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The Influence of TiN-Sputtering on Hardness and Corrosion Rate of AISI 304 for Biomaterials Application

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Abstract

This study examines the effect of hardness and corrosion resistance of Titanium Nitride (TiN) sputtering treatment on AISI 304 as alternative biomaterials. TiN sputtering was done a 25-30 mA, 2.5-3 kV and a distance between the substrate with a target of 10 mm. The variations of the ratio between argon gas (Ar) and nitrogen gas (N_2) were 70:30; 80:20 and 90:10. The variations in the duration of the sputtering process were 30, 60, 90, 120 and 150 minutes. The Vickers hardness test was performed with 5 grams of load for 10 seconds. The corrosion test was performed on a bovine serum solution as a substitute for human body fluids. Hardness and corrosion resistance increased by sputtering. The hardness of the treatment material with the 70:30 ratio of Ar and N_2 for 150 minutes is 48% higher than the hardness of non treatment material. The corrosion rate of the material with the 70:30 ratio of Ar and N_2 for 120 minutes is 875% lower than the corrosion rate of non treatment material.

Keywords: Sputtering, Hardness, Corrosion Rate, AISI 304

Introduction

TiN-Sputtering is the process of inserting TiN atoms on the surface of the substrate by firing high-energy ions on the target surface causing the target surface atoms to decompose and insert on the surface of the substrate [1]. The TiN layer deposition has hard properties, corrosion resistance, abrasion resistance, high temperature resistance, low friction coefficient, biocompatible and has good mechanical properties [2-5]. The increased hardness occurs when there is a change in the residual stress tension that can inhibit the dislocation movement [6-7].

The process of thin film formation is influenced by various parameters. As follows inter-electrode voltage, distance between electrode, gas pressure, deposition time and substrate

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temperature. The electrode voltage affects the amount of ionic energy to strike the target surface. The distance between the electrodes affects the number of atoms attached to the surface of the substrate. The gas pressure affects the collision of pound ions with air particles which is still present in the vacuum chamber. It affects of the rate of deposition of the atoms in the sputtering process. The length of deposition time greatly affects the thickness of the resulting film. Increasing temperature causes the number of vacancies to increase rapidly. It allows foreign atoms to infiltrate deeper between the atomic spaces, so that can occupy an existing void.

TiN belongs to an inert ceramic material, which is widely used as a surface coating material and has an advantage in terms of hardness [8]. It is resistant to high temperature, wear resistant and has good mechanical properties [9]. The majority of this layer is a nano crystalline compound obtained by layer deposition by sputtering or arc evaporation process. A thin layer of TiN on the surface of the specimen is formed by depositing titanium. The N_2 gas is inserted at the same time, so that a chemical reaction occurs $Ti + 1/2\ N_2 \rightarrow TiN$ [10].

The effect of new coating in terms of hardness, corrosion rate, and microstructure for alternative biomaterials applications is investigated.

Experimental Procedure

Materials

Austenitic stainless steels AISI 304 was used as material. The material composition was presented in Table 1 and the mechanical properties are shown in Table 2. The specimens of plate-shaped 3 mm thick were cut in a circle of 14 mm in diameter and polishing on the surface.

Sputtering TiN

TiN Sputtering was done by adjusting the current parameters of 25-30 mA, 2.5-3 kV voltage, the distance between the substrate and the target of 10 mm, and the ratio of Ar and N_2 was 7: 3. Ar used as a gas sputter and N_2 as reactant gas. Pure titanium was used as a target coating material. The duration of the sputtering process was varied 30, 60, 90, 120, and 150 minutes.

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Hardness test

The Vickers hardness test is used to determine the hardness of the specimen's surface [10]. The indentation load was used 5 gf for 10 seconds.

Corrosion test

The corrosion rate test was performed with a cell type three potentiometric electrode type M 273 electrode instrument [11]. The serum bovine solution was used as a Simulated Body Fluid (SBF) with a 25% bovine serum composition and 75% sterile aquades [12-14]. The corrosion test parameters were performed with scan properties: Step Height (4 mV); Step Time (2 s) and Scan Rate (2 mV/s).

Microstructure test

Microstructure test was performing using optical microscope 200 x magnifications. Cross section cross-sectional observations were also performed to determine the effect of sputtering on the surface of the specimen.

