Hydroxyapatite and Titania (HA-TiO_2) powder mixed EDM for surface modification.

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
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Mechanical

Approved by,

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January 2020

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

afhamrazuki

(Muhamad Afham bin Razuki)

ABSTRACT

Titanium dioxide (TiO_2) is remarkable in biomedical field since its applications by surface modifications on metallic implant can prevent release of metal ions after long exposure to body fluids. Its combinations with hydroxyapatite powder can further enhance the biocompatibility as well as mechanical properties of implants. In this study we aimed to apply surface modification on stainless steel by powder mixed EDM using HA and TiO_2 powder. It was found that material removal rate for the experiments conducted was higher than its respective electrode wear rate which indicate proper EDM as well as surface modification were successfully done. However, further analysis is required to determine the uncertainties of the surface modifications like its surface topography, surface roughness as well as elements and oxide compounds deposited.

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Chapter 1: Introduction

1.1 Background Study

Biomedical engineering also known as bioengineering is one of the multidisciplinary Science, Technology, Engineering and Mathematics (STEM) that merge biology with engineering, practicing engineering rules and materials to medicine and healthcare. This sector aims to narrow the gap between engineering and medicine, merging engineering and clinical biological science development and problem-solving skills to improve health care services, including evaluation, monitoring and therapy. Contrary to many other fields of science, biomedical technology has recently emerged as its own research. Such an evolution is typical as a new field move from being an interdisciplinary specialization of already developed fields to being regarded as a field in itself. Many of the research and development practice of biomedical engineering covers a wide range of subfields. Notable developments of biomedical engineering include the advancement of biocompatible prostheses, numerous diagnostic and therapeutic medical equipment varying from surgical equipment to micro-implants, popular scanning technology such as MRIs and EKG / ECGs, growth of regenerative tissue, medicinal and therapeutic biologics.

There are several subfields of biomedical engineering which are related to this project such as biomaterial, tissue engineering and medical devices (implants). Figure 1.1 shows X-ray image of hip implants after surgery. Any matter that interact with living systems is known as biomaterial. Meanwhile, for the tissue engineering its aim is to construct artificial organs using biomaterial.

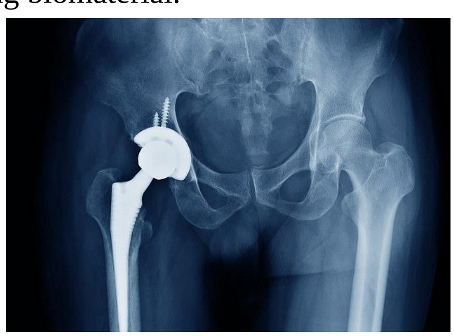


Figure 1.1 X-ray image of hip implants

For medical devices, it covers a broad area. However, there is only one that are related to the research which is implants. It is medical devices which require premarket approval (PMA) to assure the device's safety and effectiveness.

1.2 Problem Statement

Stainless steel is used widely in present industries. It is prominent for its properties which is resistance to corrosion, which can be elevated by increasing chromium content. In terms of implants, the most commonly used are austenitic SAE 316 and SAE 316L stainless. They consist of chromium, nickel, molybdenum alloy of steel which demonstrate high strength and corrosion resistance. Figure 1.2 shows various components of implants made from stainless steel.

Figure 1.2 Stainless steel implants

However, stainless steel has its own weaknesses. Throughout time, steel implants can induce allergic or toxic reactions and be rejected by the skin, and in less sanitary surgical conditions steel may not withstand harmful bacteria accumulation sufficiently. Throughout the study, we would like to examine whether HA-TiO_2 composite coating can fully enveloped the implant, improving its biocompatibility and prevent such problems to rise.

1.3 Objectives

The main aim of this research is to:

(a) To analyse the material removal rate (MRR) and electrode wear rate (EWR) of EDM to determine proper machining.

(b) To analyse surface modification of SAE 316L stainless steel after electro-discharge machining (EDM) in terms of:
   i. Surface topography
   ii. Elements and compounds deposited

1.4 Scope of Study

1. Understanding the important properties for implants manufacturing.

Acknowledge the properties that crucially need to be considered in implant manufacturing such as biocompatibility, bioactivity and osseointegration. This guided on proper selection of materials for implant.

2. Perform surface modification using EDM machining.

Details study of the process and how EDM effect the workpiece structure in term of surface modifications. Standard relevant for EDM is ISO 11090-1: 2014. MRR and EWR was used to determine successfulness of surface modifications meanwhile for further analysis SEM, EDX with XRD were needed.

