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THE EFFECT OF THE GAS MIXTURE RATIO ON 316L STAINLESS STEEL BIOMATERIAL'S MECHANICAL PROPERTIES AND CRYSTAL STRUCTURES USING DC SPUTTERING TECHNIQUE

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ABSTRACT

THE EFFECT OF THE GAS MIXTURE RATIO ON 316L STAINLESS STEEL BIOMATERIAL'S MECHANICAL PROPERTIES AND CRYSTAL STRUCTURES USING DC SPUTTERING TECHNIQUE. Stainless steel type of 316L is widely used as an orthopedic implant due to its high corrosion resistance and biocompatibility, but the weakness of these materials is low hardness and high wear. The surface must be modified to improve the material. For the purpose, a titanium nitride (TiN) thin film was deposited on the surface of stainless steel 316L using DC sputtering technique. The sputtering process was carried out for various of a gas mixture of argon (Ar) and nitrogen (N_2) of 90:10, 80:20, 70:30, and 60:40, while the other parameters kept constant. The objective of the gas mixture variation was to find out the optimum condition of ratio Ar: N_2 gas mixture with the highest hardness and lowest wear resistance. From experiment done it was found that the highest hardness in order of 232.02 VHN, while before being coated the hardness was 133.61 VHN, or there was an increase in hardness by factor of 1.73, while the wear resistance reduces from 11.6×10^{-8} mm^2/kg to 1.17×10^{-8} mm^2/kg or there was a reduce in wear resistance by factor of 9.9. The optimum conditions were achieved at Ar:N_2 ratio = 70:30. Based on XRD analysis, it can be concluded that the crystal structure of TiN thin film is cubic with the peaks (111), (200), (202), (311) and (222). From cross-section microstructure analysis using Scanning Microscope Electron (SEM), it was found the thickness of the thin film is 744 nm. The study showed that it was possible to deposited a titanium nitride (TiN) thin film on the surface of stainless steel 316L. The TiN thin film was successfully carried out to increase the hardness and to reduce the wear resistance.

Keywords: DC sputtering, 316L stainless steel, Titanium nitride

ABSTRAK

PENGARUH PERBANDINGAN CAMPURAN GAS TERHADAP SIFAT MEKANIK DAN STRUKTUR KRISTAL PADA BIOMATERIAL STAINLESS STEEL 316L DENGAN TEKNIK DC SPUTTERING. Stainless steel 316L banyak digunakan sebagai implan ortopedik karena mempunyai ketahanan korosi dan biokompatibilitas yang tinggi, tetapi kelemahan dari material ini adalah nilai kekerasan yang rendah dan keausan yang tinggi. Oleh karena itu, permukaan harus dimodifikasi untuk memperbaiki bahan. Untuk itulah, film tipis titanium nitrida (TiN) ditumbuhkan pada permukaan stainless steel 316L menggunakan teknik DC sputtering. Proses sputtering dilakukan untuk berbagai campuran gas argon (Ar) dan nitrogen (N_2) pada 90:10, 80:20, 70:30, dan 60:40, sementara parameter lainnya dibuat konstan. Tujuan dari variasi campuran gas adalah untuk mengetahui kondisi optimum dari perbandingan campuran gas Ar: N2 dengan nilai kekerasan tertinggi dan ketahanan aus terendah. Dari percobaan yang telah dilakukan, didapatkan bahwa kekerasan tertinggi sebesar 232,02 VHN, sedangkan sebelum dilapisi kekerasan adalah 133,61 VHN, atau terjadi peningkatan kekerasan sebesar 1,73 kali dibandingkan kekerasan awal, sedangkan ketahanan aus berkurang dari 11,6 × 10-8 mm^2/kg menjadi 1,17 × 10-8 mm^2/kg atau ada penurunan ketahanan aus sebesar 9,9 kalinya. Kondisi optimal dicapai pada rasio perbandingan gas Ar : N_2 = 70:30. Berdasarkan analisis XRD, dapat disimpulkan bahwa struktur kristal film tipis TiN adalah kubik dengan puncak (111), (200), (202), (311) dan (222). Dari analisis struktur mikro penampang lintang menggunakan Scanning Microscope Electron (SEM), didapatkan ketebalan film tipis sebesar 744 nm. Penelitian menunjukkan bahwa dimungkinkan untuk menumbuhkan film tipis titanium nitrida (TiN) pada permukaan stainless steel 316L. Film tipis TiN berhasil dilakukan untuk meningkatkan kekerasan dan mengurangi ketahanan aus.

