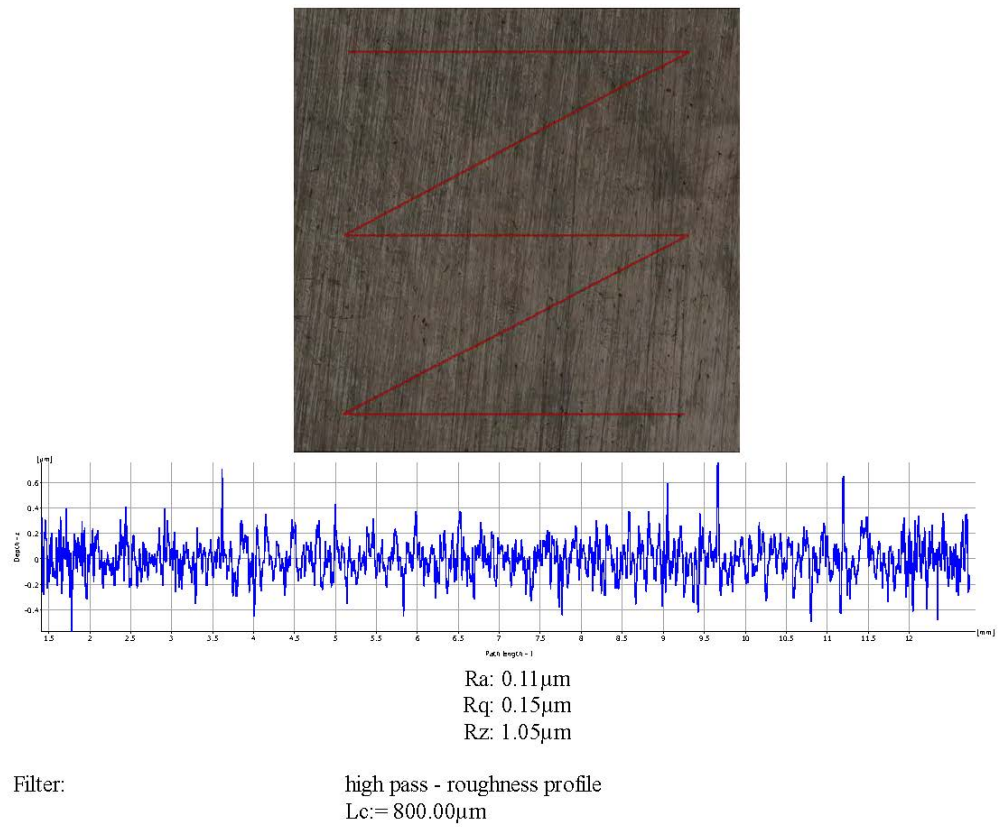


Figure 4. 15 Profile measurement of the sample grinded with P500 grid paper, showing the optical micrograph of the position of measurement and the roughness profile.

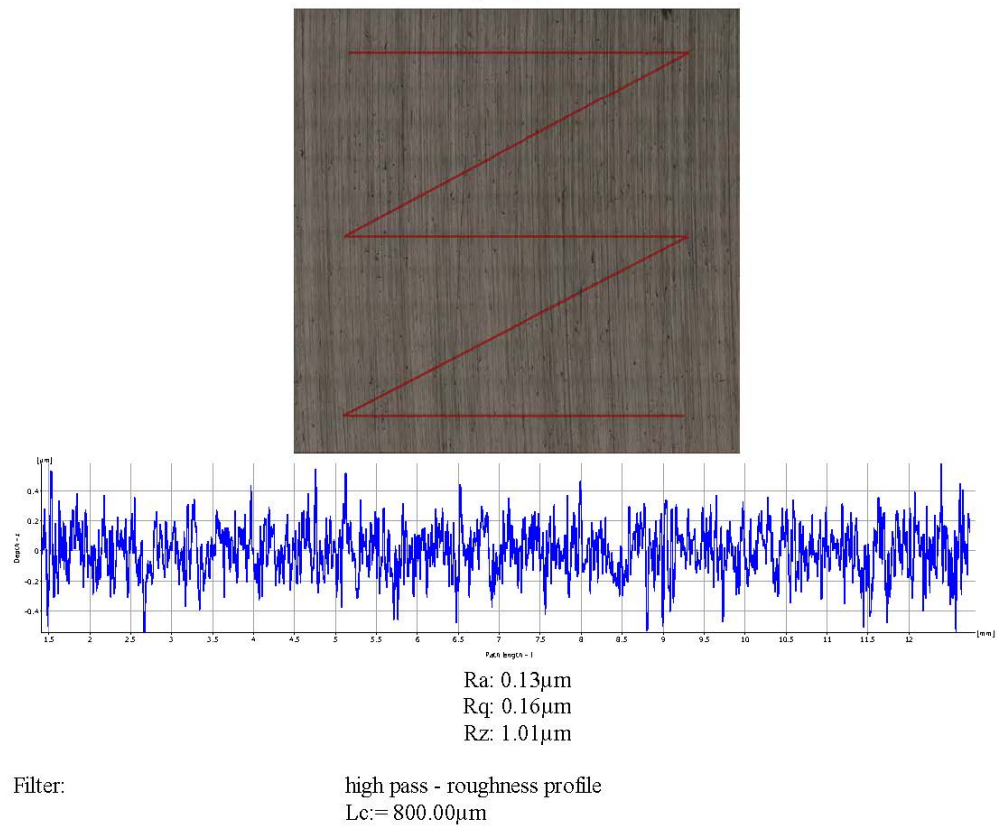


Figure 4. 16 Profile measurement of the sample grinded with P800 grid paper, showing the optical micrograph of the position of measurement and the roughness profile.

