The Effect of Sodium Hydroxide Concentration on Physical and Mechanical Properties of Magnesium AZ31 Coating for Biodegradable Bone Implant Application

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Abstract

Anodizing is a metal coating technique by converting a metal surface to form an oxide layer by electrolysis, one of which is to increase the hardness of a material. This research was carried out to know the effect of variations in electrolyte solution on the hardness of the coating resulting from the anodizing process. The electrolyte used is a solution of NaOH (Sodium Hydroxide) with a concentration of 1 M solution of 68% purity. The specimen used is magnesium AZ31, voltage 10 Volts, soaking time 10 minutes at room temperature. Based on the data analysis results, the magnesium layer's hardness value at 10 minutes at a voltage of 10 volts is 69 HV.In comparison, the coating thickness result at 10 minutes with a constant voltage of 10 volts is 6 μm. While the concentration of the solution is 0.5 M, the purity is 68%. The specimen used is magnesium AZ31, voltage 10 Volts, soaking time 10 minutes at room temperature. Based on the results of data analysis, the hardness value of the magnesium layer at 10 minutes at a voltage of 10 volts is 67 HV. In comparison, the coating thickness at a time of 10 minutes with a constant voltage of 10 volts is 4 μm. With variations in stress and time in different concentrations of the solution, there will be differences in the hardness value and thickness value of the AZ31 magnesium coating material.

Keywords: *anodizing, coating, electrolyte, hardness, coating thickness.*

I. INTRODUCTION

Material technology is widely used in various circles and institutions, one of which is in the field of bone-implant health. In particular magnesium-based alloys have attractive combinations that are potentially biodegradable due to their outstanding biological properties. Properties such as low density, high strength, excellent biocompatibility, biodegradability, no need for a second operation for implant removal [1].

The magnesium used in this research is AZ31 which has a mixture of 3% aluminum and 1% zinc. The use of magnesium is widely used in various studies, including a substitute for human bones in the medical world. The type of magnesium material AZ31 is research being developed with various tests in powder metallurgy of biomaterials. Mg alloys have a specific density (1.74-2 g/cm3) and Young's modulus (41-45GPa) close to that of the human breastbone (1.8-2.1 g/cm3, 3-20 GPa) [3].

The rapid corrosion of Mg and Mg Alloys implants cannot meet the bone repair level. Thus, it is crucial to control the corrosion rate of Mg-based implant materials to match the bone healing rate and ensure that Mg in biomedical applications corrodes to a certain degree by the anodizing system [4].

Various factors can affect the anodizing process, one of which is the effect of immersion time on the anodizing process. It was found that the longer the holding time of anodizing immersion, the thickness of the oxide layer will increase. The hardness value for variations in the holding time of anodizing immersion increases, respectively, with the length of holding time for anodizing immersion of 30, 40, and 50 minutes. Increasing immersion holding time also causes a tendency to increase the hardness value [5].

II. Materials and Methods

Process of coating magnesium with NaOH solution using a magnesium AZ31 cathode and platinum anode with a length of 50 mm x width 20 mm x thickness 5 mm, Ti6Al4V plates with 50 × 50 × 3 mm size[6] then with 0.5 Molar and 1 Molar NaOH solution.

A. *Anodizing Process*

Conclusions are written in the form of one or several.

