HYDROXYAPATITE-CHITOSAN COMPOSITE COATING ON TiAl ALLOY ELECTROPHORETIC DEPOSITION METHOD

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ABSTRACT

TiAl alloys is commonly used for bone implant applications because it has good biocompatibility. However, in long term usage of metal implants, metal release, which can harm the body, may occured. The metal release can be inhibited by hydroxyapatite-chitosan composite coating on the metal surface using Electrophoretic Deposition (EPD) method. EPD method carried out with 200 v for 40 and 60 minutes, to compare the impact of different interval time in producing the best product. The coated alloy was observed physically by SEM and showed that 60 minute-treatment produced better result. The XRD and FTIR analysis shows that the composite of hydroxyapatite-chitosan has successfully coated on TiAl alloy. The coated TiAl alloy also has low corrosion rate and could potentially be used as bone implants.

Keywords: chitosan, electrophoretic deposition, hydroxyapatite, TiAl

ABSTRAK

Paduan logam TiAl biasa digunakan untuk aplikasi implan tulang karena memiliki biokompatibilitas yang baik. Namun penggunaan implant logam dalam jangka waktu yang panjang, pelepasan ion dapat terjadi. Hal ini dapat membahayakan tubuh. Pelepasan ion logam dapat diatasi dengan pelapisan komposit hidroksiapatit-kitosan pada permukaan logam untuk menghambat pelepasan ion logam. Metode elektroforesis deposisi dilakukan dengan interval waktu berbeda, yaitu 40 dan 60 menit, tetapi dengan nilai tegangan yang sama sebesar 200 V untuk membandingkan pengaruh lamanya waktu perlakuan pada hasil pelapisan logam. Hasil pelapisan tersebut diamati secara fisis dengan menggunakan SEM dan menunjukkan bahwa waktu proses pelapisan selama 60 menit menghasilkan lapisan yang cukup baik. Hasil pencirian dengan difraksi sinar-X dan inframerah menunjukkan bahwa komposit hidroksiapatit-kitosan berhasil terlapisi pada paduan logam. Paduan logam TiAl yang telah terlapisi ini juga memiliki laju korosi yang rendah, yaitu sebesar 0.0186 mpy dan berpotensi digunakan sebagai implan tulang.

Kata kunci: elektroforesis deposisi, hidroksiapatit, kitosan, TiAl

I. INTRODUCTION

Biomaterials in the health sector growing rapidly along with the increasing need for an alternative to the substitution of damaged tissue, especially damage to the bone. Bone implants have to show the identical response as the original bone and also facing biocompatible behavior with the surrounding tissue. Commonly one of biomaterial used for bone implant is a metal, such as stainless steel, cobalt alloys, and titanium alloys [1]. The metal alloy of titanium facing compatibility and corrosion resistance better compared to stainless steel and alloy cobalt. Stainless steel may cause irritation of the content of the elements Ni, while the metal alloy cobalt, for example CoCrMo, corrosion resistance is not good and the coefficient

friction is low [2]. Titanium alloy commonly used are TiAl, TiAlV, and TiAlNb. For the application of permanent implants, metal alloy Ti have toxic effects that may result from the release of aluminum. Its needed a layer of film on the metal surface which can inhibit the release of metal ions [3].

Hydroxyapatite is a bioactive material which has bioactivity, biocompatibility and able to induce bone growth because it has chemical and mineralogical composition similar to natural bone. Hydroxyapatite can form a strong chemical bond with natural bone after implantation into the body [4]. Hydroxyapatite can be synthesized by various methods, including the wet method (via precipitation), dry method, and hydrothermal. The method used in this study, the method of wet through precipitation. This method was chosen because of the reaction involved is a simple reaction, namely the reaction between calcium hydroxide $Ca(OH)_2$ with phosphate salts $(NH_4)_2HPO_4$. In addition, the cost of synthesis of hydroxyapatite in this way is relatively inexpensive, and has a relatively high purity. Precursor synthesis of hydroxyapatite as a source of calcium can be used shell of (*Bellamya javanica*) Tutut (conch) for containing $CaCO_3$ [5].