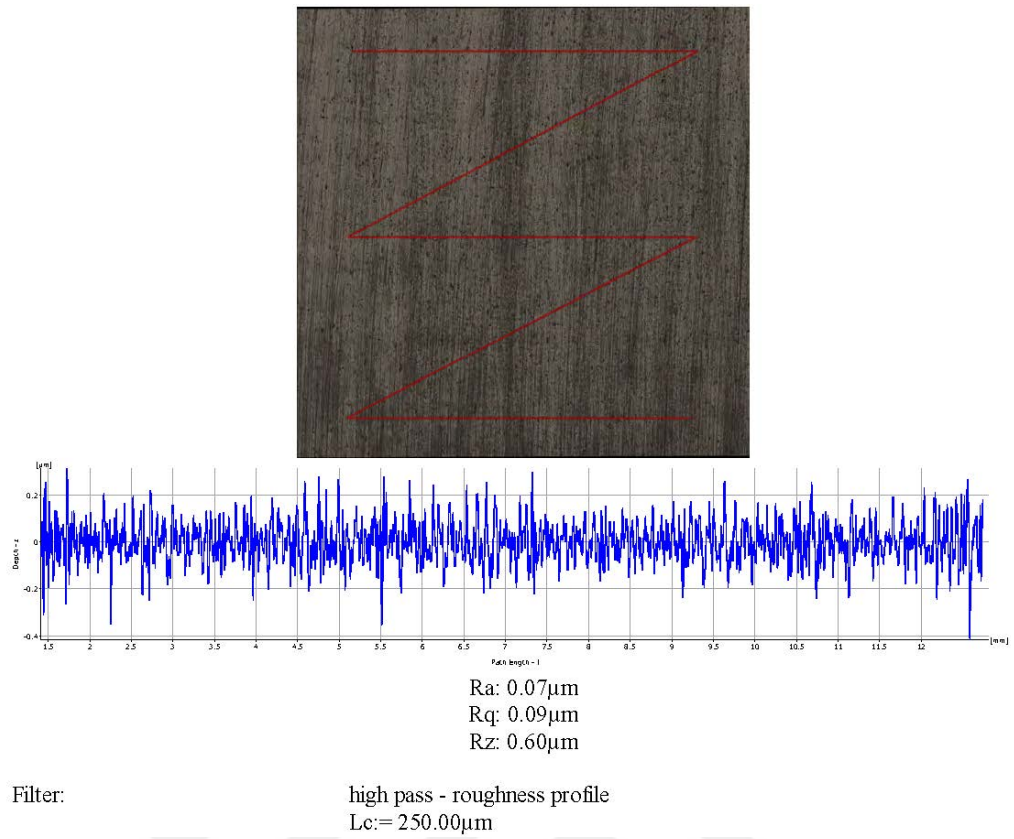


Figure 4. 17 Profile measurement of the sample grinded with P1200 grid paper, showing the optical micrograph of the position of measurement and the roughness profile.

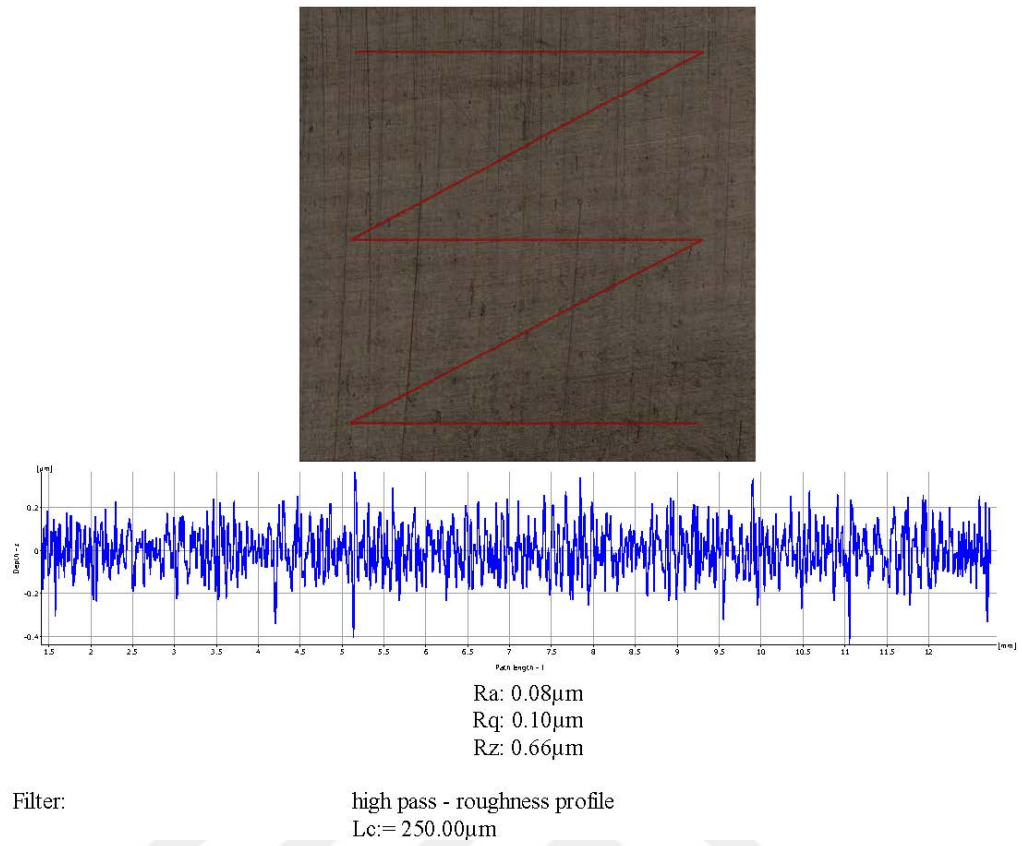


Figure 4. 18 Profile measurement of the sample polished with 9 μm diamond paste, showing the optical micrograph of the position of measurement and the roughness profile.

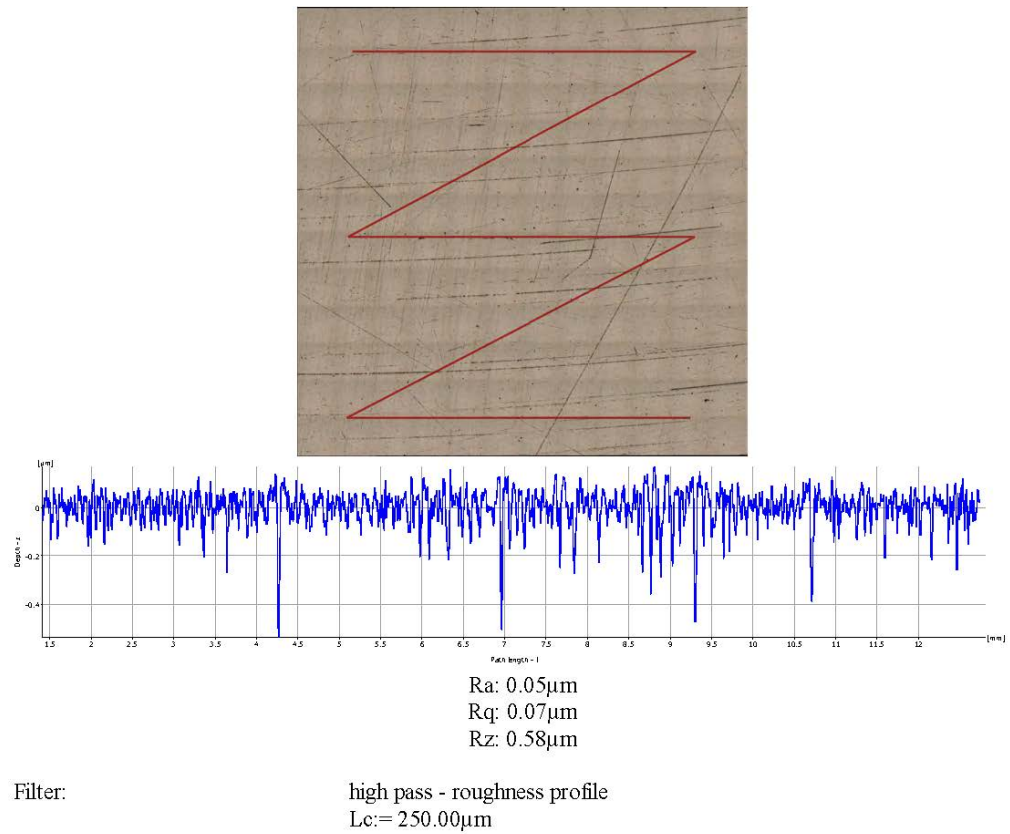


Figure 4. 19 Profile measurement of the sample polished with 3 μm diamond paste, showing the optical micrograph of the position of measurement and the roughness profile.