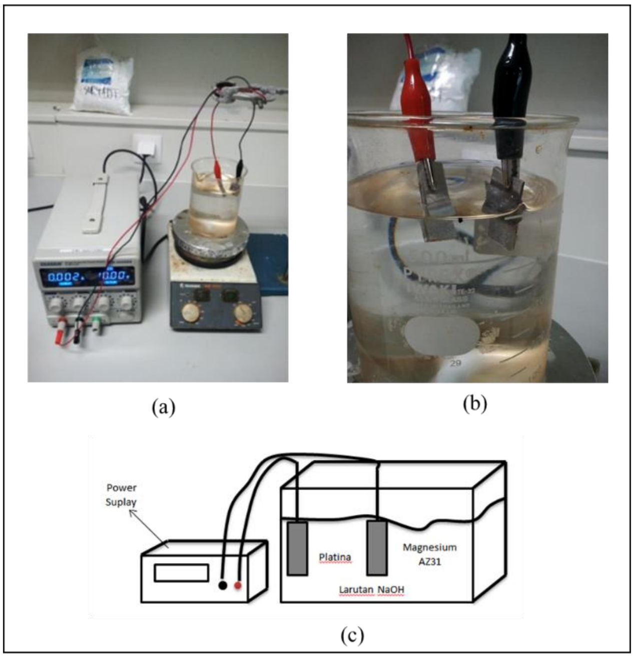

Figure 1. (a) Anodizing Process At 10 Volt; (b) Coating Forming Process; (c) Schematic of the Anodization Process

In the first experiment, magnesium AZ31 was immersed for 20 seconds in a pre-treatment solution and then anodized in 100 ml of 1 M and 0.5 M NaOH solution with a magnetic stirrer speed of 100 rpm with a fixed, variable voltage of 10 volts and for 10 minutes. At the time of anodizing, bubbles will appear on the platinum, which means that the coating on magnesium AZ31 has been successful and can be explained by the chemical reaction of reduction and oxidation, which is as follows.

B. *Chemical Process*

The chemical reactions that occur in the process of coating magnesium az31 with NaOH solution are as follows:

Reduction reaction at Pt
Oxidation reaction:

0 reduction +2

$Pt \rightarrow Pt^{2+} + 2e^-$ oxidator

Oxidation reaction on Mg
Reduction reaction:

0 oxidation +2

$Mg + 2e^- \rightarrow Mg^{2+}$ reducing agent

Platinum has a potential of +1.50 and Magnesium –2.37, so that platinum is a reducing agent of magnesium, and magnesium is an excellent oxidizing agent so that platinum has the potential to oxidize magnesium which has a lower potential than platinum. So that at the anode, an oxidation reaction occurs, and a reduction reaction occurs at the cathode. On oxidation by platinum will encourage magnesium to form Mg^{2+}.

The reaction of NaOH and H_2O on platinum

$$4NaOH_{(aq)} \rightarrow 4Na^+_{(aq)} + 4OH^-_{(aq)}$$
$$4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$$
$$4H_2O + e^- \rightarrow 2H_{2(g)} + 4OH^-_{(aq)}$$

$$NaOH_{(aq)} + H_2O \rightarrow Na^+_{(aq)} + OH^-_{(aq)} + H_{2(g)} + O_{2(g)}$$

The reaction of magnesium with NaOH

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$$
$$Mg(OH)_2 \rightarrow MgO + H_2O$$

In the NaOH reaction, H_2O in platinum will produce Na^+ ions, dissolve in water, H_2 and O_2 gases will evaporate, and OH- which will react with Mg^{2+}. The reaction of magnesium with NaOH results in forming an oxide layer on magnesium MgO (magnesium oxide), and H_2O has formed again and will react again with NaOH. This reaction will last for 10 minutes under the influence of a voltage of 10 volts.

III. Results and Discussions

The results and discussion of practical work regarding the effect of the concentration of NaOH electrolyte solution on the coating result from the anodizing process on magnesium AZ31 for bone implant applications are as follows:

A. *Coating Hardness Test*

Data on the average value of the hardness of the magnesium oxide layer AZ31 without anodizing treatment and anodizing treatment using various concentrations of 1 M and 0.5 M electrolyte solutions are presented in graphical form as follows. From graphic image 4.3, about the graph of the hardness value of the non-anodizing magnesium AZ31 layer and the anodizing treatment using a concentration variation of 1 M and 0.5 M solution at a constant voltage of 5 volts within 10 minutes it can be seen that there is an increase in the layer hardness value between magnesium AZ31 which did not get anodizing treatment with magnesium AZ31 received anodizing treatment with the average value of the layer hardness from the highest to the lowest was anodizing using a concentration of 1 M electrolyte solution and 0.5 M NaOH.