Chapter 2: Literature Review

2.1 Electrical Discharge Machining (EDM)

Electrical discharge machining (EDM), also known as spark machining, spark eroding, burning, sinking, wire burning or wire erosion, is a production process whereby electrical discharges (sparks) are used to produce a desired shape. Figure 2.1 shows the schematic diagram of EDM. It is designed to shape conductive materials that are incredibly difficult to cut [1, 2, 3]. Material separation is accomplished by transforming electrical energy into thermal energy by means of a series of high frequency, 103–106 Hz, independent electrical discharges between two electrodes, with a limited gap length of 10–100 μm, submerged in a dielectric fluid medium [3]. The dielectric fluid used usually is minerals oil which later will burned and emit carbons and react with alloy element and create surface of extremely hard carbide [4]. The open voltage is introduced between the two electrodes before discharge, after which the activation delay duration for dielectric breakdown occurs, which signifies the numerical time lag required to generate initial electrons and the time for dielectric ionization. This lag period varies and relies on the circumstances of the distance of gap [3].

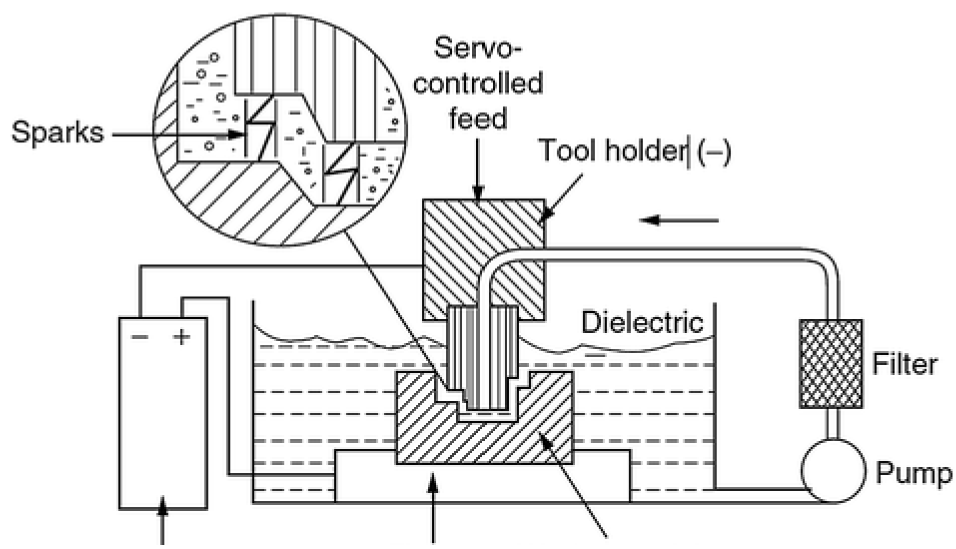


Figure 2.1 Schematic Diagram of EDM

EDM quality depends heavily on the modification of electrical parameters (discharge current, discharge duration, OFF-time, supply voltage, and tool-electrode polarity) and nonelectrical parameters (flushing size, machining time, machining depth, dielectric medium and electrode speed) [4]. Furthermore, EDM capability can be improved to reduce surface cracks, better surface finish, and high machining stability, this process was advanced using magnetic-field, dry EDM, and tool-electrode rotation [2].

Disintegration happens from the acceleration of electrons to the anode, with the origin of electrons either originating from the cathode under the applied field or stray electrons in the space. The electron interacts on neutral atoms and molecules found in the dielectric fluid, producing1 positive ions and extra electrons which accelerate towards cathode and anode, respectively. Each spark creates a high-temperature localized plasma stream, measured at between 8000 which 12,000 ° C, and causes a strong localized pressure of 200 atm [3].

EDM methods have been widely used in the production of cutting tools, moulds and dies in recent decades. However, according to the research by Aliyu, A.A.A., et al [1], they mentioned that EDM process not only can be used to shape the metallic implant, but it simultaneously can be applied for shaping and surface coating. Another statement was found stated that, EDM process is also considered as surface modification due to proof of material migrate between electrodes and dielectric fluid with additives [4]. Figure 2.2 shows material migrate upon machining and deposited on workpiece. It is known as Additive Mixed EDM (AM-EDM) which increase its performance by mixing various metallic powder into dielectric fluid. It has been largely documented that AM-EDM is widely used in manufacturing sectors of automobiles, aerospace and nuclear components [1].