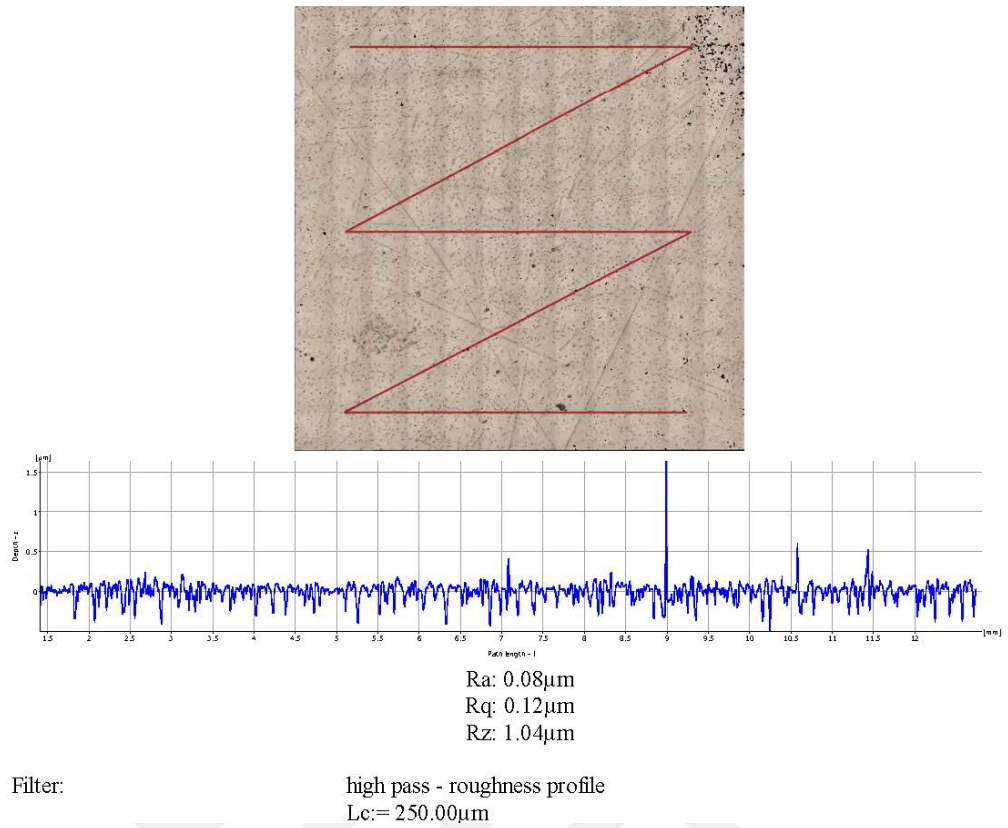


Figure 4. 20 Profile measurement of the sample polished with 1  $\mu\text{m}$  diamond paste, showing the optical micrograph of the position of measurement and the roughness profile.

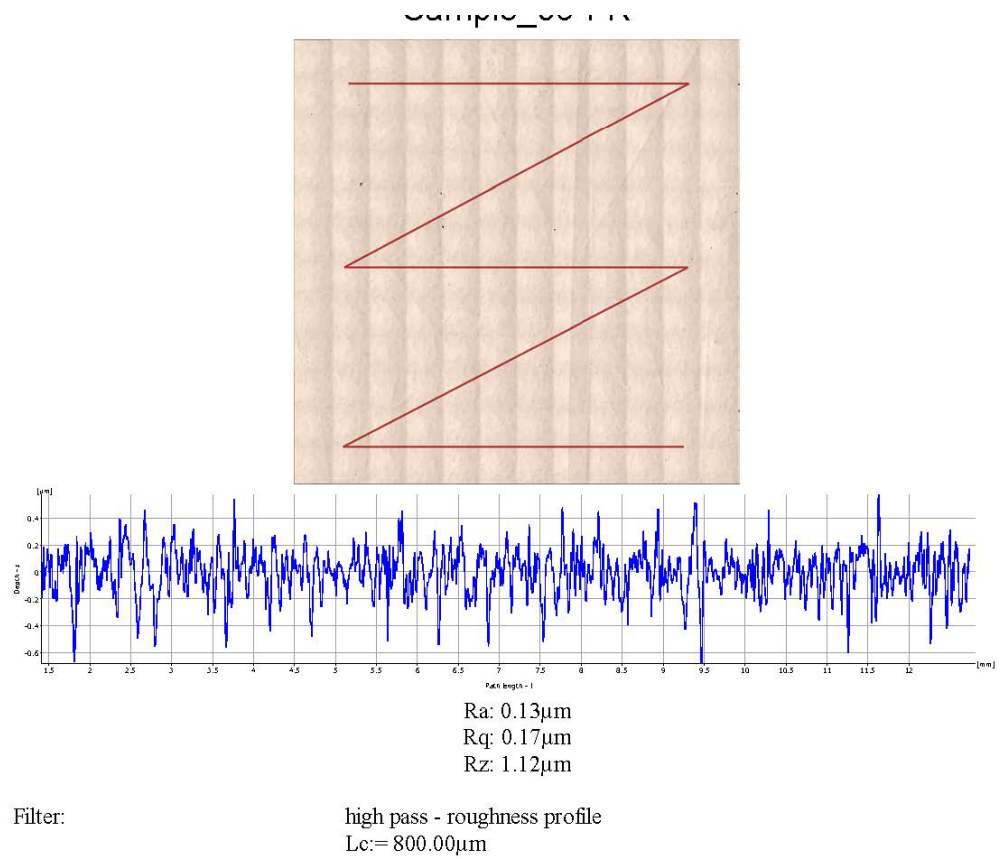


Figure 4. 21 Profile measurement of the sample polished with OP-S solution, showing the optical micrograph of the position of measurement and the roughness profile.