The surface hardness test aims to compare the value of the surface hardness of the raw material, the thickness of the oxide layer after anodizing on magnesium AZ31. This test was carried out using the Vickers Micro Hardness (HV) method with a loading of 0.5 HV.

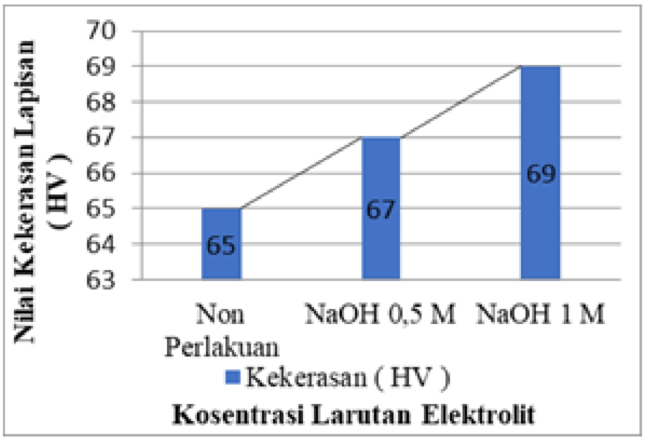

Figure 2. Graph of Average Hardness Results of AZ31 Magnesium Oxide Layer with Anodizing Treatment Electrolyte Solution Concentration of 1 M and 0.5 M NaOH

The results of these tests are then calculated to determine the hardness level on the surface of magnesium AZ31, which has been anodized with a variation of 0.5 M concentration solution in anodized solution. The following are the steps for calculating the hardness value (VHN) of the thickness of the oxide layer on raw materials, 0.5 M and 1 M anodizing materials with a hardness tester. Hardness testing using the Vickers microhardness (VHN) method using a DuraScan type device with the Struers brand with the ASTM E 92 test standard for magnesium AZ31 material with dimensions of 300 mm long, 150 mm wide, and 50 mm thick. The tests were carried out at an average temperature of 23.5°C and average humidity of 42%.

After installing the equipment, set the Vickers hardness test parameters on the control unit, then select 'single measurement' in the 'specimen' menu by selecting 0.5 HV loading and lens magnification on the autofocus objective lens. Then put the sample on a test base that has been cleaned using alcohol by placing a flat surface on the bottom and a smooth surface on top. After that, select the 'position' 'turret' menu, select the diamond indentation, and lower the indenter to a distance of ±2 cm above the sample surface.

Then choose 'AF Touch' to change the visual indenter into a lens then it will automatically autofocus on the monitor screen then start the hardness test by continuing to lower the indenter and selecting the 'measure' menu then the tool will work automatically when finished then the monitor will display the hardness value, and the image is saved . After that, test sample 2 magnesium AZ31 with an anodizing voltage process of 10 volts.

Figure 3. Vickers Hardness Test Tool

The calculation of the Vickers hardness refers to ISO 6507/2, which is adjusted to the verification of the tool against the standard. However, the Vickers hardness value will automatically appear on the control unit screen by using this tool. For manual calculations, the Vickers hardness value is calculated using equation 2.1, and it can be shown as follows,

$$HV=1.8544(P/d^2) \quad (1)$$

With :
P = load, kgf
d = average length of two indented diagonals, mm

The results of the one way ANOVA test to answer the hypothesis that there is an effect of variations in electrolyte solution on the hardness of the coating resulting from the anodizing process with the normality and homogeneity prerequisite test, which states that the data is normally distributed and the population is identical, with the fulfillment of these prerequisites, one way ANOVA can be performed.