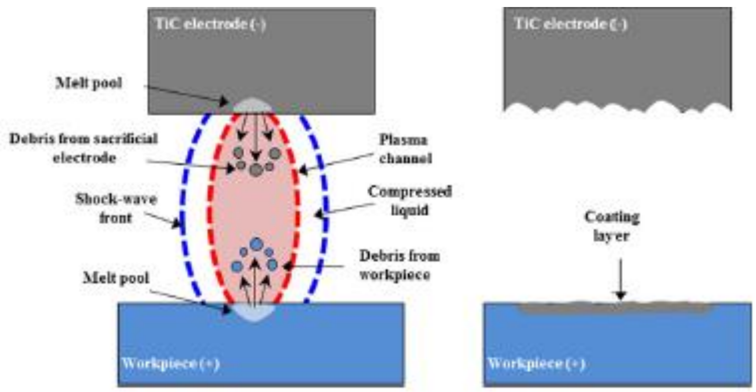


Figure 2.2 Condition on gap between EDM during EDM (left) and after EDM (right).

Materials from the tool electrode and the suspended dielectric fluid additives are transported and accumulated on the surface of the workpiece, thereby modifying its chemical composition, mechanical properties and enhancing surface quality. The previous statement can also be supported by another research by Aliyu, A.A.A., et al [1] which stated that tool electrode's material and the powder suspended inside dielectric fluid, migrate to machined Bulk Metallic Glass (BMG) surface in elemental or compound form. Calcium and Oxygen from decomposed Hydroxyapatite (HA) powder joined to Zirconium (Zr) and reinforced on matrix of BMG, creating calcium enriched, nanoporous bio ceramic Lakargite ($CaZrO_3$) coating (Figure 2.3) [2]. This state will increase cell viability and wear rate due to deposition of hard carbide and biocompatible oxide layer on its surface [1].

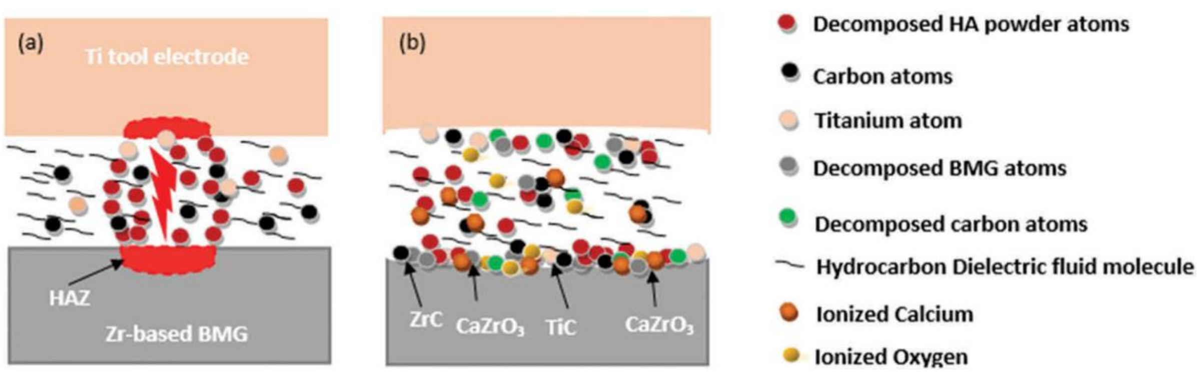


Figure 2.3 Another migration and deposition of elements on workpiece.

2.2 Titanium Dioxide (TiO_2)

Titanium dioxide which are also known as Titanium (IV) oxide or titania is a compound that can be formed naturally from titanium due to reaction with oxygen. It can exist in 3 kinds of polymorphs which are brookite, anatase or rutile. Titania is often desirable in surface modification of titanium implant since it can prevent metal ions released to the environment. Izman S., et al stated that titanium and its alloy cannot fully guaranteed their biomedical properties after long period exposure to body fluid. There was already an evidence on bare titanium vanadium alloy which emit vanadium after long exposure [5]. The release of metal ions inside the body can cause toxicity and must be avoided. Hence, surface modifications by titania on metallic implants can minimise the toxicity after long period of usage.

According to Hanaor et, al. rutile can be irreversibly converted from anatase. Initially, when synthesising $TiO_{2,}$ the crystalline phase produced is mostly anatase [6]. This happened due to recrystallization of anatase is much faster because of surface free energy is lower. Rutile is transformed irreversibly from anatase at temperature about 600 ^{o}C, but the temperature reported is varied from 400 to 1200 ^{o}C depending on the raw materials and processing methods [6]. Furthermore, transformation of anatase to rutile does not occur in a short time as it is reconstructive and time dependent [6,7,8].