Although hydroxyapatite has good bioactivity and biocompatibility, hydroxyapatite has its drawbacks, as it is fragile and poor mechanical properties. It hinders clinical use as a load-bearing long-term. Therefore it needs to be made of composite material from some of the material has good biocompatibility, mechanical strength and good toughness. Ceramics can be composited with a polymer to produce a composite which has better mechanical properties. Polymers can be used are the PLA, poly (β-hidroksialkanoat) (PHA), or polysaccharides [1]. In the present study, hydroxyapatite composite with chitosan. Chitosan is a natural polysaccharide largely derived from the shells of crabs, but also can be obtained from shrimp, corals and jellyfish ubur.Kitosan is an ideal polymer for biomedical applications because it is biocompatible and biodegradable properties were good. Chitosan has been applied in cartilage tissue engineering and wound healing of bone or orthopedic applications [6].

Hydroxyapatite-chitosan composite is good blend to improve corrosion resistance and biocompatibility. These composites was coated on a metal surface by using electrophoretic deposition (EPD). The advantage of the EPD is the equipment used is quite simple, flexible in the use of the substrate material and the coating, and can easily control the uniformity and thickness of the layer [7]. This study aims to coat the metal alloy TiAl by composites of hydroxyapatite-kitosandengan using EPD method. Furthermore, these materials are characterized using X-ray diffraction (XRD), FTIR (fourier transform infra red), SEM (scanning electron microscope), and corrosion test.

II. EXPERIMENTAL SECTION

2.1 Materials

TiAl alloys, conch shell *Bellamya javanica* (from Cianjur, West Java), $(NH_4)_2HPO_4$, NaOH, HNO_3, chromic sulfate, strontium, $CaCO_3$, infusion solution ringer lactate, glacial acetic acid, pH universal indicator , ethanol and distilled water.

2.2 Instrumentation

Glassware, water bath, analytical balance, thermometer, magnetic stirrer, furnace, oven, desiccator, sonicator, centrifuge, milling machines, tool EPD, atomic absorption spectroscopy (AAS) brand Shimadzu AA7000, XRD Philips brand, optical microscopy, FTIR, and SEM.

2.3 Synthesis of hydroxyapatite using wet method

$(NH_4)_2HPO_4$ 0.3 M dropped on the suspension of $Ca(OH)_2$ 0.5 M with condition kept to a temperature of 40 ± 2 ° C, while stirring using a magnetic stirrer. In this synthesis, the pH is monitored and corrected to obtain a pH of 10. The reaction mixture was allowed to stand for 24 hours at room temperature. Furthermore, the solution sonicated and centrifuged at 4500 rpm for 15 minutes and then rinsed with distilled water. Then, the precipitate is dried at 105° C for 3 hours. Once dry, the precipitate is finely pulverized in a mortar and then sintering at 900 ° C for 2 hours. Hydroxyapatite powder is allowed to cool in a desiccator. Furthermore, hydroxyapatite were characterized using XRD.

2.4 Synthesis of TiAl alloys

Sample preparation starts with calculating the exact composition to obtain a sample of pellets prepared melted. The first calculation of the atomic composition of the powder Al purity of 95% with a purity of 95%

Ti powder. Here is used the weight ratio of Ti and Al as 54% and 46% with a total weight of 16 grams. Furthermore, both types of metal powders are mixed thoroughly. Tools used for mixing is Ball Mill. This tool mix and grind the powder material by collisions between the steel balls and ceramic inside. Milling is done for 30 minutes at 500 rpm with a round number 5 ball size pieces are the same diameter.

After that, the powder is formed into pellets by compacting using Enerpac press machine 10T, with great pressure of 800 kgf / cm 2 for 60 seconds. The compacted pellets results in melting by arc melting furnace. Once the melted pellets is then reduced in thickness so that the coin with a diameter of 14 mm and a thickness of 2.5 mm.

2.5 Hydroxyapatite-Chitosan Composite Coatings on TiAl Alloys

EPD conducted prior to coating with pre-treatment on the metal. TiAl metal formed with a diameter of 14 mm and a thickness of 2.5 mm. Metal sanded with 800-grit sandpaper, then washed with water and didegrease with ethanol, and air dried. After the alkali treatment given to the metal with metal soak in a solution of NaOH 10% during 24 hours.