Keywords: DC sputtering, Stainless steel 316L, Titanium nitrida

INTRODUCTION

The use of metal materials as medical implants began in the 19th century, cross-section with the development of the metal industry era during the Industrial Revolution. The discovery of metal implants was strongly driven by demands for bone repair, especially in the fixation of fractured inner bones. In 1860 aseptic lister surgical techniques successfully implanted metal in a bone. Since then, metal material has been used in orthopedic implants [1]. Biomaterials are employed in components implanted into the human body for replacement of diseased or damaged body parts. These materials must not produce toxic substances and must be compatible with body tissues (i.e., must not cause adverse biological reactions). All of the above materials-metals, ceramics, polymers, composites, and semiconductors-may be used as biomaterials [2].

Some types of biomaterials from metals commonly used in orthopedic surgery are stainless steel, cobalt mixture, titanium mixture [3]. Stainless steel type of 316L is widely used as an implantable biomaterial because it has a relatively low cost, easy availability, and corrosion resistance [4]. The weakness of biomaterial 316L stainless steel is that it is not resistant to wear, so it cannot be used for long periods. One of the requirements for biomaterials is wearing resistance. If the material becomes worn, it frees metal ions and causes toxicity to the body. Therefore, to prevent failure, the hard coating can be deposited on the surface of 316L stainless steel biomaterial [5].

The titanium nitride (TiN) layer [6] is a hard layer and has biocompatibility properties. The titanium nitride layer has been used for coatings on stainless steel biomaterials such as Priyambodo et al [7] research on the effects of TiN coating on 304 and Yazici et al [8] researching on TiN coatings on 316L stainless steel biomaterials.

Sputtering [9] is the process of evaporation or production of the gas phase of condensed material using the impact of high-speed particles such as accelerated ions. Some benefits of DC sputtering are it can produce a thin layer of material which has a high melting point (where the melting point TiO_2 is =1853 ^{o}C), can deposit solid materials, able to save material from being deposited, has strong adhesion, the thickness of the layer can be accurately controlled, cheap operations, can do multiple layers of deposition, the adhesion force between the film and the surface of the substrate is stronger so as to extend the life of the use of components made, and the thickness of the layer can be controlled precisely.

The advantage of this technique compared to the coating technique [10] is that the material to be coated does not have to be heated to melt, so it is advantageous to deposit materials that have high melting points such as the TiN layer. One variation that can be done in the DC sputtering process is the gas mixture ratio. Priyambodo and Wiwien [7] [11] stated that the gas mixture ratio could increase the hardness of a material.

The current study aims to obtain optimum TiN layer deposition, in terms of hardness and wear resistance, on the surface of 316L stainless steel using the DC sputtering process with the right gas mixture ratio. The gas mixture used is argon gas and nitrogen gas. The target used by the DC sputtering process is titanium.

EXPERIMENTAL METHOD

Materials and Sample Preparation

The material used in this study was 316L stainless steel with the first three highest elements are Fe (65.33), Ni (11,64) and Cr (17,22) [12].

This material was cut into cylindrical specimens with a diameter of 14 mm and 5 mm thick. The making of the test object aims to ensure that the test object can be placed on the DC sputtering machine holder. The specimens were grounded and polished to produce a smooth and flat specimen. The grinding process is carried out using abrasive paper with a value of 800 mesh, 1000 mesh, 1500 mesh, and 3000 mesh and polished mechanically with autosol. The polished specimens were washed with 70% alcohol for 15 minutes in an ultrasonic cleaner machine and dried at room temperature.

