Growth of TiN thin film on Al 5083 deposited using dc sputtering technique for improving their hardness and corrosion resistance

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Abstract. Aluminium 5083 is an Al-Mg alloy commonly used in ship hull construction. Although it has good corrosion resistance, this aluminium alloy is susceptible to corrosion in extreme environments for a long time. This research aims to improve the ability of aluminium 5083 deposited by TiN to increase hardness and corrosion resistance using dc sputtering process. This research was carried out with several processes, namely the study of literature, preparation of tools and materials, manufacturing of test objects, coating process, characterization, data analysis, and report making. Hardness testing was done by Vickers method, corrosion testing was carried out by electrochemical method, and crystal structure test using diffraction X-ray. The results of this study were sputtering time 120 minutes increasing hardness 81.6% or becoming 94.7 VHN. The best corrosion rate at 90 minutes sputtering time is 0.0001 mpy. The formation of the TiN phase in the direction of 111, 200, and 202 planes respectively, was shown through peaks at 2-theta at 36.68°, 42.72° and 61.98°.

1. Introduction

Seawater covers 70 percent of the earth’s surface and is generally considered the most corrosive natural environment. Indonesia is a maritime country that 75 percent of its territory is sea, so it requires sea transportation to support the survival of the population. Based on the construction aspect of the ship, the hull is the area that was first exposed to seawater. One of the biggest sources of damage to marine plates is seawater corrosion. Aluminium and aluminium alloys include light metals that have high strength and are resistant to rust[1]. Aluminium alloys that are widely used for shipbuilding are the 5xxx series (Al-Mg-Mn) and 6xxx series (Al-Mg-Si)[2]. Although aluminium alloy has good corrosion resistance due to the natural oxide layer that aluminium has, but in a corrosive environment this layer becomes unstable. This instability makes aluminium alloys can also be attacked by corrosion, as in the aluminium shipbuilding industry[3].

A solid material surface when bombarded by high energy particles then the atoms on the surface of the material get enough energy to escape and scattered from the surface, this phenomena is called the sputtering process. DC sputtering method uses DC voltage in its to generate plasma. Therefore this method can only be used on conductor or semiconductor objects [4]. Some types of compounds that can be grown through the sputtering method include TiO₂, TiN and others. One of them is Titanium
Nitride (TiN) and its a compound that is hard and often used for coating on the material to improve the mechanical properties of the material[5].

The advantage of the sputtering method compared to other methods is that the process is faster and cleaner because the process is carried out in a vacuum, can produce a thin layer of material that has a high melting point, almost all solid materials such as semiconductors, metals, metal alloys and ceramics can be grown, have stronger adhesion so that it can extend the service life of the components being made, and the thickness of coating can be precisely controlled[6].

Based on the previous description, it is known that the method of sputtering can increase the property of the material. So, the aim of this research is to investigate the effect of time variation and gas ratio an aluminium alloys 5083 deposited by TiN using DC sputtering process.

2. Experimental Procedure

The plate of aluminium alloys 5083 was cut using water jet cutting machine into disc shape 5 mm thick and 14 mm diameter. The surface substrate was smoothed using SiC paper from 800-grade up to 2000-grade. After the substrate becomes smooth, the substrate was polished by diamond paste and then washed using liquid soap and alcohol by ultrasonic cleaner for 10 minutes and 20 minutes for each process.

Parameters that need to be considered during the sputtering process are pressure, voltage, current, time, and the ratio of a mixture of argon gas and nitrogen. The parameters that were kept constant were the pressure in the order of 10⁻² Torr, a voltage of 3 kV, a current of 10 mA. In this study, TiN thin films was deposited using DC sputtering for 60 minutes; 90 minutes; 120 minutes; 150 minutes of time as well as variation of argon and nitrogen gas ratio such as 60:40; 70:30; 80:20; and 90:10. The sputtering process was carried out at PSTA – BATAN Yogyakarta, Indonesia.

The microhardness test was done at PSTA – BATAN using microhardness tester Vickers Matsuzawa MMT-X7. The hardness test was carried out for raw and coated materials. For hardness test, the applied load was 10 gf for 10 seconds of indentation time. The corrosion test was done at Material Engineering Laboratory, UGM. The electrochemical method was performed using potentiostat Princeton Applied Research Versastat 4 instrument. The corrosion test was applied for raw and coated material with highest hardness value. The test was carried out in simulated solution such as seawater namely 3.5% NaCl solution. The testing process for each substrate was carried out for 10 minutes and the NaCl solution was replaced for each substrate tested, then the corrosion rate was analyzed in mpy (mils per year) unit.

The crystal structure for raw and coated material for highest hardness value was analyzed by X-ray Diffractometer (XRD) at Chemistry Laboratory, UNHAS. The operation was carried out at 40 kV and 15 mA. The source used was Cu-Kα with the wavelength was 1.54 Å. The 2-theta angle used was at 15° - 75°. This characterization was performed to see the existence of TiN layer after the sputtering process.