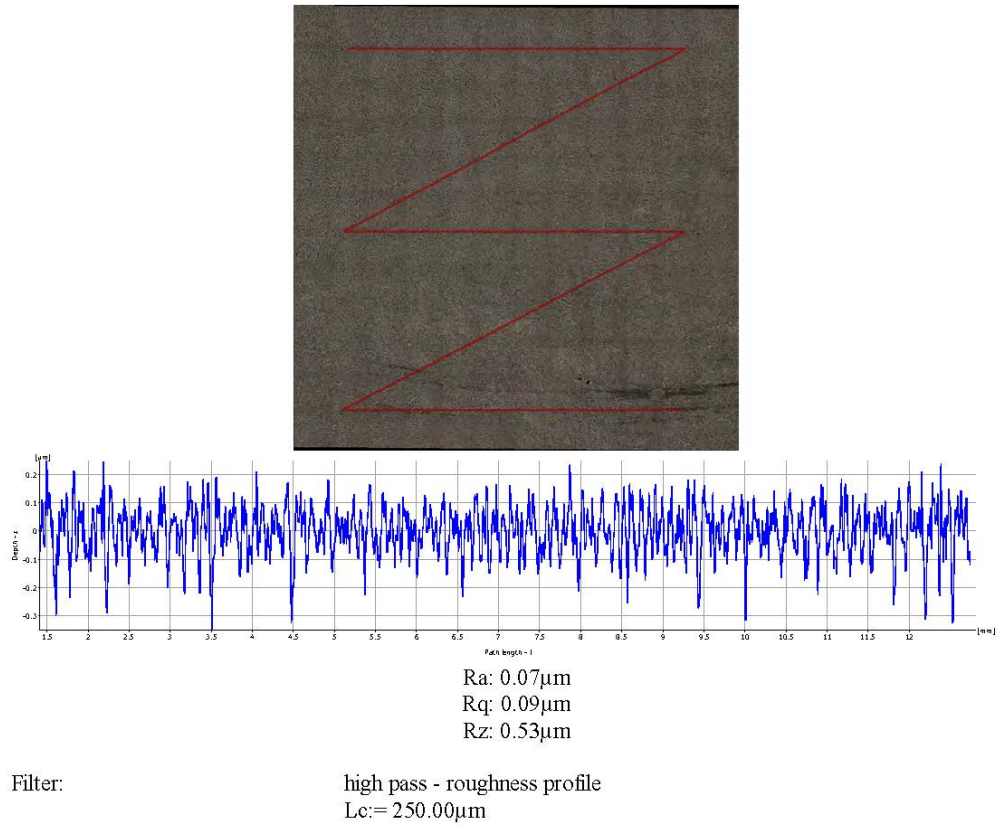


Figure 4. 22 Profile measurement of the sample etched with 100ml distilled water, 80 ml HNO<sub>3</sub>, and 10 ml HF solution, showing the optical micrograph of the position of measurement and the roughness profile.

For imaging, the surfaces of different pre-treated samples of titanium alloy are shown in 3d by AFM in Figure 4.23.

The average roughness of the samples can be observed from the figure. The first sample's roughness is graded at eight, from -4 to 4 micron. The second sample's roughness is graded at three, from -1 to 2 micron, while the first grinding stage for TiAlSiZr alloy is graded at 2.5 grades from -1.25 to 1.25 micron [77].

The third sample's roughness is graded at two , from 0 to 2 micron, whereas the fourth sample's roughness is graded at three, from -1 to 2 micron. The second grinding stage for TiAlSiZr alloy is graded at 3.75 grades from -2 to 1.75 [77].

The fifth sample's roughness is graded at two, from -1 to 1 micron. The sixth sample's roughness is graded at two and a half, from -2 to 0.5 micron. The seventh sample's

roughness is graded at three, from -2 to 1 micron. The eighth sample's roughness is graded at three, from -2.5 to 0.5 micron. The ninth sample's roughness is graded at zero, hence no readings are attained. The tenth sample's roughness is graded at four, from -1.5 to 2.5 micron.

It is clear from the etched samples that the surface appearance is random due to the fact that the chemical solution dissolves the turning tracks, while the other samples are more uniform [74,75].

## **4.2 Characterizations the Samples after Coating with PCL**

In this section, a detail about the characterization of the sample after coating with PCL is provided.

### **4.2.1 Thickness Measurements**

The thickness of the samples are measured via caliper before and after treatment; and after coating, as shown in Table 4.12.

The samples having thickness of 2 mm are selected, and as a result of grinding and polishing, the thickness decreased a little. The PCL scaffolds are defined in the literature as  $0.019 \pm 0.006$  [7]. It is assured that all samples' coating was made sure to be more than 0.01 mm.

Because the coating adhesion is poor in some samples so some of samples its take more of solution to reach to this thickness.

All the samples is needed 6.5 mm of the solution to obtain 0.01 mm thickness while the sample 10 and 5 is needed just the normal 4.6 mm of the solution to obtain 0.01 mm thickness.