DC Sputtering Process

The TiN layer deposition process was carried out using a DC sputtering machine in PSTA (Centre for Accelerator Science and Technology)-BATAN, as shown in Figure 1. The duration of the deposition process [11][13] was 90 minutes, with a variation of the ratio of the mixture of ultra high purity argon and ultra high purity nitrogen gases of 90:10, 80:20, 70:30, 60:40.

Figure 1. DC sputtering in PSTA-BATAN Yogyakarta.

The vacuum process was carried out to remove the air in the reactor until it reaches a pressure of 10^{-4} Torr. This vacuum process aims to remove impurities such as dust and gas which can disturb the system.

Characterization

The characterization was carried out by performing hardness and wear test, X-Ray Diffraction (XRD), and SEM-EDS. Hardness test was carried out on raw material and all DC sputtered specimens.

The hardness measurement tool used is the micro-hardness of the Matsuzawa MMT-X7 type. Wear resistance testing was carried out on all specimens that have been pressed DC sputtering and raw material. The wear level measurement tool used was Ogoshi High-Speed Universal Wear Testing Machine. XRD testing was only done on specimens that have the optimum hardness and wear resistance after DC sputtering, and untreated specimens are carried out. XRD testing was carried out to determine the presence of TiN phase on the surface of 316L stainless steel specimens. The diffractogram analysis of the XRD test results using the Match-2 application. SEM-EDS testing is carried out on specimens that have the optimum hardness and wear resistance values after TiN deposition is carried out on surfaces and test objects without a coating process. SEM-EDS testing was carried out to determine the thickness of the TiN layer and the elements content of the raw material and the specimens that had been processed by DC sputtering.

RESULTS AND DISCUSSION

Results of the Coating Process

The results of the specimens that have been carried out by the DC sputtering process show that there is a color difference with the specimen without the DC sputtering process. Figure 2 shows the surface appearance of 316L stainless steel raw material before and after the sputtering process was carried out with

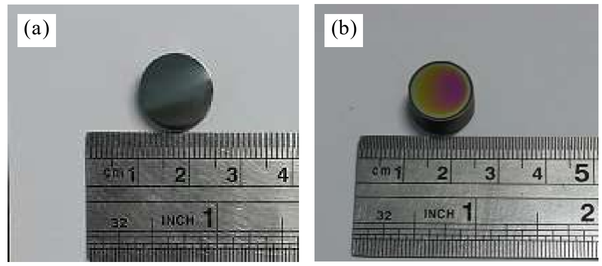


Figure 2. The surface of the test objects (a). raw material (b). specimen that has deposited TiN.

the specimen that has TiN deposition on the surface. In visual terms, there were color differences on each surface after the DC sputtering process, i.e., the raw material changes color to gold. The TiN layer [14] has a specific golden color so that in terms of visual, TiN layers have been deposited on 316L stainless steel surfaces. The colour of the specimen that has deposited TiN was not completely gold, this is probably due to the presence of oxygen in the reactor. The oxygen content is possible due to corrosion that arises because the substrate is not stored under vacuum.

Hardness Test Results

Figure 3 shows the results of the hardness of the TiN layer with variations in the gas mixture ratio. The results of the hardness test obtained that the hardness of 316L stainless steel raw material is 133.77 VHN. The hardness value obtained has calculated with the hardness measurement tool's correction factor of 1.3. The optimal hardness value in this study was obtained in the 70Ar: 30N2 gas mixture test with a hardness value of 232.02 VHN or an increase of 73.65%. The same results were also obtained by Priyambodo [7], who had deposited TiN layers on AISI 304 by producing optimum hardness in the ratio of Argon gas and Nitrogen gas mixture to 70:30.