Results and Discussion

Mechanical properties of AISI 304

The constituent elements of the material are shown in Table 1. The element is used as a basis for corrosion test data. The corrosion rate is also affected by the alloying elements in the material. Mechanical properties of AISI 304 are shown in Table 2. This data is used as a comparison with the material already treated.

Table 1. Composition test

Fe	Cr	Ni	Mn	Si	Cu	Mo	Co	V
70.9400	17.2633	8.3640	1.8614	0.4961	0.3342	0.2666	0.1876	0.0990
Zn	**W**	**P**	**C**	**Nb**	**Al**	**Sn**	**Ti**	**Ca**
0.0368	0.0320	0.0315	0.0278	0.0274	0.0205	0.0125	0.0040	0.0015

Table 2. Mechanical properties

Material	Tensile Strength (MPa)	Yield Strength (MPa)	HV (kgf/mm^2)
AISI 304	634	277	248

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Hardness test

The effect of sputtering duration and composition on the hardness of AISI 304 is shown in Figure 1. The TiN coated AISI 304 has a higher hardness than non-treatment material. AISI 304 hardness value without treatment is 248 HV. The highest hardness increased to 366 HV or about 48% at the composition of 70:30 ($Ar:N_2$) with a duration of 150 minutes.

The more duration on the sputtering increased hardness. As the sputtering duration increases, more and more TiN atoms are inserted on the surface of AISI 304. The depleted TiN atoms fill in the blank space on AISI 304 so that the surface density increases.

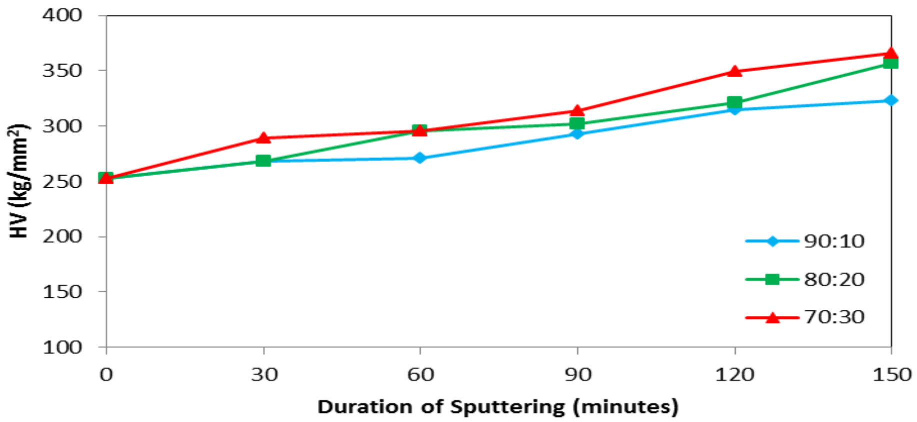

Figure 1. Effect of duration and sputtering layer composition against hardness of AISI 304

TiN layer composition was affected by nitrogen gas amount as reactant gas in sputtering process. Nitrogen atoms which react with titanium atoms formed TiN. Hardness increased by adding nitrogen atoms that are illuminated with Titanium atoms [15].

Corrosion test

AISI 304 anodic polarization curve in serum bovine solution is shown in Figure 2. Analysis of Tafel slope values indicates the corrosion current (I_{corr}) value of the specimen. The smaller the I_{corr} value, the smaller the corrosion rate [16]. Similarly, corrosion rate decrease with increasing corrosion potential value (E_{corr}). E_{corr} values increase with increasing duration of sputtering. It can be observed that treated AISI 304 tends to be more corrosion resistant than AISI 304 non treatment. E_{corr} of AISI 304 non treatment is -0.1923 V, while AISI 304 with TiN sputtering (70:30) duration of 120 minutes has the highest value E_{corr} is -0.0267 V. The corrosion resistance of stainless steels can be enhanced by the presence of nitrogen elements [15-18]. Nitrogen can be a direct passivation or indirect it can stabilize passivation [19]. TiN thin layers was proved to be able to protect the the substrate from surface corrosion attacks.