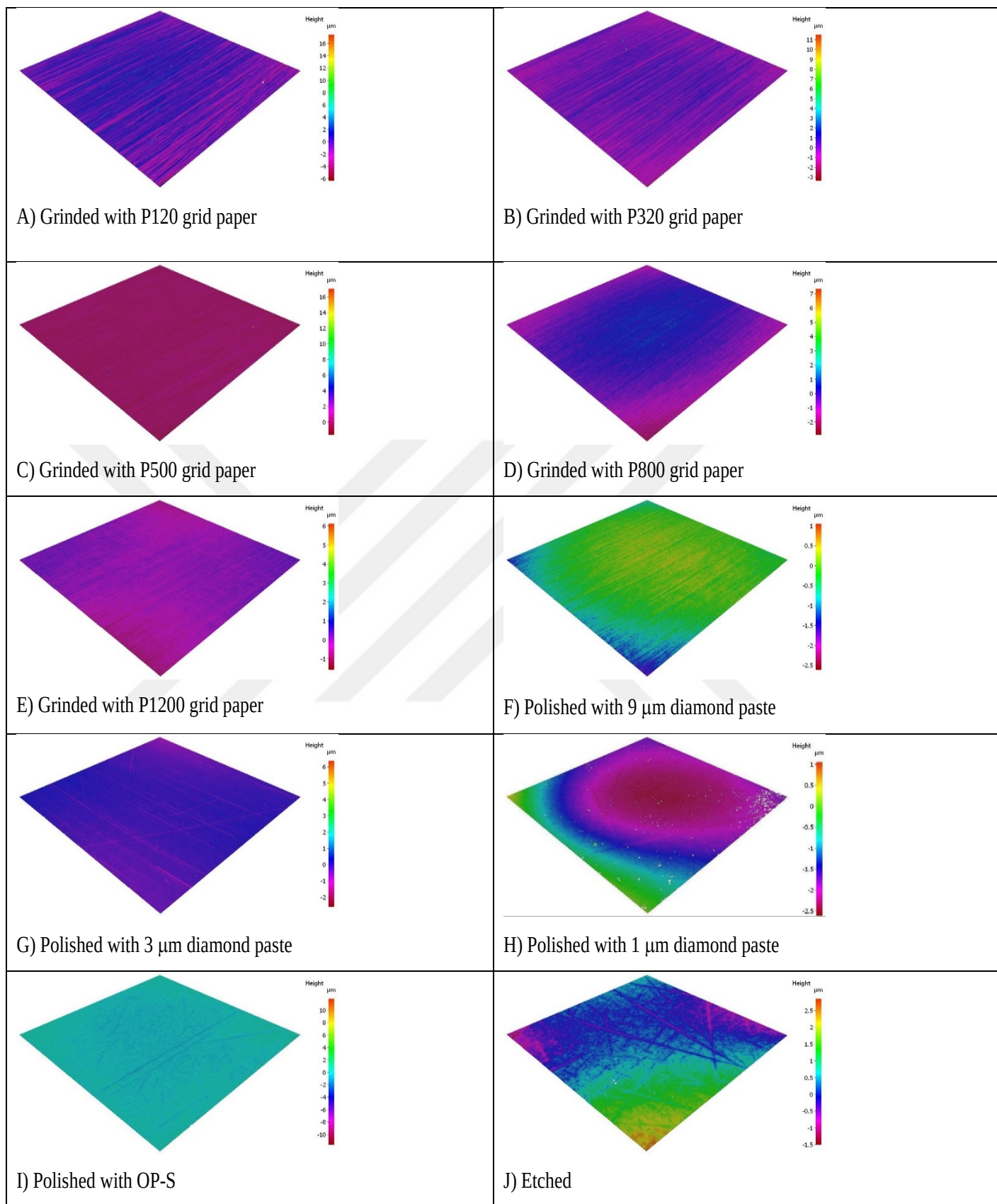


Figure 4. 23 AFM images of titanium alloy after treatment

Table 4. 12 The thickness of the samples before and after the coating

| Condition          | Before coating (mm) |                    | After coating (mm) | Difference between after / before (mm) |
|--------------------|---------------------|--------------------|--------------------|----------------------------------------|
| P120 grinded       | 2.00                | Pcl/P120 grinded   | $2.019 \pm 0.002$  | $0.019 \pm 0.002$                      |
| P320 grinded       | 1.99                | Pcl/P320 grinded   | $2.007 \pm 0.002$  | $0.017 \pm 0.002$                      |
| P500 grinded       | 1.98                | Pcl/P500 grinded   | $1.993 \pm 0.002$  | $0.013 \pm 0.002$                      |
| P800 grinded       | 1.97                | Pcl/P800 grinded   | $1.805 \pm 0.002$  | $0.019 \pm 0.002$                      |
| P1200 grinded      | 1.96                | Pcl/P1200 grinded  | $1.978 \pm 0.002$  | $0.018 \pm 0.002$                      |
| 9 $\mu$ m polished | 1.96                | 9 $\mu$ m polished | $1.976 \pm 0.002$  | $0.016 \pm 0.002$                      |
| 3 $\mu$ m polished | 1.95                | 3 $\mu$ m polished | $1.964 \pm 0.002$  | $0.014 \pm 0.002$                      |
| 1 $\mu$ m polished | 1.95                | 1 $\mu$ m polished | $1.969 \pm 0.002$  | $0.019 \pm 0.002$                      |
| OP-S polished      | 1.94                | OP-S polished      | $1.958 \pm 0.002$  | $0.018 \pm 0.002$                      |
| Etched             | 1.94                | Etched             | $1.954 \pm 0.002$  | $0.014 \pm 0.002$                      |

#### 4.2.2 CA-Contact Angle Measurements

The biological macromolecules adhesion like proteins on the implants is influenced by the wettability of the sample's surface; hence, considered as one of the important things for cells immobilization[81].

CA values of the coated titanium alloy by PCL are shown in Table 4.13, and the shape of the water droplet on the specimens are shown in the Figure 4.24.

It is concluded that PCL is a hydrophobic material with a contact angle of 115, whereas the contact angle of uncoated  $\text{TiAl}_6\text{V}_4$  is 70.1. Also, the contact angle of the other pre-treatments to the titanium alloy are more than 90, so that made them a poor choice in hydrophilicity.

While the contact angle in the etched alloy with PCL is less than all (uncoated  $\text{TiAl}_6\text{V}_4$ , PCL, Pcl/120 grinding  $\text{TiAl}_6\text{V}_4$ , Pcl/320 grinding  $\text{TiAl}_6\text{V}_4$ , Pcl/500 grinding  $\text{TiAl}_6\text{V}_4$ , Pcl/800 grinding  $\text{TiAl}_6\text{V}_4$ , Pcl/1200 grinding  $\text{TiAl}_6\text{V}_4$ , Pcl/9 micron polishing  $\text{TiAl}_6\text{V}_4$ , Pcl/3 micron polishing  $\text{TiAl}_6\text{V}_4$ , Pcl/1 micron polishing  $\text{TiAl}_6\text{V}_4$ , Pcl/OP-S polishing  $\text{TiAl}_6\text{V}_4$ ). The reason might be the usage of distilled water,  $\text{HNO}_3$ , and HF to remove the contaminants and native oxide from the surface and that will generate the free surface energy. Hence, excellent bonding strength to the alloy substrate and good adhesion to the coating is achieved. Moreover, this will aid for proliferation, better cell growth, cell attachment, increase in hemolysis ratio, and platelets adhesion because it has higher wettability and the liquid would have more expansion on the material surface [7, 8, 3, 28, 77].

As mentioned in the literature, the hydrophilic surface helps migration, proliferation, and cell adhesion[81].

The average contact angle of the coated samples is 105.79 and this illustrates how much the etched sample is subsiding from the average.

When compared with other studies on graphene oxide (GO) modified electrospun poly ( $\epsilon$ -caprolactone) (PCL), the contact angle is slightly decreased only by  $\sim 5^\circ$ [46].

Table 4. 13 The amount of average contact angle for the samples

| sample                                                   | Contact angle (°) |
|----------------------------------------------------------|-------------------|
| PCL                                                      | 115               |
| TiAl <sub>6</sub> V <sub>4</sub>                         | 70                |
| PCL/120 grinding TiAl <sub>6</sub> V <sub>4</sub>        | 113               |
| PCL /320 grinding TiAl <sub>6</sub> V <sub>4</sub>       | 114               |
| PCL /500 grinding TiAl <sub>6</sub> V <sub>4</sub>       | 105               |
| PCL /800 grinding TiAl <sub>6</sub> V <sub>4</sub>       | 95                |
| PCL /1200 grinding TiAl <sub>6</sub> V <sub>4</sub>      | 122               |
| PCL /9 micron polishing TiAl <sub>6</sub> V <sub>4</sub> | 112               |
| PCL /3 micron polishing TiAl <sub>6</sub> V <sub>4</sub> | 110               |
| PCL /1 micron polishing TiAl <sub>6</sub> V <sub>4</sub> | 98                |
| PCL /OP-S polishing TiAl <sub>6</sub> V <sub>4</sub>     | 126               |
| PCL /Etch TiAl <sub>6</sub> V <sub>4</sub>               | 58                |

The difference between samples are clarified in the figure 4.24.