Hydroxyapatite-chitosan colloid solutions that have been formed are connected to two electrodes, as the negatively charged electrode used metal TiAl which is the target of coating and as a positively charged electrode used platinum. During the process of electrophoretic deposition, hydroxyapatite and chitosan are dispersed will move under the influence of an electric current so that it will stick to metal surfaces TiAl. Source voltage used is 200 V for 40 and 60 minutes. After coating, TiAl alloys are characterized using X-ray diffraction (XRD) for phase analysis, FTIR (fourier transform infra red) for functional groups, SEM (scanning electron microscope) for morphology analysis, and corrosion test.

2.6 Corrosion test

Potensiostat corrosion test using a device or galvanostat 273 models with potential used is -20mV to 20mV in media corrosion. Media corrosion used is the infusion solution of NaCl 0.9%. Samples with a diameter of 1.4 cm is placed on the working electrode, then put on the device potentiostat or galvanostat. The process of corrosion caused by the movement of electrons in an electrochemical reaction, so that the corrosion rate can be determined.

III. RESULTS AND DISCUSSION

3.1 Hydroxyapatite formation

Shell powder which has passed through the stages of conversion to be $Ca(OH)_2$ is used as a source of calcium in the synthesis of hydroxyapatite. The method used in the synthesis of hydroxyapatite is a wet method through precipitation because of the reaction involved is a simple reaction, namely the reaction between calcium hydroxide Ca (OH) $_2$ with phosphate salts $(NH_4)_2HPO_4$, in addition to the cost of synthesis of hydroxyapatite in this way is relatively inexpensive, and has a relatively high purity. Synthesis of hydroxyapatite runs through reaction [8].

$10Ca(OH)_2 + 6\ (NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 6H_2O + 12NH_4OH.$

Based on the results of hydroxyapatite powder difractogram (Figure 1) shows that the hydroxyapatite thus obtained with the appearance of the typical peak of hydroxyapatite in 2θ about 30 ^{o} -35 ^{o,} precisely look at 2θ 31.77 $^{\circ,}$ 32.18 $^{\circ,}$ 32.91 ^{o} with highest intensity. As reported by Singh [5] the synthesis of hydroxyapatite from the fields conch shell, the three highest peaks appear at 2θ 31.7 $^{\circ,}$ 32.2 $^{\circ,}$ and 32.9 $^{\circ.}$ It is also appropriate when compared to data JCPDS, which shows three distinctive peaks of hydroxyapatite appears at 2θ 31.77 $^{\circ,}$ 32.19 $^{\circ,}$ 32.90 $^{o.}$

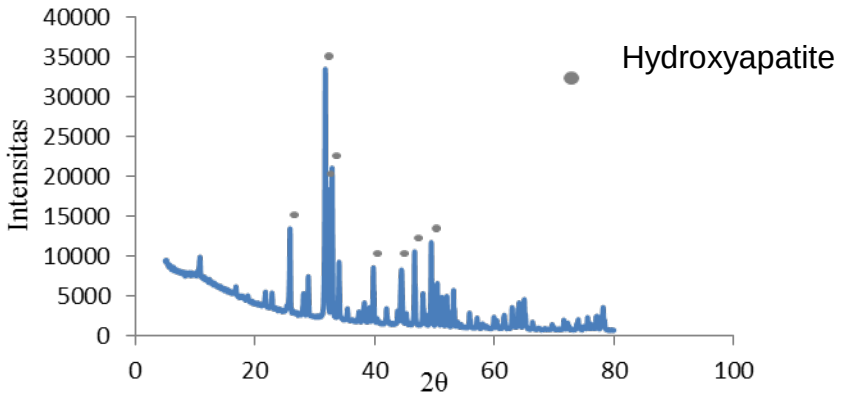

Figure 1 X-ray diffractograms synthesized of hydroxyapatite

3.2. Synthesis of TiAl Alloys

Ti-based alloys used for bone implants because it has good strength and a low density [9]. In the present study used the composition of 52% Ti and 48 Al% with a total weight of 13 grams. In manufacturing, the first two ingredients are mixed with a ball mill for 30 minutes. When the stirring is done for too long, the effect is that the powder may be attached to the surface of the balls stirrer and not pursuant to cause the composition ratio of the expected [10]. After being mixed, and then carried out the process of compacting and then melted at a temperature of 1800 ^{o}C. Remelting (Figure 2a) then shaped manually with a grinding machine so that the coin with a diameter of 14 mm and a thickness of 2.5 mm. However, because the metal TiAl has a high hardness, metal refining processes and the formation of less than optimal (Figure 2b).