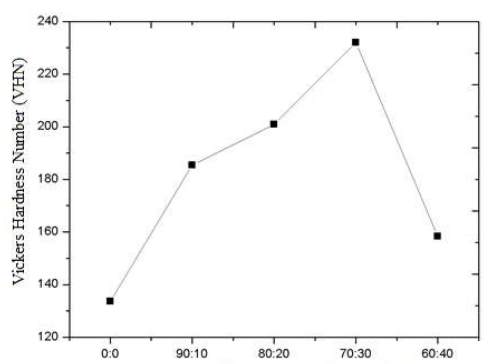


Figure 3. Hardness test result of the TiN layer with variations in the gas mixture ratio

The formation of TiN compounds is influenced by nitrogen concentration and the duration of the process. The nitrogen absorbed at the surface diffuses into the titanium forming interstitial solution of nitrogen in the hcp α-titanium phase. The surface layer formed is called the diffusion zone (α(N)). This process can continue as long as the α-titanium matrix can dissolve nitrogen at the nitrogen medium/solid interface (where the nitrogen concentration is the highest). If the concentration of nitrogen at the gas/metal interface becomes higher than the α phase is able to retain in interstitial solution, a reaction at the interface occurs leading to the formation of a new phase Ti_2N. There is a concentration jump of nitrogen at the sample surface, and as a result, the total nitrided layer consists of a compound layer (Ti_2N) on the top and a diffusion zone underneath. Following the same rules when the concentration of nitrogen at the gas/metal interface becomes higher than the one acceptable in Ti_2N, there is a phase transformation at the sample surface and the Ti_2N transforms to TiN. The sublayer with titanium nitrides only (TiN and Ti_2N) forms the compound layer, while α(N) is the diffusion zone. In this study, the duration of the deposition process is constant for 90 minutes so that the process of forming the TiN layer is only influenced by the concentration of nitrogen, which can be regulated by the ratio of the gas mixture [15].

At the ratio of $70Ar:30N_2$ gas mixture has formed the optimum TiN layer resulting in optimum hardness. At the ratio of $90Ar:10N_2$ and $80Ar:20N_2$ gas mixtures, nitrogen concentrations in this process have not reached optimum conditions, and the possibility of TiN layers has not formed so that the increase in hardness is not optimum. The increase in hardness is proportional to the increase in nitrogen concentration, and this is following Mahieu's study in 2008 [16]. At the ratio of the $60Ar:40N_2$ gas mixture, there is a phenomenon of a decrease in hardness when compared with a variation of the other gas mixture ratio. This phenomenon is possible because a little argon gas in the reactor makes nitrogen gas dominate. It means that only nitrogen atoms are deposited on 316L stainless steel specimens so that the harder TiN compounds do not form [10].

Wear Test Results

Wear test was used to determine the wear resistance of a material. The smaller the wear specific value, the higher the wear resistance of the material. If the material has high wear resistance, the width of the wear footprint is smaller. Figure 4 shows the decrease in specific wear between specimens that have been carried out by the sputtering process for various variations of the gas mixture. Before the treatment, the wear specific was 11,6 x 10-8 mm²/kg. After the treatment, the wear specific was in range 7,46 x 10-8 - 1,17 x 10-8 mm²/kg. The optimum value of wear specific was at $70Ar:30N_2$ of the gas mixture. At this optimum condition, the wear specific decreased ~ ten times, which is a significant improvement.

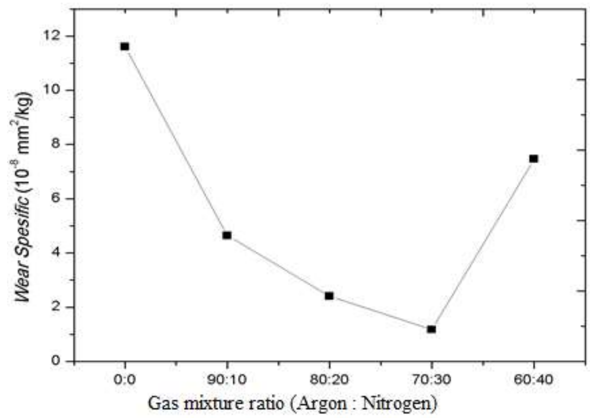


Figure 4. Wear test result.