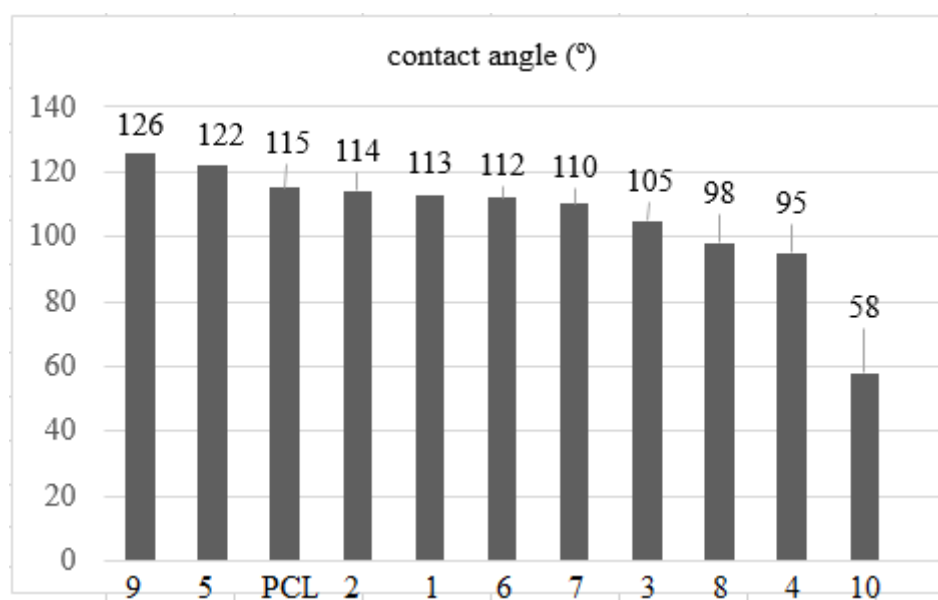


Figure 4. 24 the differences in the contact angle between the samples

By comparing the effects of the surfaces, roughness of the titanium alloy on the contact angle of coated sample, it becomes clear that the surfaces' roughness (profiles arithmetical deviation ) has much less effect on the hydrophilicity on the coating. The exception was observed for the etched one and is regarded as an outlier due to the effect of surface chemistry in addition to its low contact angle, and that means it is a hydrophilic sample [78].

Table 4. 14 A Comparison between the surface roughness and contact angle

| Contact angle (°) | Surfaces roughness (profiles arithmetical deviation ) (micron) |
|-------------------|----------------------------------------------------------------|
| 113.9             | 0.56                                                           |
| 114.78            | 0.28                                                           |
| 105.64            | 0.11                                                           |
| 95.8              | 0.13                                                           |
| 122               | 0.07                                                           |
| 112.3             | 0.08                                                           |
| 110.2             | 0.05                                                           |
| 98.3              | 0.08                                                           |
| 126.4             | 0.13                                                           |
| 58.63             | 0.07                                                           |

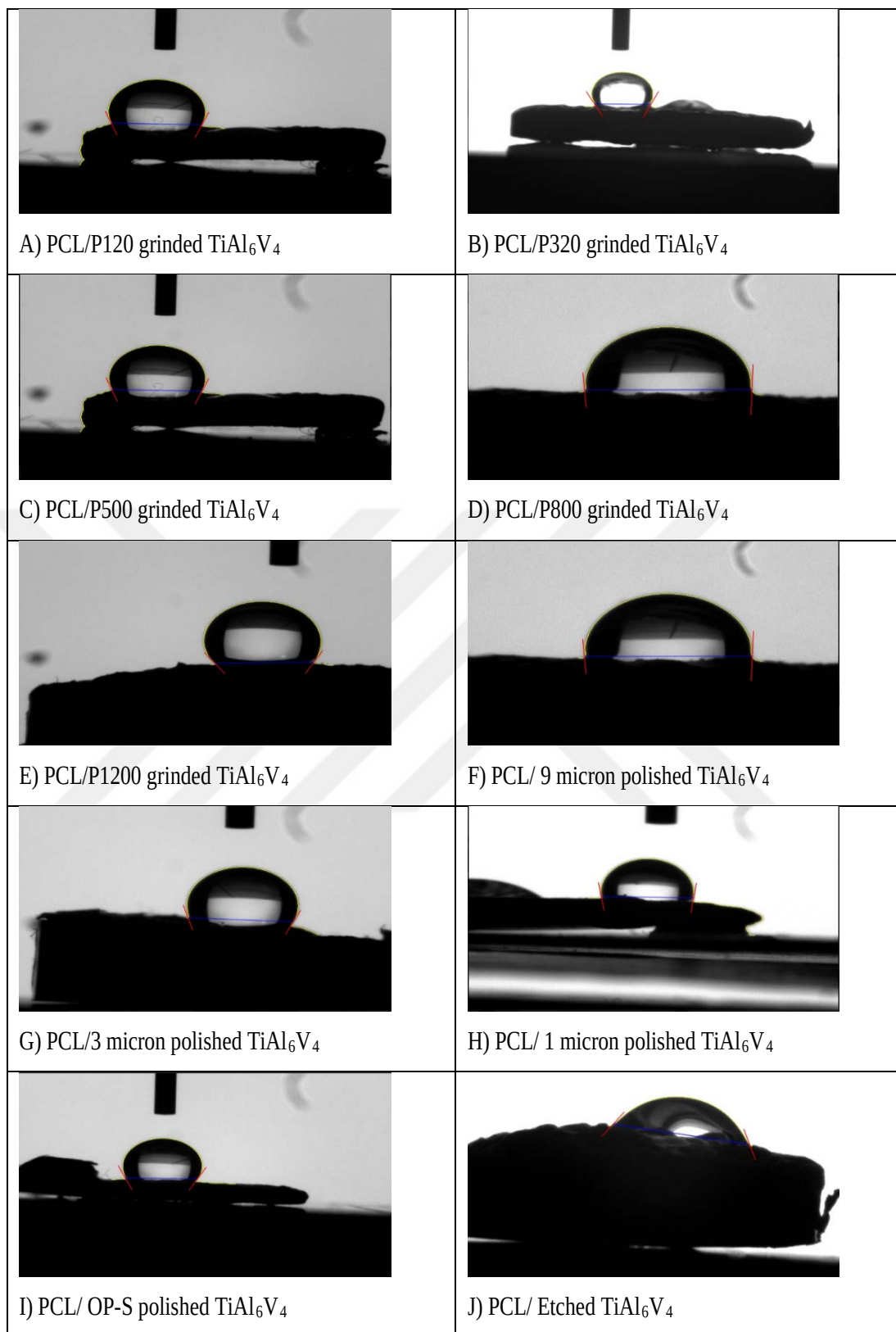


Figure 4. 25 The shape of the water droplet on the specimens

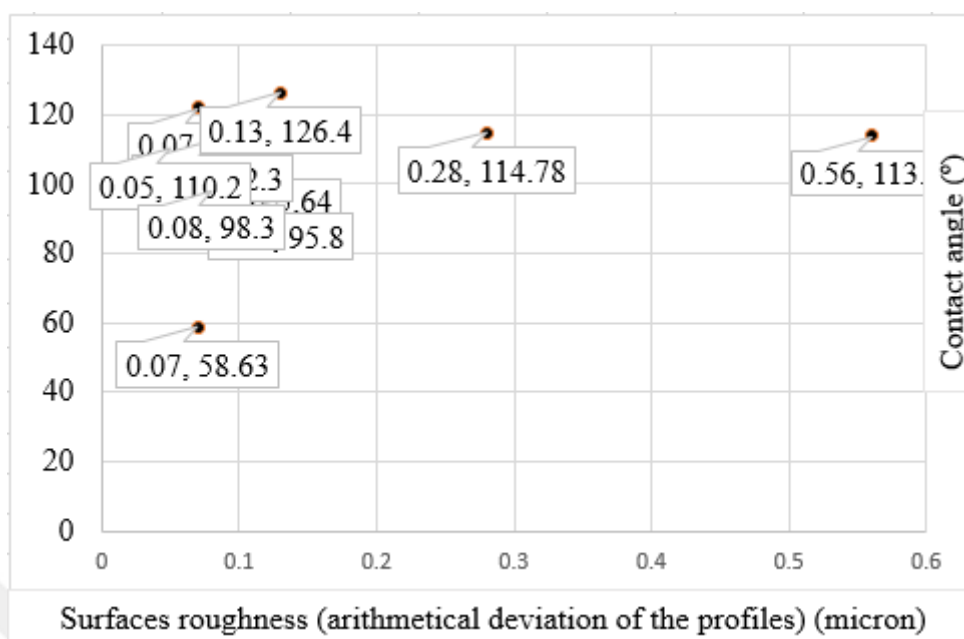


Figure 4. 26 A diagram explain the relation between surface roughness of the alloy and the contact angle