Figure 2 TiAl Alloys remelting a) before smoothing b) after smoothing

3.3. Hydroxyapatite-Chitosan Composite Coatings on TiAl

The use of bone implant in the form of metal on a certain period of time can cause side effects that can harm the body implant users. One reason is the release of metal ions into the body fluids which can be carcinogenic [1]. To avoid the release of metal ions and adding a metal implant wear, do biomaterial coating on the metal surface. Coatings used in this study is hidroktiapatit-chitosan composite of hydroxyapatite which has been synthesized from a snail shell fields. Hydroxyapatite is fragile when in contact with blood or body fluids, then by dikompositkannya hydroxyapatite with chitosan, biocompatibility and mechanical properties of hydroxyapatite will increase. In addition, chitosan also has good bioactivity and be antimicrobial [6]. At the time of hydroxyapatite and chitosan combined into a composite will be interactions between calcium ions in the hydroxyapatite group NH_2 on chitosan that form coordination complexes (Figure 3).

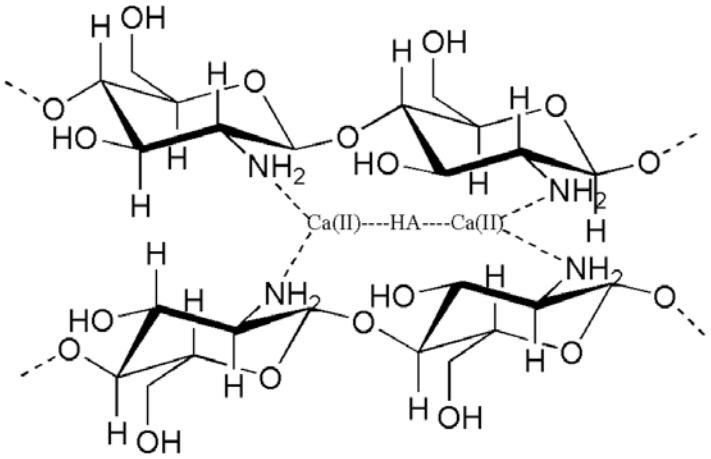

Figure 3 Interaction on hydroxyapatite-chitosan composite

3.4. Hydroxyapatite-chitosan composite may be prepared by the method of in situ or ex situ.

In this study, a composite made with ex situ methods, by mixing a solution of chitosan with hydroxyapatite powder in ethanol solvent to form a colloidal mixture. This colloidal mixture will be used for superimposing the metal with EPD method. Prior to coating, TiAl alloys given treatment by sanding the metal surface with sandpaper 160 grid in order to facilitate attachment of the composite. After the metal is washed with water and soaked with ethanol in order to remove impurities, such as grease on the metal [11]. Furthermore, given the alkali treatment by immersing the metal in a solution of NaOH 10% for 24 hours to allow the metal surface more hydrophilic, so that the composite easier to stick to metal surfaces. Hydrophilic metal surface will be faster stimulates bone growth. After pre-treatment and given metal composite solution has been prepared, and then do the coating by EPD method. In this method, there are two stages of the process, namely the migration phase of charged particles that are in a liquid solvent by the action of the use of the electric field (electrophoresis stage) and the stage of coagulation of particles form a layer on the electrode (phase deposition) [10].