From the one-way ANOVA test, it is stated that the average value of the hardness of the magnesium AZ31 layer after receiving anodizing treatment with various types of electrolyte solution NaOH (Sodium Hydroxide). At concentrations of sulfuric acid solution

(H_2SO_4) 10%, 11%, 12%, 13%, 14%, and 15% carried out on aluminum material resulted in hardness levels of 66.26 VHN, 73.67 VHN, 64.84 VHN, 64 .93 VHN, 65.15 VHN, and 68.43 VHN [7].

The significance of the difference in the mean of each treatment can also be seen in the post hoc test, which shows that the mean treatment using 1 M and 0.5 M NaOH electrolyte solution does not show a significant difference. The thickness and hardness of the oxide layer depend on the type and composition of the electrolyte used. From the electrolyte factor used in the anodizing process in this study, the difference in the hardness value of each treatment was influenced by several factors, namely the electrolyte solution group, the degree of ionization of the solution, the concentration of [H+] ions in the solution.

Table 1. Results of testing and calculating surface hardness after the anodizing process with variations in the concentration of anodized electrolyte solution.

No	Variation	Test Point Position	Violence
1.	Raw Material	Random	65 HV
2.	NaOH 0.5 M	Anodizing	67 HV
3.	NaOH 1 M	Anodizing	69 HV

The table above shows the results of micro Vickers testing on anodizing aluminum surfaces with variations in sulfuric acid concentration. From the table above, it can be analyzed that the 1 M NaOH electrolyte solution concentration has a higher surface hardness value than the 0, NaOH solution variation. 5 M.

The most hardness with a hardness of 69 HV, while at a concentration of 0.5 M electrolyte solution has a hardness of 67 HV, the lowest hardness value is at a hardness of 65 HV without anodizing. However, overall, the hardness test results without anodization are minor. At a concentration of 0,5 M, NaOH has a surface hardness of magnesium AZ31, which can start to increase, and at the concentration of 1 M solution has the highest value. It is suspected that this is because the concentration of NaOH used is higher so that the workpiece opens the pores more evenly. The oxide layer is flatter than 0,5 M.

From the results above, it can be concluded that the electrolyte solution with a high concentration can affect the increase in the hardness value of magnesium AZ31, as evidenced by the results of 1 M NaOH. From the results of his research, it can be concluded that the higher concentration of NaOH electrolyte solution with the immersion time interval in the anodizing process for 10 minutes can increase the hardness value of the anodizing magnesium AZ31 surface.

In the results of this test, the highest surface Vickers hardness was at a concentration of 1 M at 69 HV and the lowest at a concentration of 0.5 M at 67 HV. The results of other studies that have been carried out by [10] with variations in the concentration of sulfuric acid solutions of 10, 15, 20, and 25%, that the effect of variations in the concentration of sulfuric acid electrolyte used in the anodizing process affects the hardness of the material with the highest hardness obtained at a concentration of 10% Of 100.2 (VHN), the lowest hardness was at a concentration of 25% with 95.5 (VHN). Differences in hardness values can be caused by several factors, including aluminum metal used as an anode, current strength, and anodizing time.

B. Visual Test Results

After the anodizing process in this test are photos from the smartphone's 13 MP (Mega Pixel) camera capture. The following is a description of the results of the tests carried out. The following is the coating color with anodizing treatment with variations of 1 M and 0.5 M NaOH electrolyte solutions. The following is a picture of the color results of the specimen surface with anodizing treatment using a concentration of 1 M solution.

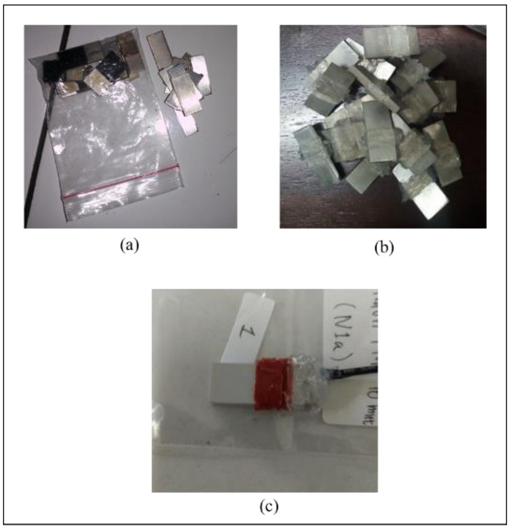

Figure 4. Color Comparison (a). before sanding (b). After sanding (c). Specimen Surface Anodizing Treatment with 1 M Electrolyte