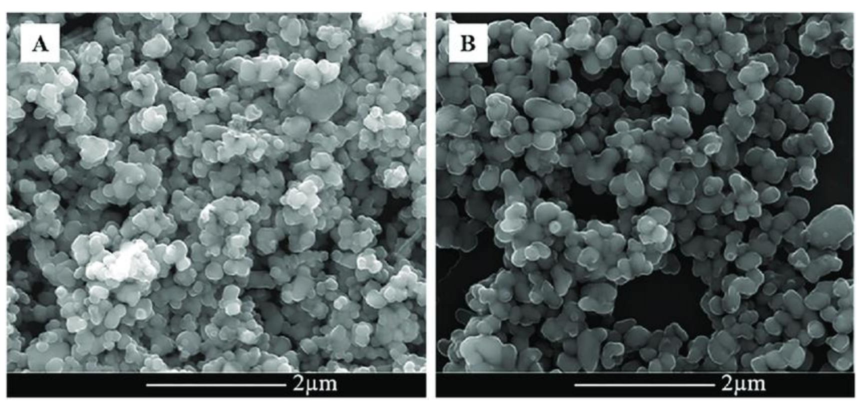


Figure 2.4 SEM image of anatase (left) and rutile (right side)

Nowadays, researchers can analyse phase and ratio of anatase rutile by using modern technology. X-ray diffraction is commonly used for phase proportion quantification by using Spur and Myers method. This method uses the rutile ratio (110) peak at 27.355º 2θ to anatase (101) peak at 25.176º 2θ. Another method of differentiating anatase and rutile is by Laser Raman micro spectroscopy. The key strength of Raman Laser micro spectroscopy is its applicability to thin films on nanoscale. By using XRD glancing angle, the instrument needs considerable adjustment, the peaks are very diffuse, and the context is such that no amorphous phase can be ascertained, if present [6,10]. Thus, the analysis would be more sensitive and accurate.

Among brookite, anatase and rutile, the most recommended oxide structure is rutile [11,12]. They are different based on their properties and photo catalytic performances. Izman S., et al claimed that rutile oxide layer is more resistant towards bacteria, possess high hardness and wear resistant compared to brookite and anatase. This statement is also supported by Biswas et al. In their study, they justified that hardness value is proportional to oxidation time and temperature. Moreover, rutile structure is more superior due to its young modulus which close to that of the bone [13]. This is crucial to avoid stress shielding effect which might lead to bone density losses.

2.3 Hydroxyapatite (HA)

Hydroxyapatite (HA) is one of the calcium phosphates that is frequently used for biomaterials. It has the most stability compared to other calcium phosphate in term of physiological conditions like temperature, pH and composition of body fluids. For the past years, Nano HA is used widely in prosthetic and bone tissue applications due to its similarity in size, crystallography and chemical composition with human hard tissues [16]. It can be prepared naturally or synthesized through several processes. Its properties which mimics the phase of the bone and characterized as naturally biocompatible, bioactive and osteoconductive [14]. Moreover, it can be used to control the degradation and resorption rate [16].

Figure 2.5 Partially HA coating on metal implant

However, HA also has its own downside. It is mentioned that they have brittle nature, lack sufficient tensile strength in bulk [16] and poor mechanical strength which that obstruct its usage for load bearing applications [15]. In order to overcome it fracture toughness, HA is often added with CNTs, alumina (Al_2O_3), yttria-stabilized zirconia (YSZ), Ni_3Al and Ti alloys [15]. HA is also used as coating on metallic implants and as reinforcement to polymer scaffolds material for tissue regeneration (Figure 2.5) [14]. By reinforced such material with HA, it is not only enhancing its biological properties but also block toxic elements from being released and promote cell proliferation on the implant surface [1]. Within this approach, biocompatibility can be provided by HA while the mechanical properties can be enhanced and ensured by the metal substrates. Therefore, it can be used for applications involving load-bearing conditions [15].

2.4 TiO_2 – HA composites coating

Few researches on titania-hydroxyapatite composite coating on titanium substrate have been found but there have been no reports on it been produced by powder-mixed EDM. According to Kim et, al. they have produced the composite coating using sol-gel, and the advantages using that way is the coating layers formed were highly dense, homogenous and high strength of adhesion. Cell growth activity on composite coating recorded were also much higher than bare commercially pure titanium (CPTi) and even on pure HA coating [21,23].