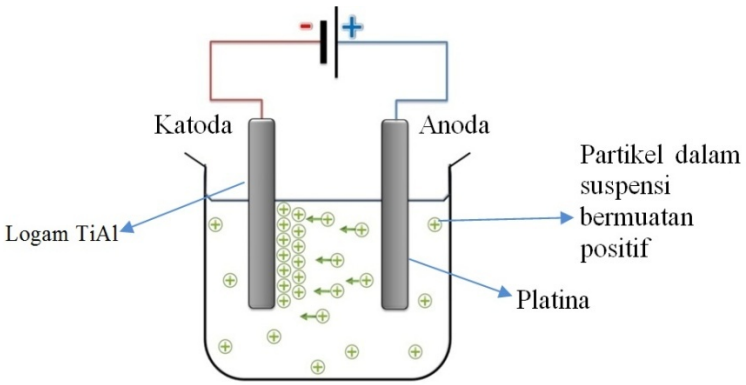

Figure 4 Illustration of hydroxyapatite-chitosan composite coating on TiAl using EPD. This process uses an electric voltage of 200 V for 40 and 60 minutes. Metal tial associated with negative flows or as a cathode, while the platinum working electrode is used which is connected with the positive current or as the anode. At the time of electrified particles of hydroxyapatite and chitosan will migrate toward the metal TiAl and will be deposited to form a layer on the metal surface TiAl. After the metal is coated by a hydroxyapatite-chitosan composite then air dried.

Coating results from the second time (Figure 5) showed that the coating for 60 minutes to produce a more uniform coating than the coating time of 40 minutes. But in that part of the metal edge (Figure 5b) composite layer looks thicker than in the middle. This can happen because at the edge of the metal contained more rugged part due to less optimal metal refining process. This shows that the rough surface of the metal will be more and more particles will stick to and coat the surface.

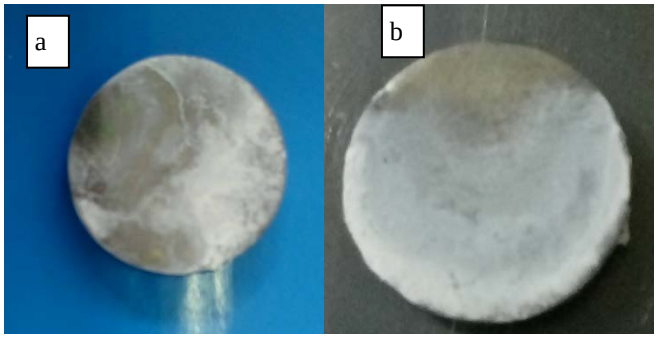

Figure 5 hydroxyapatite-chitosan composite coating on TiAl during a) 40 minutes b) 60 minutes.

3.5. Characterization using SEM

Morphology TiAl Alloys that has been coated with hydroxyapatite-chitosan composite was observed using SEM. The results of the morphological characterization of layers shown in Figure 6. In Figure 5a and 5b do not indicate that the porous structure of the composite layer, but it appears that the composite layer distributed fairly evenly on the metal as well as when viewed with magnification of 1000 times (Figure 6b). But on the edge of a metal with 1000 times magnification (Figure 6c), it can be seen that the composite layer is not distributed evenly, as indicated by the number of clusters that form hydroxyapatite. This can occur because the surface of the metal is less smooth edges so that more hydroxyapatite attached and form a cluster than in the central part of the metal.

In Figure 6a and 6b can also be aesthetically that the density of hydroxyapatite crystals well enough. Adding chitosan 20% in the composite composition will increase the density of hydroxyapatite.

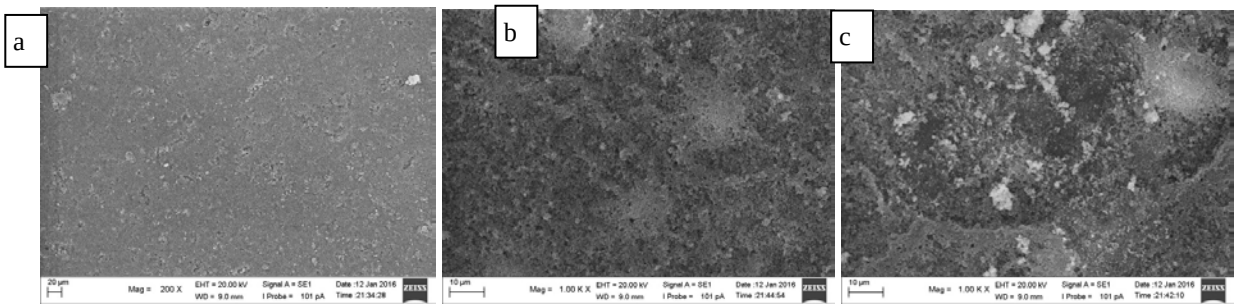

Figure 6 morphology of the metal surface a) magnification of 200 times, b) magnification of 1000 times, and c) the edges of the metal magnifications of 1000 times