#### 4.2.3 Adhesion Test

The adhesion test results are tabulated in Table 4.15. A test is performed for every sample type and the failure between the substrate and most of the coating layers is removed for the samples (2,3,6,7,9). The first layer of coating is removed for the sample (8) and 12% of coating is removed for sample (4). About 5% of the coating is removed from the sample (1), and a very small amount of the coating is removed from the sample (10), whereas the sample (5) was found to be the best[67,76,ASTM: D 3359 – 97 Adhesion by Tape Test].

The percentage of remained paint is determined by the ImageJ software program. The details of the comparison of adhesion strength for all samples are shown in Figure 4.26.

Table 4. 15 The adhesion test results

| sample no | The remaining paint | Total sample area | The percentage of paint remaining after removing the tape % |
|-----------|---------------------|-------------------|-------------------------------------------------------------|
| 1         | 206251 pixels       | 215425 pixels     | 95.7                                                        |
| 2         | 231 pixels          | 179056 pixels     | 0.1                                                         |
| 3         | 6212 pixels         | 173498 pixels     | 3.5                                                         |
| 4         | 244996 pixels       | 275706 pixels     | 88.8                                                        |
| 5         | 181276 pixels       | 182257 pixels     | 99.4                                                        |
| 6         | 33618 pixels        | 179056 pixels     | 18.7                                                        |
| 7         | 21198 pixels        | 170468 pixels     | 12.4                                                        |
| 8         | 129774 pixels       | 172555 pixels     | 75.2                                                        |
| 9         | 7242 pixels         | 171056 pixels     | 4.2                                                         |
| 10        | 172330 pixels       | 173869 pixels     | 99.1                                                        |

For evaluation the samples from 1-5, One is very bad and five is very good. Samples (2, 3, 6, 7, and 9) are considered very bad and their evaluation is zero. The samples (4, 8) is better and evaluated is three. The samples one is evaluated four. The samples (5, and 10) is considered the best and evaluated 5

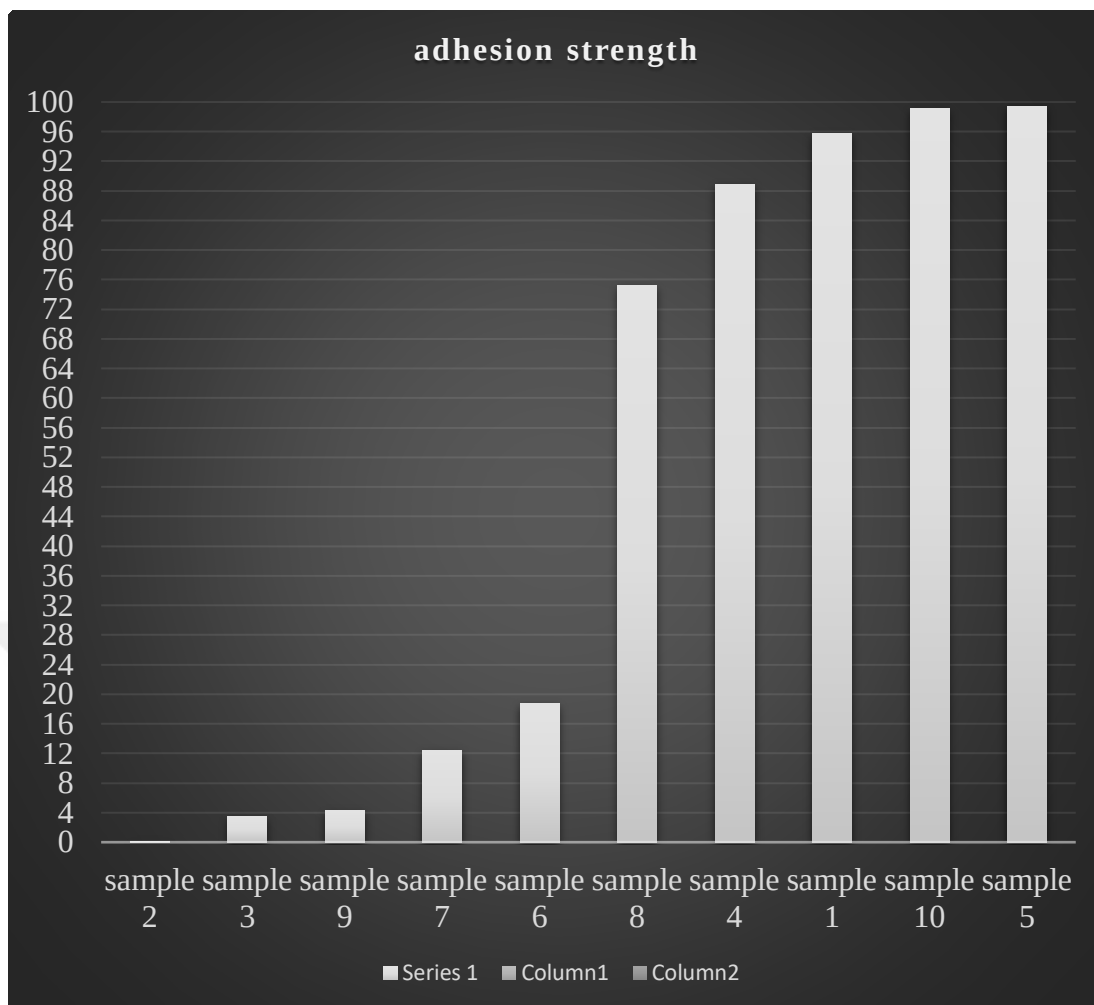


Figure 4. 27 Comparison of adhesion strength for the samples of PCL/  $\text{TiAl}_6\text{V}_4$