Another simple yet successful technique of producing the composite coating was by microwave processing done by Siddharthan A. et, al. CPTi metal was packed in HA and undergo microwave at 800 W for 22 minutes to produce the composite coating [19]. The coating produced were mostly Titania in rutile structure together with HA as minority. The advantages of this process are it required less time, save energy and the composite coating obtained had better osteoblast adhesion and cell proliferation.

Other alternative ways of producing the titania-hydroxyapatite composite coating were by high velocity oxy-fuel (HVOF) spraying [20], pulse electrolysis [22] and electrophoretic deposition [24]. Generally, they acquired the same finding in which the composite coating produced by each respective method are much superior in terms of hardness, adhesion strength and cell proliferation.

2.5 Porosity of Coating

Bone growth and stress distribution can be facilitated by porous coatings. Porous coating that was made up from hydroxyapatite for example can help different types of ions and molecules like collagen and protein to be adsorbed into their surface and will produce biological films [25]. It is mentioned that for optimum biocompatibility of the implant, the most desirable pore size ranges from 50 to 400 μm [26]. Therefore, we can use these parameters to determine biocompatibility.

Chapter 3: Methodology

The procedure started with preparation of 316L stainless steel workpiece and copper tool electrode. Both materials initially exist as metal plate and need to be cut into desired dimensions. Wire-cut EDM was used as the metals possess high mechanical strength thus it was more convenient for such purpose. Stainless steel workpiece was cut into dimension of 10mm x 10mm x 5mm. For copper tool electrode, the dimension was 12mm x mm x mm.

After cutting process have been done, both workpiece and tool electrode need to be grinded using grinding polishing machine. Such action needed to remove impurities and copper debris that might deposited on stainless steel workpiece due to wire-cut EDM and to make sure copper tool electrode had smooth and even surface for proper machining.

Figure 3.1 Stainless steel workpiece

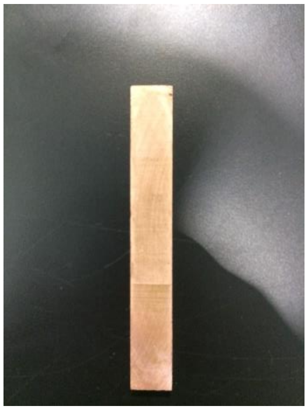


Figure 3.2 Copper tool electrode

Next, HA and TiO_2 powder were weighted respectively and begun setup the machining and electrical parameters of the die-sink EDM (refer table for respective weight and parameters). Run the powder mixed EDM to machine 0.7 mm of the workpiece thickness. Once finish record the final weight of workpiece and tool electrode. Analyse the surface modification using SEM, EDX and XRD.