The correlation between the effect of the ratio of the mixture of argon and nitrogen gas to the hardness and wear resistance of 316L stainless steel is shown in Figure 5. Figure 5 shows that the higher the level of hardness, the lower the wear specific value or, the better wear resistance. If a material has a higher level of hardness, the smaller the wear will occur if the friction force is applied on the surface. Thus the effect of the right ratio of the mixture of argon and nitrogen gases can increase hardness and increase wear resistance optimally. To prevent the loss of constituent components on 316L stainless steel biomaterials that are used as orthopedic implants and extend the life of the material.

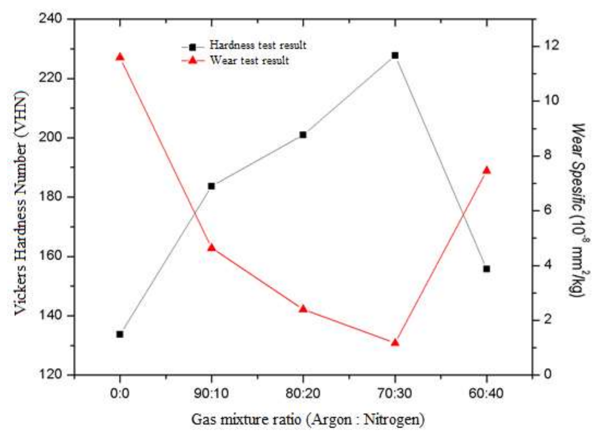


Figure 5. Correlation between the effect of gas mixture ratio on hardness and wear resistance on 316L stainless steel.

XRD Test Results

XRD analysis is done with the Match-2 application that uses a database from the Crystallography Open Database (COD). By matching the 2-theta measurement data against the 2-theta database, the phase of the surface of the test object will be known. For strengthening XRD analysis, related journals can also be used. From the journal, it can also be seen that 2-theta in the phases of the formed phase can then be adjusted to 2-theta measurements so that the phase fields that appear in this test can be known.

The dominant element in the raw material is Fe, so XRD testing in raw material must have Fe phase. Figure 6 shows a diffractogram of the results of XRD raw material testing. Figure 6 shows there is peak suitability between the 2-theta angle of measurement with the 2-theta angle of Fe phase based on the COD database. In this figure, there are three peaks of the Fe phase, which are fields 111, 200, and 202. However, the peak suitability between the 2-theta angle of measurement with the 2-theta angle of Fe phase based on the COD database only in fields 111 and 200, while the fields 202 did not obtain the peak suitability.

Figure 2 points (b) shows that there is a golden color, a typical color of a TiN compound, on a 316L stainless steel surface. However, this must be proven by XRD testing. From the results of XRD testing, the TiN phase is formed. The diffractogram of specimens deposited by TiN is shown in Figure 7. Figure 7 also shows the suitability of the peak between the 2-theta angle of measurement and the 2-theta angle of the TiN phase based on the COD database (entry number 96-900-8749). Friexas in 2015 [17] stated that five diffraction peaks at 2-tetha 36.6 °; 42.4 °; 61.9 °; 74.2 ° and 78.7 ° are similar to the Titanium Nitride (TiN) phase in fields 111, 200, 220, 311 and 222. This study proves that the TiN phase has formed in specimens resulting from the sputtering process.