3.6. Characterization using XRD

Metal that has been coated with hydroxyapatite-chitosan composite characterized by XRD. The diffraction pattern obtained (Figure 7) shows that the hydroxyapatite-chitosan coating succeeded performed with the emergence of a distinctive peak at an angle 2θ 32.01 hydroxyapatite,˚32.09, and 32.22˚. It is also appropriate when compared to data JCPDS, which shows three distinctive peaks of hydroxyapatite appears at 2θ 31.77 °, 32.19 °, 32.90 o. With the chitosan, the crystallinity of the composites were also reduced [12]. Chitosan peak does not appear in the results due to peak chitosan diffractogram will appear on the X-ray diffractogram composite of hydroxyapatite-chitosan when chitosan is contained in the composite of more than 30%. It can be seen that the diffractogram obtained metal legible also peaks at an angle 2θ tial 36.11, 38.97˚,˚ 41.20, 53.88˚. It can be caused due to a metal composite layer is still thin that the diffraction pattern of the metal are also accepted.

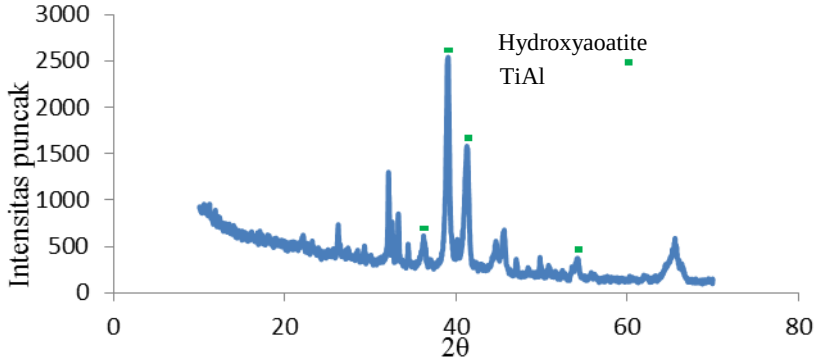

Figure 7 X-ray diffractograms hydroxyapatite-chitosan composite coatings on TiAl

3.7. Characterization using FTIR

TiAl alloys that has been coated with hydroxyapatite-chitosan composite then characterized by FTIR. This characterization is aimed to prove that the composite of hydroxyapatite-chitosan has been coated on the surface of the metal. It can be seen from the functional groups that are legible on the FTIR spectra obtained. Based on the resulting spectrum (Figure 8) shows that the absorption band v_2 PO_4^{3-} in wave numbers 572.86 and 601.79 cm^{-1} $cm^{-1,}$ at 960.55 cm^{-1} wave number contained absorption bands of $v_1PO_4^{3-,}$ and the wave number 1053.13 cm^{-1} and 1093.64 cm^{-1} there is an absorption band $v_3PO_4^{3-}$ of hydroxyapatite. It is also shown in the FTIR spectra synthesized hydroxyapatite by Peon *et al* (2004) [13] that there are absorption bands at wavelengths of 566 and 601 cm^{-1} for $v_2PO_4^{3-,}$ $v_1PO_4^{3-}$ at 954 $cm^{-1,}$ and $v_3PO_4^{3-}$ at 1087 and 1022 $cm^{-1.}$ Absorption band o3 hydroxyl on hydroxyapatite and chitosan is the wave number 3390.86 cm $^{-1}$ [14]. Additionally, the chitosan also show the emergence of CH vibration serpan ribbon at wave number 2856.58 cm^{-1} and 292.87 cm^{-1} and an absorption band for NH at wave number 1567.83 cm $^{-1.}$ This is consistent with those reported by Kumirska *et al* (2010)[14] that the absorption band to appear on the CH stretching vibration wave numbers 2921 and 2867 cm^{-1} and an absorption band for NH appears at wave number 1650-1580 $cm^{-1.}$