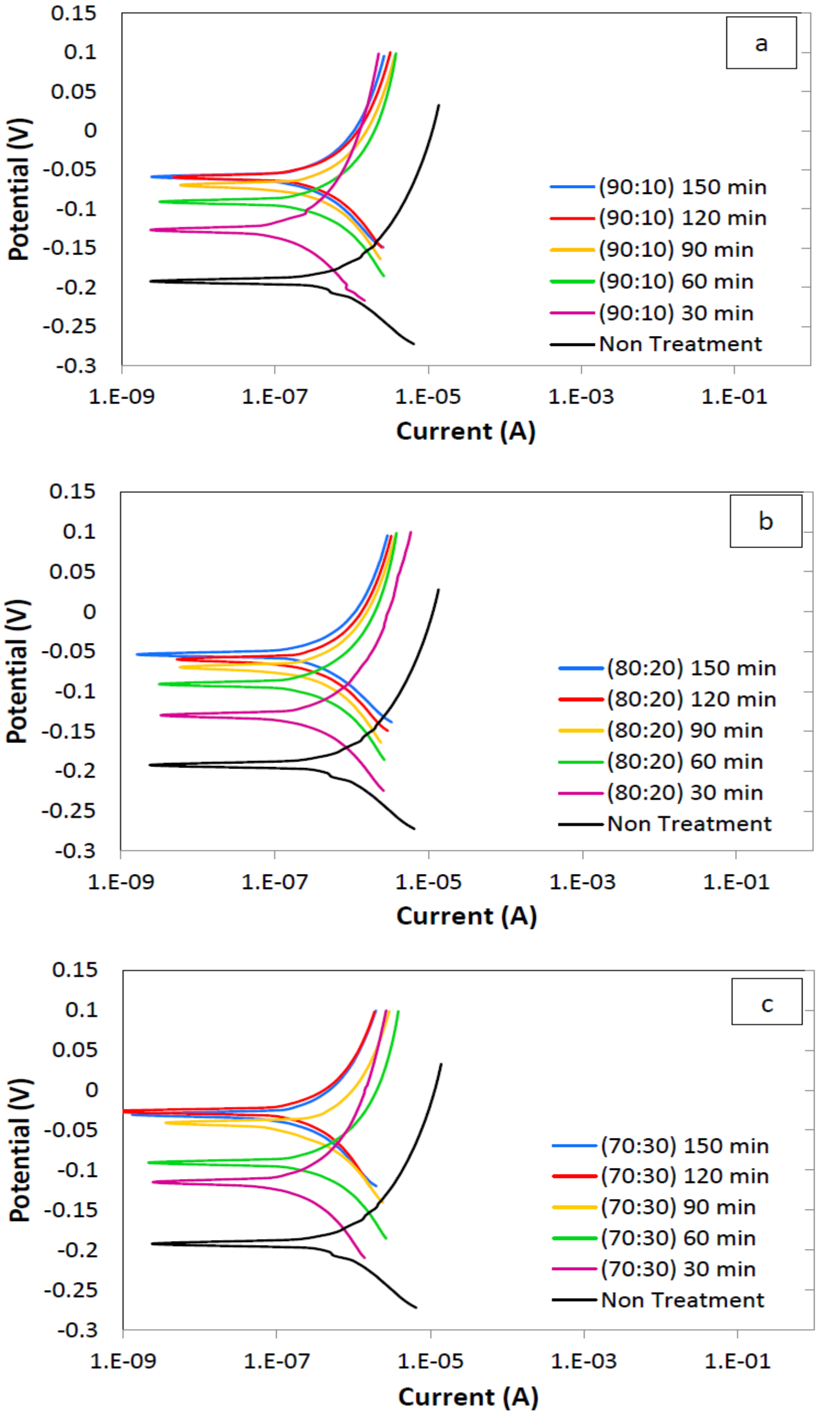

Figure 2. The anodic polarization curves of TiN sputtering film on AISI 304 of (a) Ar:N_2 (90:10), (b) Ar:N_2 (80:20) and (c) Ar:N_2 (70:30) in bovine serum solution

The effect of sputtering duration on AISI 304 corrosion rate is shown in Figure 3. Corrosion rate decreases with increasing duration of sputtering. Deposition time is an important parameter in the sputtering process. The longer the sputtering process, the more target quantity (Ti) splashed onto the surface of the substrate. However, the time of sputtering deposition had an optimum limit. Maximum sputtering duration was 120 minutes. If the duration was added it can increase its corrosion rate. AISI 304 non treatment corrosion rate was 0.35 mpy and the best value of 0.04 mpy on the TiN specimen (70:30) was 120 minutes. This result shows relative corrosion resistant is outstanding [20]. Comparison of the initial specimen with the treatment specimen decreased the corrosion rate about 875%.