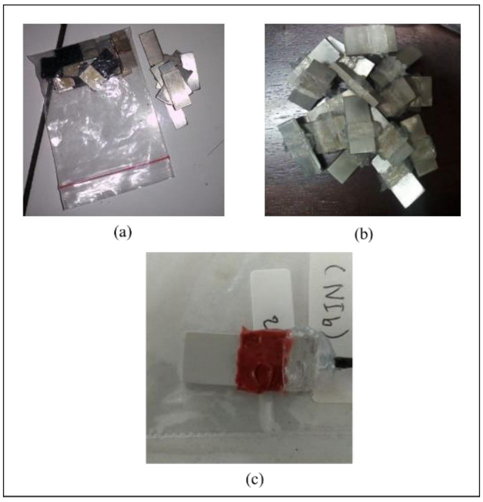

Figure 5. Color Comparison (a). before sanding (b). After sanding (c). The surface of Specimens Result of Anodizing Treatment with 0.5 M Electrolyte

Let us look at the Figure (4) of the specimen above. We can see that the color produced from the anodizing treatment using a 1 M NaOH electrolyte solution produces reasonably thick ash to the white layer. The higher the concentration of the solution used, the pigment's color formed on the material's surface can increase.

Let us look at Figure (5) of the specimen above. We can see that the color resulting from the anodizing treatment using a 0.5 M NaOH electrolyte solution produces ash to the white layer of color. It is caused by differences in the structure of the oxide layer in the form of porous size formed from each concentration of electrolyte used, also influenced by the thickness of the oxide layer, whose value is directly proportional to the hardness of the oxide layer. It was concluded that the characteristics of the formed oxide layer would significantly affect the staining adhesion.

C. *Oxide Layer Thickness Test*

Table 2. Test results and calculation of the thickness of the oxide layer after the anodizing process with varying concentrations of 1 M and 0.5 M in the anodized solution.

Variation	Thickness	Thickness Result (µm)
No Treatment	Random	0
0.5 M NaOH	Anodizing	4
1 M NaOH	Anodizing	6

To test the thickness of the anodizing oxide layer using a coating thickness tester anodizing type CM8826FN. This measuring instrument can be used to measure the thickness of the galvanic and the anodizing process. This tool is equipped with two kinds of thickness measuring probe sensors, namely type F Probe is used to measure the thickness of non-magnetic materials such as copper, zinc, aluminum, chrome, etc. attached to magnetic materials such as iron, nickel etc.

While the NF probe is used to detect the thickness of the non-magnetic layer on non-magnetic metal materials, it can be used in the anodization process, electro plating, etc. which are used on aluminum, brass, platinum, titanium, stainless steel, and magnesium materials.

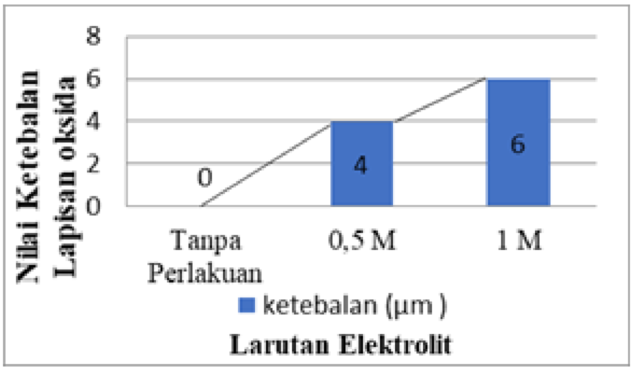

Figure 6. Comparison graph between the average thickness (µm) and the concentration of NaOH in the anodizing solution

The graph above shows that the variation of 1M and 0.5 M NaOH concentrations after the anodizing process resulted in a thickness of the oxide layer on the magnesium AZ31 surface of 6 µm, 4 µm, respectively. From the test results described in the graph above, it can be concluded that variations in the concentration of NaOH in the anodizing solution in the anodizing process affect the thickness of the oxide layer of magnesium AZ31.