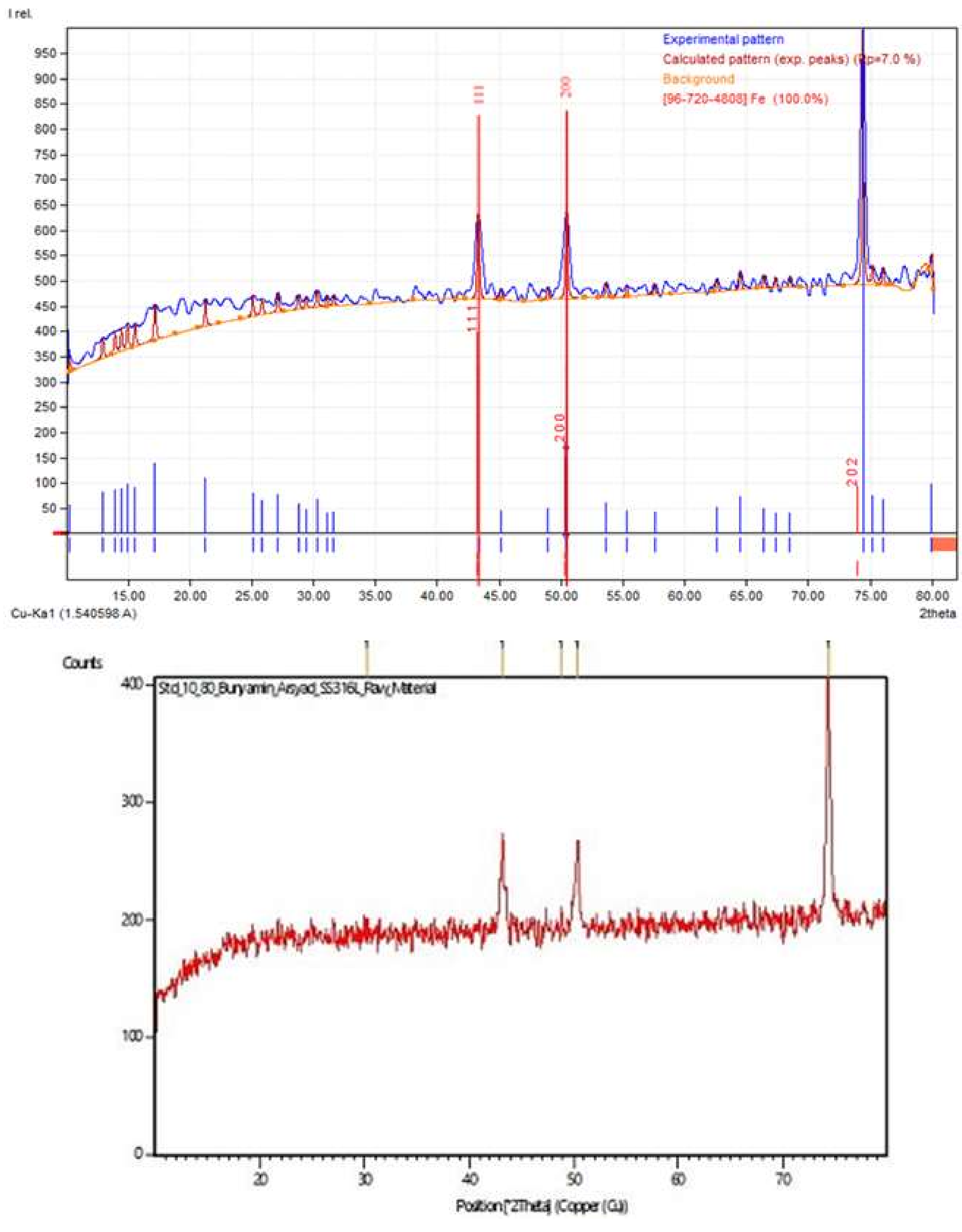


Figure 6. The results of the Fe phase analysis on the raw material .