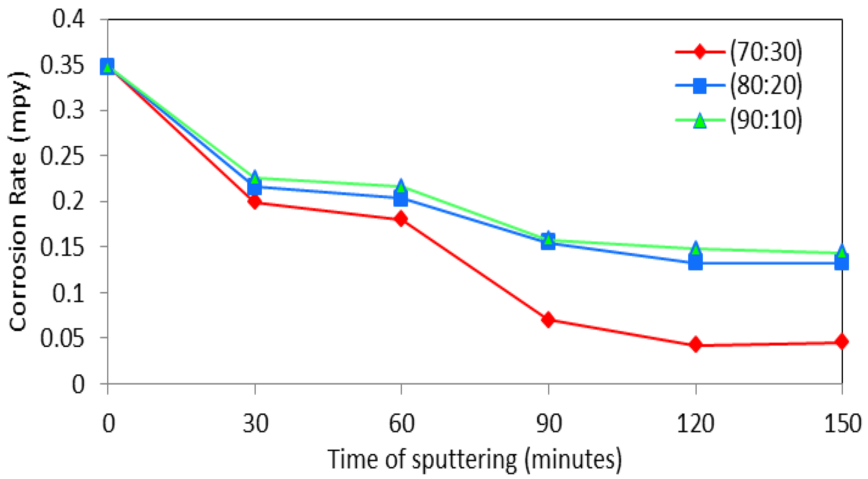

Figure 3. Corrosion rate ratio of AISI 304 and AISI 304-TiN (70:30; 80:20 and 90:10) with duration of (0; 30; 60; 90; 120 and 150 minutes)

Microstructure

The observation of the microstructure was performed by 200X enlargement of the cross section of the specimen shown in Figure 4. The TiN atoms in the sputtering process diffused into the specimen surface and formed a thin layer with a thickness of about 5µm. The vacancies on the surface of the specimen are inserted with TiN atoms, thereby increasing the density of the specimen's surface. The TiN thin film is hard and serves as a protective film layer of oxidation on the surface of the substrate. This is in accordance with the results of hardness tests and corrosion tests, that TiN coating can increase hardness and corrosion resistance.

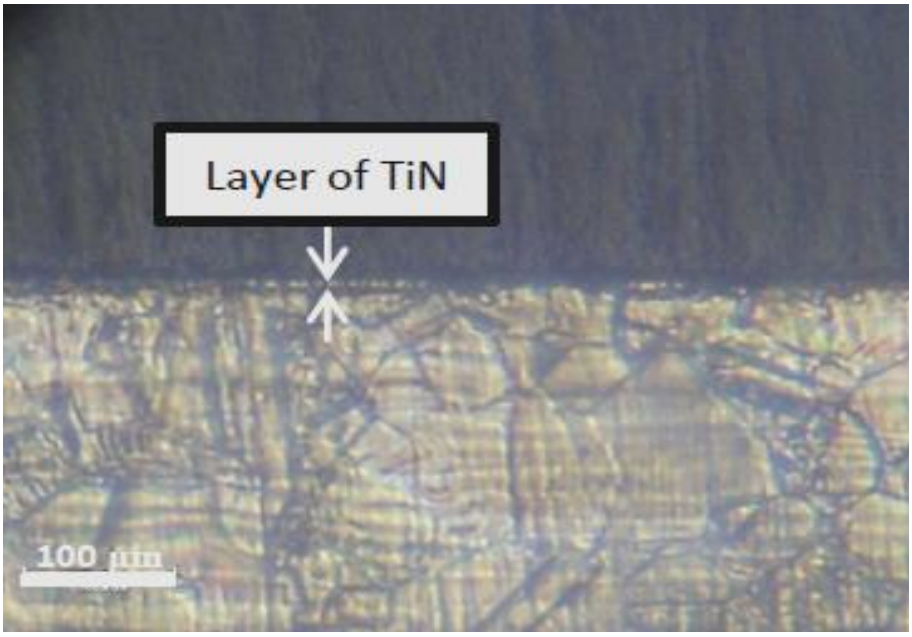

Figure 4. Cross-section microstructure of sputtering (70:30) 120 minutes AISI 304

Conclusions

Sputtering TiN can increase the surface hardness and decrease the corrosion rate significantly in AISI 304. The best AISI 304 corrosion rate is treated 8 times lower than AISI 304 non treatment. The surface hardness can also be increased by 48%.

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