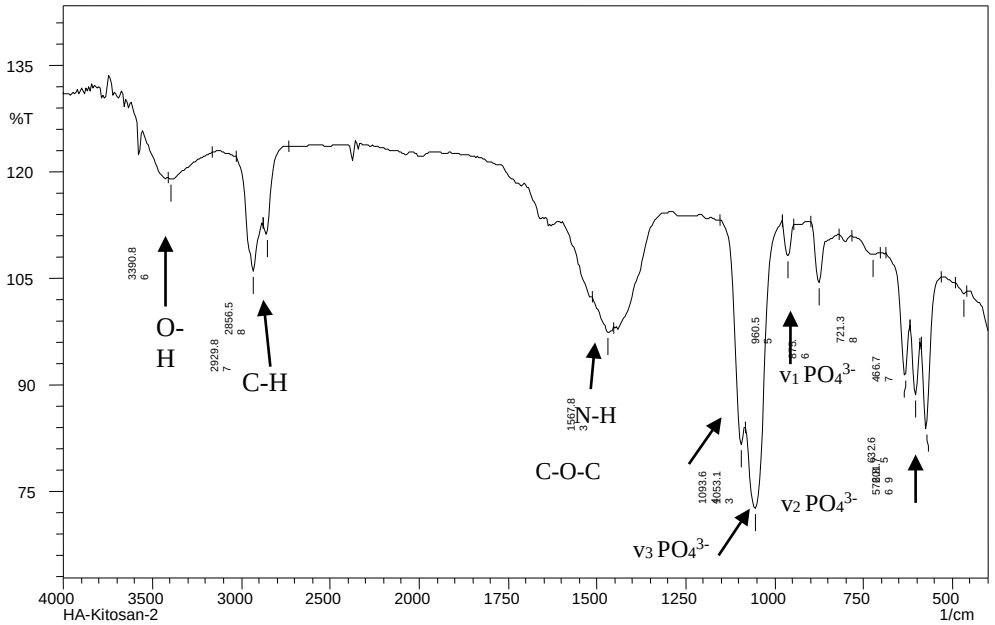

Figure 8 FTIR spectra coating

3.8. Corrosion Analysis

Hydroxyapatite-chitosan composite coating on a metal alloy TiAl done one of them in order to inhibit metal corrosion rate TiAl. With the composite layer, in addition to improving the mechanical properties of the metal, the expected rate of corrosion of metal TiAl can be reduced. Therefore, the corrosion rate was measured before and after coating to prove it. Results of corrosion tests were obtained (Table 1) shows that the corrosion rate of 0.0338 mpy TiAl metal can be reduced by the presence of hydroxyapatite-chitosan composite layer. In theory, prior to coating, metal TiAl potentially be used as an implant material because it has a corrosion rate of less than 1 mpy and 0.457 mpy be under if it refers to the European standard for medical applications [15]. But with the hydroxyapatite-chitosan composite coating expected to increase the biocompatibility of the metal. With the hydroxyapatite-chitosan composite layer as well, the metal corrosion rate decreases to 0.0186 mpy.

Table 1 Results of Corrosion Test

Sample	Rate corrosion mpy)
TiAl alloy without coating	0.0338
TiAl alloy coated with hydroxyapatite-chitosan composite	0.0186

CONCLUSION

TiAl alloy successfully coated on a hydroxyapatite-chitosan composite by electrophoretic deposition method. The best coating is produced during use voltage of 200 V for 60 minutes. However, due to lack ratanya metal surfaces at the edges, coating in this section is thicker than the other parts. This is evidenced in the results of SEM, that on the side of the metal edge formed many cluster. Characterization by XRD and the identification of functional groups by FTIR showed the composite metal has been coated by a hydroxyapatite-chitosan. TiAl alloy that has been coated it also has a low corrosion rate, in the amount of 0.0124 mpy and could potentially be used as implants bone.

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