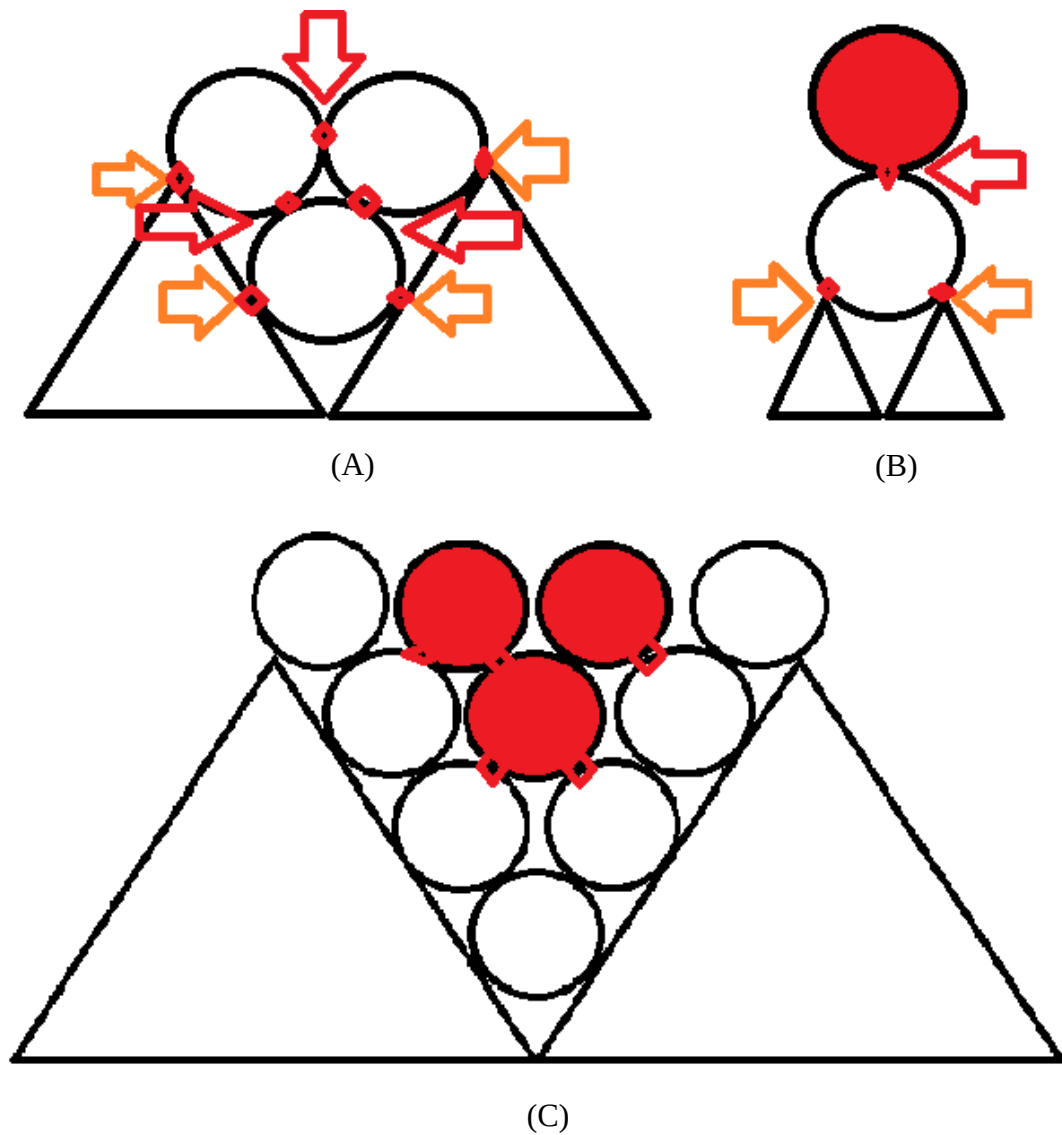


Figure 4. 28 (A) Acceptable roughness (B) Low micro-roughness (C) large micro-roughness

From Figure 4.28, the balls represent the fibers and the triangle represent the metal. The big and small triangles represent the high roughness and low roughness, respectively. The weak points are marked using red arrows, the orange arrows represent the strong points, and the red balls identifies the weakest balls.

In the high roughness, the balls in the middle are considered as weak because of not being linked to the substrate; hence, steak off easily. In the low roughness, it is more easy to steak of due to the presence of large flat areas, as they contribute to the separation of large coating's portions that makes possible the adhesion to the tape

much better and separation of large coating's portions [83]. In the acceptable roughness, there are many contact points to the substrate, and that results in the much stronger adhesion of coating to the substrate, which is 0.07 for PCL fibers. The samples after steak of the tape are displayed in the Figure 4.29

Comparing with the titanium oxide Nano coating on titanium surface failed in lower micro-roughness (800 grindings) and succeed in high micro-roughness (300 grindings) [83]. The coating material is different so that 300 grinding is good for CP Ti coating and for PCL 1200 grinding is appropriate.



Sample (10)

sample (1)

sample (9)

Figure 4. 29 The samples after steak of the tape

## CHAPTER 5

### 5. CONCLUSIONS

- For fabrication of PCL/TiAl<sub>6</sub>V<sub>4</sub> biomaterials, different pre-treatment like grinding, polishing, and etching is performed. PCL is electro-spun by a plastic syringe (capacity of 5ml) at 15.5-20 kV with the flow rate of 15  $\mu$ L/min. PCL is prepared by dissolving it with chloroform/methanol (75/25 v/v) at 30 °C.
- EDS is used to detect the elements on the surface of titanium alloy. It shows that the surface is free from any strange elements and the percentages of alloy composition is within the standard range of about ~90% for titanium, ~6% for aluminum, and ~4% for vanadium.
- Titanium alloy microstructure after grinding, polishing, and etching is investigated by the optical microscopy to confirm the microstructure of titanium alloys.
- SEM is also investigated in detail. Through results, it is determined that the degrees of grinding, polishing, and etching through the smears existed on the surface of the samples, and it also confirmed the change in the microstructure of the etched sample.
- AFM is used to obtain 3D shapes of the alloy surfaces after pre-treatment.
- The surface-area-to-volume ratio is enhanced using this study by increasing the roughness of the sample surface to 3 microns. This provides space for bone attachment and subsequently increases cellular proliferation.

- The mean roughness values are obtained to confirm the roughness values numerically; the results shows that the best roughness for the coating adhesion is found to be 0.07.
- The thickness of the coating is specified depending on the scaffold's measurements in the range of  $0.019 \pm 0.006$ .
- The osseointegration with the bone is improved in this study by decreasing the hydrophobicity in the Pcl/Etch TiAl6V4 sample by more than 47.16. This will prevent fracture, implant loosening, patient's pain, and unnecessary costs when it's necessary to change the implants
- The adhesion of nanofibers to the metallic surfaces is increased by modifying the surface roughness of titanium alloy. The samples Pcl/Etch TiAl6V4 and Pcl/1200 grinding TiAl6V4 have the best adhesion strength: more than 99% of coating did not stick out from the metal after removing the tape and that makes them distinctive to be chosen in the long term for body applications.
- The electrospinning device is used for coating the PCL on the titanium alloy, and grinding and polishing machine is utilized for the surface improvement of the alloy.
- To measure the PH of simulated body fluid, PH meter is used, and to mix the solutions and fix the temperature, a magnetic mixture device is used.
- As a result of all characterization studies, it is inferred that coating PCL on etched TiAl<sub>6</sub>V<sub>4</sub> is the most suitable approach in orthopedic applications and in tissue engineering applications.

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