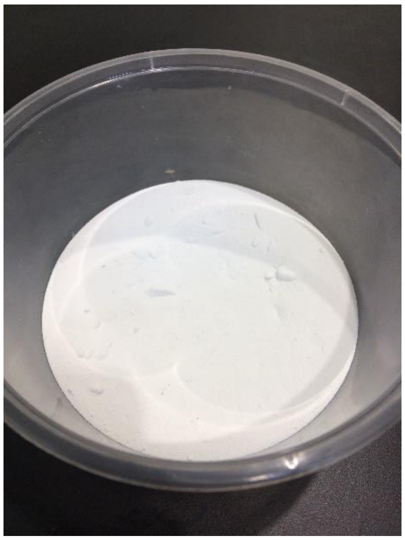


Figure 3.3 Hydroxyapatite powder

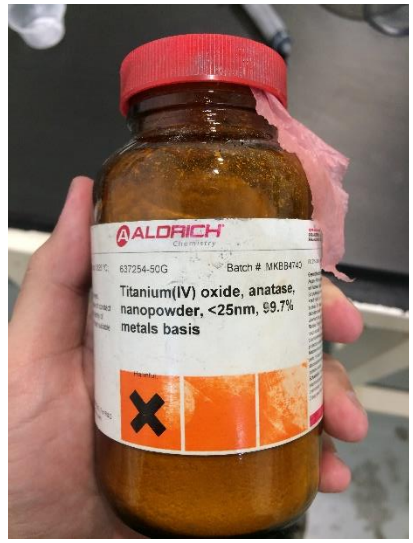
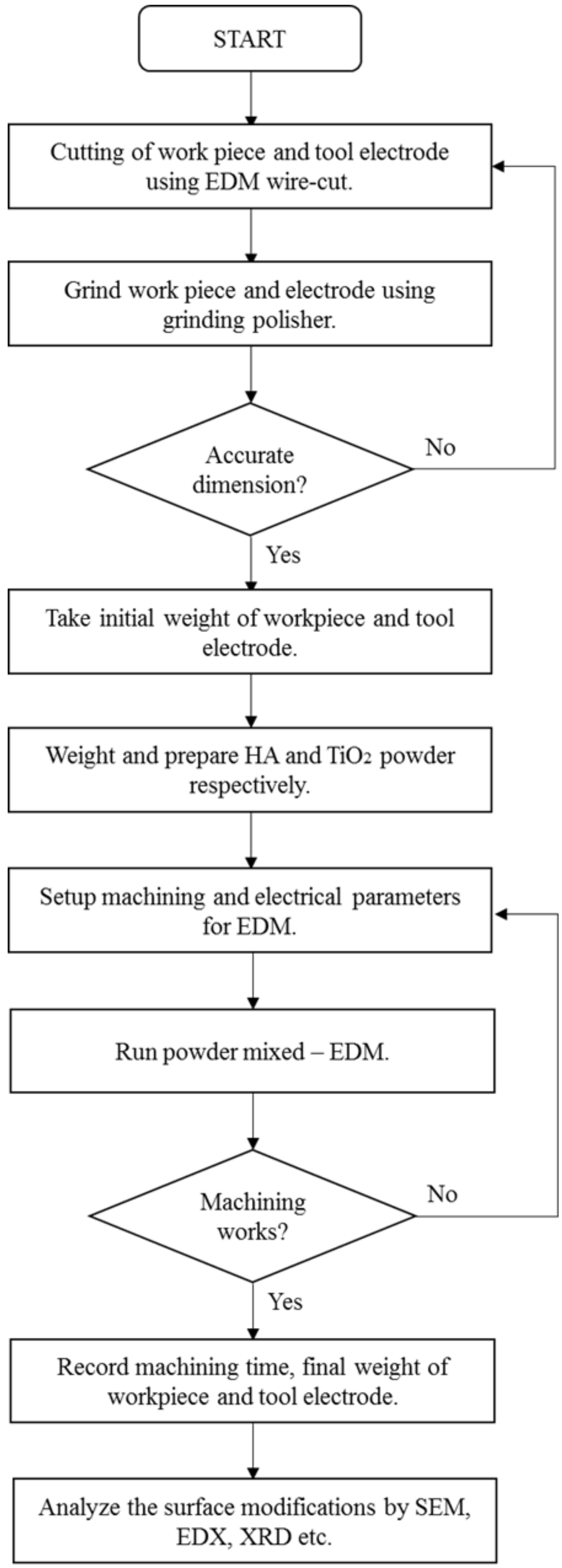


Figure 2.4 Titania powder

DOE #1	DOE #2
Peak current: 10 A	Peak current: 7 A
Pulse on time: 8 μs	Pulse on time: 8 μs
Gap voltage: 150 V	Gap voltage: 150 V
HA concentration: 7 g/L	HA concentration: 10 g/L
TiO_2 concentration: 0.4 g/L	TiO_2 concentration: 1 g/L
Dielectric volume: 7L	Dielectric volume: 7L

Table 3.1 Machining parameters

3.1 Project Timeline



3.2 Gantt Chart

Task	Final Year Project 1														Final Year Project 2													
	Academic Calendar Week														Academic Calendar Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Planning																												
Identification of Problem																												
Literature Research																												
Report Prep																												
Experimental Approach																												
EDM Preparation																												
EDM																												
Analyse EDM-ed workpiece																												
Report Submission																												
Interim Report																												
Viva																												
Dissertation																												

Project progress Project key milestones

Chapter 4: Result and Discussion

4.1 Findings

From EDM, we have recorded few data that would help for our analysis.

DOE 1	
Total mass hydroxyapatite (HA) powder in dielectric	49 g
Total mass titania (TiO_2) powder in dielectric	2.8 g
Tool electrode mass	Before machining: 89.68 g
	After machining: 89.45 g
Workpiece mass	Before machining: 3.57 g
	After machining: 3.23 g
Machining time	12.9 minutes

Table 4.1 Findings of DOE 1

DOE 2	
Total mass hydroxyapatite (HA) powder in dielectric	70 g
Total mass titania (TiO_2) powder in dielectric	10 g
Tool electrode mass	Before machining: 89.65 g
	After machining: 89.41 g
Workpiece mass	Before machining: 3.56 g
	After machining: 3.21 g
Machining time	18.1 minutes

Table 4.2 Findings of DOE 2

From the tabulate data, we can calculate material removal rate (MRR) and electrode wear rate (EWR) of each experiment using this formula:

$$\boxed{\text{MRR or EWR} = \frac{\text{Initial weight} - \text{final weight (g)}}{\text{Machining time (min)}}}$$