3. Result and Discussion

3.1. Hardness Measurements

For hardness test, the used load was 10 g for 10 seconds of indentation time. Figure 1 shows three different forms of surface indentation for (a) the raw material substrate and (b) sputtered substrate. Figure 1 (a) has a large indentation trace and (b) has a small indentation trace, it means that the hardness of the sputtered substrate is higher than raw material substrate. This indicates that a thin layer has formed on the sputtered substrate. The raw material substrate has a smooth and flat surface so that the indentation formed is large. While the sputtered substrate has a dense surface due to the formation of a thin layer so that the indentation formed is small and it indicates a high hardness value.
Figure 1. Substrate Surface of (a) raw material substrate (b) sputtered substrate

Figure 2 shows the hardness as a function of time parameters. From graph shows that the time affects the hardness on the substrate. The longer the processing time increases the hardness value of substrate[7], [8]. The optimum hardness value in this time parameters is 94.7 VHN. In the time parameters over the processing time the value of hardness increases indicates that a thin layer has formed. But after passing the optimum value, material hardness decreases significantly due to saturation. The increase of the hardness value is consistent with the amount/ thickness of TiN compound coating attached to the substrate. However, the hardness value decrease after the optimum is obtained because the TiN deposited substrate has saturation, causing the hardness value to decrease. The hardness value decreases after the optimum time because the deposition results have reached optimum density[8]. This trend can be seen in Figure 2.

Figure 2. Hardness value of time parameters

Figure 3 shows the optimum hardness is obtained at 70:30 of argon and nitrogen gases ratio. This phenomenon indicates the large percentage of Ar ions that bombarded titanium target has an effect on the number of spattered Ti atoms. The percentage of nitrogen gas is sufficient to bond with the titanium atom then form TiN compounds. The highest hardness value of the Ar70: N30 gas mixture compared to other gas mixture parameters. A higher concentration of argon will cause the forming of TiN compounds not optimum. [9].
3.2. Corrosion Test
The test was carried out using a simulated solution such as seawater namely 3.5% NaCl solution. The testing process for each substrate was carried out for 10 minutes and the NaCl solution was replaced for each test. Corrosion test results show the measured corrosion stress (Ecorr) and corrosion currents (Icorr) using Versa studio software. Then, the data is extrapolated to get the best corrosion rate. As a comparison of the corrosion rate result from Versa studio software, a theoretical calculation was performed using equation $r = K \frac{ai}{nD}$, where $r$ is corrosion rate, $K$ is a constant variable, $a$ is equivalent weight, $i$ is corrosion current, $n$ is area of the material and $D$ is material density. To calculate the corrosion rate of Al-5083 material, the equivalent weight of Al-5083 material is required. It can be estimated with the dominant composition in the Al-5083 material. The analysis result is shown in Figure 4.

The test results show that the corrosion rate of raw material is 1.47 mpy while the best corrosion resistance substrate sputtered is 90 minutes with a mixture ratio gas Ar70:N30. The formation of a thin layer of TiN on the substrate causes the substrate to resist corrosion. In addition to the TiN compounds that are formed increasing the nitrogen composition in the sputtering process can also protect the substrate from corrosion. This is possible due to the diffusion of nitrogen on the substrate.
just prior to the occurrence of a thin layer of TiN on the surface of the substrate. In DC sputtering tubes, when the plasma phase is formed, nitrogen under plasma condition will diffuse into the substrate and for nitrate bonds which have corrosion resistant properties[10]. Therefore, in addition to the thin layer of TiN formed, nitrate bonds formed on the surface of the substrate beneath the thin layer of TiN also resist corrosion.

3.3. Crystal Structure
The crystal structure for raw material substrate and sputtered substrate that were analyzed by X-ray Diffractometer (XRD). The operation was carried out at 40 kV and 15 mA. The source used was Cu-Kα with the wavelength was 1.54 Å. The 2-theta angle used was at 15° - 75°.

In raw material substrate, it is known that the database for aluminium experimental data is related to COD with entry number 96-431-3215. From this database it can be seen that the aluminium substrate has a cubic structure with peak values at 2-theta 38.49°, 44.66°, 65.06°. The 2-theta peak is formed at direct 111, 200, 202. The experimental result of sputtered substrate is related to COD with entry number 96-900-8749 which is the TiN phase database. The report shows that 2-theta are at 36.68°, 42.72°, 61.98° has a cubic structure. The 2-theta peak is formed at direct 111, 200, 202. This can be seen in Figure 5, there are XRD patterns of raw material substrate and sputtered substrate.

![XRD pattern of substrate in various sputtering parameters](image)

In figure 5 shows that there is no significant difference in XRD spectrum. The TiN is formed in a low intensity (thin layer). Another factor that causes the low intensity of the TiN phase is the interstitials of TiN atoms on the substrate, which causes x-ray diffraction which illuminates the target atoms to be destructive so that it has a low intensity. Factors such as a nitrogen gas flow rates also influence the formation of the TiN phase. The flow rate of N₂ also greatly effects the crystal structure, degree of orientation, and texture[11].

4. Conclusion
The growth of TiN thin film on Al 5032 deposited using DC sputtering technique to improving the hardness and corrosion was done. The optimum sputtering time is 120 minutes with a ratio of argon and nitrogen is 70:30. This method increased the hardness of the substrate from 52.14 VHN to 94.7 VHN or increased 81.6 %. The lowest corrosion rate is at 90 minutes sputtering processed. Its decreased 1.47 mpy to 0.0001 mpy. The improvement of hardness and the reduce of corrosion rate caused by the formation of TiN thin layer which shown by XRD result at 2-theta 36.68°, 42.72°, 61.98° which is cubic structure. The sputtering process changes the hardness and corrosion resistance of the substrate surface with a thin layer of TiN formed during the process.
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