Then for the highest MgOH oxide layer thickness at a concentration of 1 M NaOH solution after the anodizing process of 6 µm, while the smallest value of the oxide layer thickness after the anodizing process at a concentration of 0.5 M anodizing solution was 4 µm because the material that was not treated was not produced layer thickness (a knowledgeable audience might find this sentence hard to read. Consider: Removing any unnecessary words, Splitting it into two sentences). The average thickness of the coatings is 7 µm, 9.8 µm, 14.7 µm and 19.8 µm for NaOH concentration is 0.05 mol/L, 0.1 mol/L, 0.2 mol/L, and 0.4 mol/L, respectively [8].

Shows the lateral view images of the as-anodized Ti–7.5Mo specimen and those specimens treated by 0.5 M and 5 M NaOH. A cross-section SEM image of the nanotube layer of the as-anodized Ti–7.5Mo shows well-ordered tube arrays with a tube length of about 434 ± 7 nm, which was significantly greater than those of the 0.5 M and 5 M NaOH-treated Ti–7.5Mo specimens (423 ± 10 and 388 ± 9 nm, respectively). The thickness of the tube layer decreased with increasing NaOH concentration [9].

Therefore, it can be concluded that the variation in the concentration of the anodizing solution in the anodizing process dramatically affects the thickness of the oxide layer formed on the surface of magnesium AZ31. The research conducted [10] concluded that each addition of the electrolyte concentration given caused a thicker oxide layer to form after the anodizing process.

Due to the higher concentration of NaOH, the resistance in the electrolyte solution decreases. The electric current that flows is more significant at the same voltage. As a result, the reaction that occurs is faster, then the thickness of the layer increases.

The variation of the concentration of the electrolyte solution given in the anodizing process has an optimum magnitude. The graph above shows that the variation of sulfuric acid concentration in 30%, 40%, and 50% anodized solutions after the anodizing process resulted in the thickness of the oxide layer on the aluminum surface of 2 µm, 2.5 µm, and 1.5 µm, respectively. The results obtained in this study are under research conducted by [10]. Each addition the electrolyte concentration causes a thicker oxide layer to form after the anodizing process.

Due to the higher concentration of sulfuric acid, the resistance in the electrolyte solution decreases. This results in a more significant current flowing at the same voltage. As a result, the reaction occurs faster, then the thickness of the layer increases. Meanwhile, the results of other studies indicate that the reduction in the thickness of the layer is due to the rapid oxidation reaction that occurs so that the oxide layer that has been formed will melt faster and cause the depletion of the oxide layer that has been formed.

In the results of this test, the thickness of the layers of 1 M and 0.5 M is 6 µm, 4 µm, respectively. The higher the concentration of sulfuric acid in the anodized solution, the thickness of the oxide layer will increase. The highest oxide layer thickness of up to 14.51 µm is obtained at a concentration of 0.36 M. However, at a concentration of 0.48 M, the thickness is only 9.95 µm. Then, increasing concentration of sulfuric acid solution (H2SO4) results in a surface with a denser pore, marked by an increase in the gray color after the anodizing process [10].