	DOE 1	**DOE 2**
MRR	MRR = $\frac{3.57 - 3.23}{12.9}$ = 0.0263 g/min	MRR = $\frac{3.56 - 3.21}{18.1}$ = 0.0193 g/min
EWR	EWR = $\frac{89.68 - 89.45}{12.9}$ = 0.0133 g/min	EWR = $\frac{89.65 - 89.41}{18.1}$ = 0.0133 g/min

Table 4.3 MRR and EWR

4.2 Analysis

The data calculated showed that MRR were larger than it respective ERR for both design of experiment. This indicate that proper machining using EDM die-sink had been achieved. Based on past research done by Aliyu, A.A.A., et al., and few others on powder-mixed EDM, we were strongly believed that some of the hydroxyapatite and Titania powder had migrated from dielectric fluid and deposited on stainless steel workpiece, thus establish surface coating which consist of those powders.

However, there were some uncertainties regarding further details on condition of surface modification. One of them is surface roughness. From literature review, we already acknowledged that higher surface roughness of coating would promote better cell growth and adhesive strength. According to [7], higher peak current would contribute to higher surface roughness which was used in DOE 1. Even though peak current used in DOE 2 was smaller there was also small likelihood of higher surface roughness due to more powders were used and both powders are non-electrically conductive, thus it will increase insulating strength of dielectric fluid [4]. Nevertheless, the surface roughness of EDM surfaces can be determined by Atomic Force Microscope (AFM) or profilometer. For comparison, the optimum surface roughness should be in the range of Ra = 0.5 to 1.5 μm [5].

Moreover, further analysis can also be done using Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Analysis (EDX) to analyse surface topography of the coating. By SEM, we can determine the porosity, coating thickness and surface condition whether the microcrack was formed during EDM with high peak current or not. Higher peak current gave rougher surface finish, but it could also initiate microcrack on coating. Besides, details of surface modification can be more analysed using X-ray Powder Diffraction (XRD) to identify the any oxides or carbides deposited on machined surface.

4.3 Summary

The result and objective that we obtained now are MRR and EWR which indicate EDM proper machining as well as surface modification on stainless steel workpiece. However, further details on the surface modification such as surface roughness, presents of defect, elements and compound deposited only can be known by further analysed with SEM, EDX and AFM.

Chapter 5: Conclusion and Recommendation.

In the end of this semester, we have achieved one of the objectives which was analysing MRR and EWR for proper machining by EDM. Based on the hypothesis from past powder mixed EDM experiment, elements and compounds from dielectric fluid and tool electrode will migrate and deposited on workpiece surface, thus allowed surface modification if proper EDM machining can be achieved. Moreover, the methodology we used were also based on the past procedure. Although different powders and machining parameters were used, we could conclude the surface modifications were theoretically achieved.

For better confirmation, such analysis that we mentioned earlier like SEM, EDX and XRD can be used. In addition, microhardness test also can be adopted to determine the increase in hardness of composite coating compared to stainless steel itself. Another improvement can be considered was annealing of workpiece after been EDM to increase the chance of rutile crystalline phase deposited as it can further increase hardness and wear resistance. Such actions cannot be proceeded as right now we are facing pandemic COVID-19 outbreak and government had declared movement control order. However, I hope this information would be beneficial either to those who will be doing research in the same field or readers.

References

[1] Aliyu, A.A.A., et al., Characterization, adhesion strength and in-vitro cytotoxicity investigation of hydroxyapatite coating synthesized on Zr-based BMG by electro discharge process. Surface and Coatings Technology, 2019. 370: p. 213-226.

[2] Aliyu, A.A.A., et al., Hydroxyapatite mixed-electro discharge formation of bioceramic Lakargiite (CaZrO3) on Zr–Cu–Ni–Ti–Be for orthopedic application. Materials and Manufacturing Processes, 2018. 33(16): p. 1734-1744.

[3] Algodi, S.J., et al., Electrical discharge coating of nanostructured TiC-Fe cermets on 304 stainless steel. Surface and Coatings Technology, 2016. 307: p. 639-649.

[4] Aliyu, A.A.A., et al., A Review of Additive Mixed-Electric Discharge Machining: Current Status and Future Perspectives for Surface Modification of Biomedical Implants. Advances in Materials Science and Engineering, 2017. 2017: p. 1-23.