IV. Conclusions

From the research, analysis, and discussion of data that has been carried out on the effect of variations in the concentration of NaOH anodize solution on the anodizing process. Then several tests were carried out, namely coating thickness testing and Vickers microhardness testing, that Magnesium AZ31 is a material that is currently often used as a material in technology biomedical because it has a young modulus and a specific density similar to that of human bone. The coating on the Mg AZ31 material is carried out so that the Mg AZ31 material can increase the corrosion resistance properties and the healing time. As the NaOH concentration increases, the thickness of the MgO oxide layer increases. The thickness of the layer at a concentration of 0.5 M and 1 M after anodizing was 4 m and 6 m, respectively. In the study results for 2 test specimens, the higher the concentration of NaOH solution used, the more coating formed on the surface. While the hardness test showed at a concentration of 1 M NaOH, the hardness value was 69 HV, while at a concentration of 0.5 M, the hardness was 67 HV, so from the results of research with concentrations of 0.5 M and 1 M, the hardness level increased. However, during the anodizing process, Mg AZ31 interacts with NaOH solution so that it is possible to cause the porous formation and will reduce its young modulus. To prevent a decrease in its Young's modulus the Mg AZ31 material is press casting (compacted) with various variations of semi-solid temperature sintering temperature and then designing and analyzing the application of biodegradable bone implants in the form of plates and bone bolts

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References

[1] Zhang, L., Zhang, J., Chen, C.F., Gu, Y. 2015. Advances in microarc oxidation coated AZ31 Mg alloys for biomedical applications, Corros. Sci., 91 7-28.

[2] Gupta, M., Phuong, N.V., Moon, S. 2017. Enhanced corrosion performance of magnesium phosphate conversion coating on AZ31 magnesium alloy. Trans. Nonferrous Met. Soc. China 27 1087−1095.

[3] Wang, L., Chen, Li., Yan, Z., Wang, H., Peng, J. 2009. Effect of potassium fluoride on structure and corrosion resistance of plasma electrolytic oxidation films formed on AZ31 magnesium alloy. Journal of Alloys and Compounds 480 469–474.

[4] King, A.D., Birbilis, N., Scully, J.R. 2014. Accurate Electrochemical Measurement of Magnesium Corrosion Rates; a Combined Impedance, Mass-Loss and Hydrogen Collection Study, Electrochimica Acta, http://dx.doi.org/10.1016/j.electacta. 2013.12.124.

[5] Pujianta, Ary. 2008. Pengaruh Variasi Waktu Penahanan Pencelupan Terhadap Ketebalan, Nilai Kekerasan, Dan Laju Korosi Lapisan Oksida Aluminum Pada Proses Anodizing. Skripsi thesis, Universitas Muhammadiyah Surakarta.

[6] Lin, S. H., Chien, C. S., Kuo, T. Y., Hsieh, Y. H., Huang, J. W., Chin, W. H.,Lee, H. T. 2020. Biomedical evaluation of vacuum plasma sprayed tantalum coatings processed by alkali treatment and alkali-heat treatment with different NaOH concentrations. Surface and Coatings Technology, 403, 126400. doi:10.1016/j.surfcoat.2020.126400.

[7] Kristanto, A.H. 2017. Pengaruh Variasi Kosentrasi 10%-15% Larutan Asam Sulfat (H2SO4) Pada Proses Anodizing Alumunium. Universitas Sanata Dharma. Yogyakarta.

[8] Tang, H., & Gao, Y. 2016. Preparation and characterization of hydroxyapatite containing coating on AZ31 magnesium alloy by micro-arc oxidation. Journal of Alloys and Compounds, 688, 699–708. doi:10.1016/j.jallcom.2016.07.079 url to share this paper: sci-hub.se/10.1016/j.jallcom.2016.07.079

[9] Hsu, H.C., Hsu, S.K., Wu, S.C., Hung, Y.H., & Ho, W.F. 2020. Surface modification of nanotubular anodized Ti–7.5Mo alloy using NaOH treatment for biomedical application. Thin Solid Films, 710, 138273. doi:10.1016/j.tsf.2020.138273

[10] Rohman, A. K. 2012. Pengaruh Variasi Konsentrasi Elektrolit Terhadap Kekerasan Permukaan Pada Proses Anodizing Aluminium 6xxx. Skripsi. Tidak diterbitkan. Fakultas Teknologi Industri Universitas Islam Indonesia