[5] Izman, S., et al., Surface Modification Techniques for Biomedical Grade of Titanium Alloys: Oxidation, Carburization and Ion Implantation Processes. Titanium Alloys - Towards Achieving Enhanced Properties for diversified Applications, 2012. Retrieved from www.intechopen.com

[6] Hanaor, D.A.H. and C.C. Sorrell, Review of the anatase to rutile phase transformation. Journal of Materials Science, 2010. 46(4): p. 855-874.

[7] Liu, X., P. Chu, and C. Ding, Surface modification of titanium, titanium alloys, and related materials for biomedical applications. Materials Science and Engineering: R: Reports, 2004. 47(3-4): p. 49-121.

[8] Liu, W., S. Liu, and L. Wang, Surface Modification of Biomedical Titanium Alloy: Micromorphology, Microstructure Evolution and Biomedical Applications. Coatings, 2019. 9(4).

[9] Sobieszczyk, S., Surface modifications of Ti and its alloys. Advances in Materials Sciences, 2010. 10(1).

[10] Sharan, J, et.al, An Overview of Surface Modifications of Titanium and its Alloys for Biomedical Applications. Trends in Biomaterials and Artificial Organs, 2015. 29 (2): p. 176–187.

[11] Kulkarni, M, et.al, Biomaterial Surface Modification of Titanium and Titanium Alloys for Medical Applications. Nanomedicine, 2014.

[12] Esmaeilnejad, A., et al., Synthesis of titanium oxide nanotubes and their decoration by MnO nanoparticles for biomedical applications. Ceramics International, 2019. 45(15): p. 19275-19282.

[13] Lan, W.C., et al., The Potential of a Nanostructured Titanium Oxide Layer with Self-Assembled Monolayers for Biomedical Applications: Surface Properties and Biomechanical Behaviors. Applied Sciences, 2020. 10(2).

[14] Mohanta, D., et al., Carbon nanotubes: Evaluation of toxicity at biointerfaces. Journal of Pharmaceutical Analysis, 2019.

[15] Lahiri, D., S. Ghosh, and A. Agarwal, Carbon nanotube reinforced hydroxyapatite composite for orthopedic application: A review. Materials Science and Engineering: C, 2012. 32(7): p. 1727-1758.

[16] Balani, K., et al., Tribological behavior of plasma-sprayed carbon nanotube-reinforced hydroxyapatite coating in physiological solution. Acta Biomatter, 2007. 3(6): p. 944-51.

[17] Ragunathan, S., et al., Hydroxyapatite reinforced natural polymer scaffold for bone tissue regeneration. Materials Today: Proceedings, 2019.

[18] Kim, H.-W., et al., Hydroxyapatite and titania sol-gel composite coatings on titanium for hard tissue implants; Mechanical andin vitro biological performance. Journal of Biomedical Materials Research, 2005. 72B(1): p. 1-8.

[19] Siddharthan, A., T.S.S. Kumar, and S.K. Seshadri, In situ composite coating of titania–hydroxyapatite on commercially pure titanium by microwave processing. Surface and Coatings Technology, 2010. 204(11): p. 1755-1763.

[20] Gaona, M., R.S. Lima, and B.R. Marple, Nanostructured titania/hydroxyapatite composite coatings deposited by high velocity oxy-fuel (HVOF) spraying. Materials Science and Engineering: A, 2007. 458(1-2): p. 141-149.

[21] Kuroda, K., et al., Osteoinductivity of Titania/Hydroxyapatite Composite Films Formed Using Pulse Electrolysis. Materials Transactions, 2007. 48(3): p. 328-331.

[22] Milella, E., et al., Preparation and characterisation of titania/hydroxyapatite composite coatings obtained by sol gel process. Biomaterials 22, 2001: p. 1425-1431.

[23] Ramires, P.A., et al., The influence of titania hydroxyapatite composite coatings on in vitro osteoblast behaviour. Biomaterials 22, 2001: p. 1467-1474.

[24] Rath, P.C., et al., Titania/hydroxyapatite bi-layer coating on Ti metal by electrophoretic deposition: Characterization and corrosion studies. Ceramics International, 2012. 38(4): p. 3209-3216.

[25] John, K., Mechanical biocompatibility of dental materials. Biocompatibility of Dental Biomaterials, 2017. p. 9-21.

[26] Kaivosoja, E., et al., Materials used for hip and knee implants. Wear of Orthopaedic Implants and Artificial Joints, 2013. p. 178-218.

[27] Alla, R. K., et al., Review on surface roughness of implants. Trends in Biomaterials and Artificial Organs, 2011. 25(3): p. 112-118.