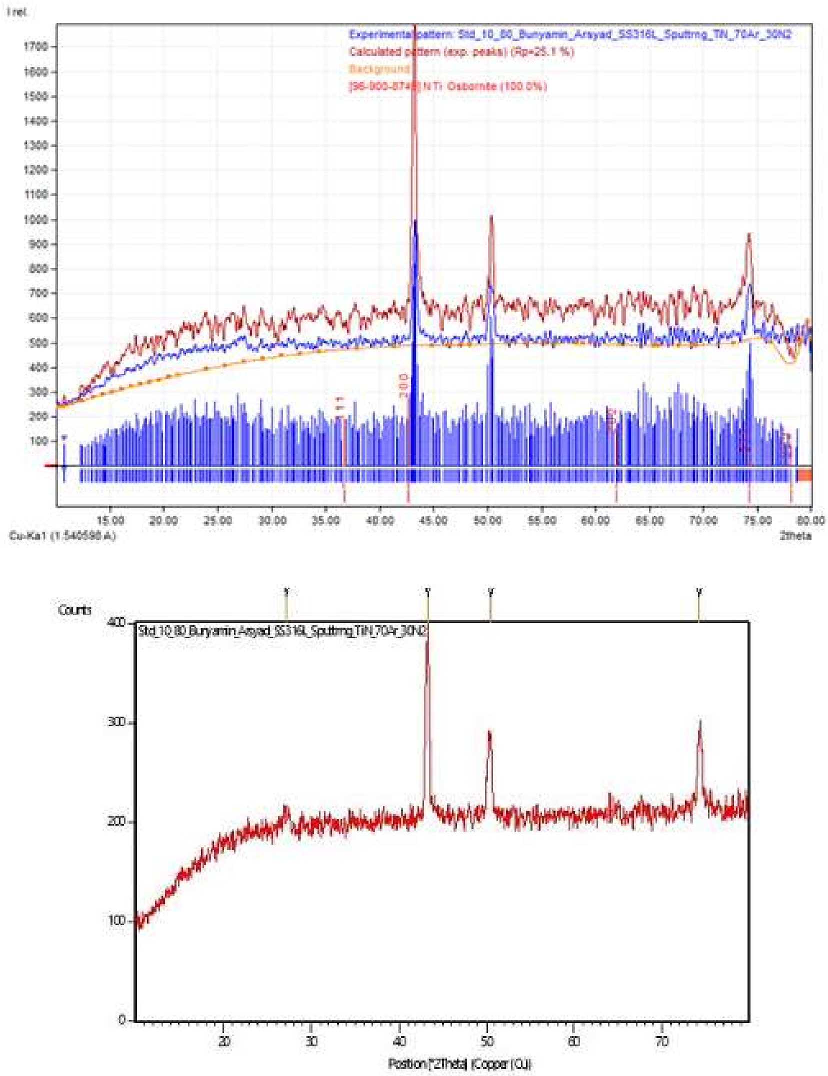


Figure 7. The results of the TiN phase analysis on specimens that have been carried out by the sputtering process.

SEM-EDS Test Results

The thickness of the layer was observed using the SEM technique at the cross-section of the raw material and the test specimens that have been carried out in the DC sputtering process. The scanning results on the cross-section of raw material and test objects that have been carried out in the DC sputtering process are shown in Figure 8.

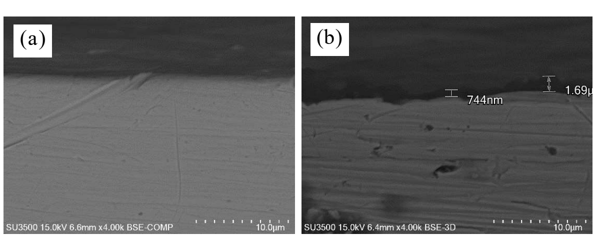


Figure 8. Cross-section image (a). raw material (b). specimens that have been carried out DC Sputtering Process.

Figure 8 shows that at the cross-section of the raw material, there is no layer on the surface, while the specimens that have been carried out DC sputtering process have layers with a thickness that is not homogeneous. This layer is the TiN phase shown in the XRD test results. The TiN layer that is grown on the surface of the substrate has a thickness that is not homogeneous. Inhomogeneous thickness is possible due to inadequate sample preparation so that the substrate layer or surface is uneven and not smooth. Another possibility that can cause TiN layers to have a non-homogeneous thickness is the influence of parameters such as substrate temperature [13]. Aziz [18] states that plasma temperature plays a vital role because it affects the solubility of TiN atoms on the surface of the substrate or affects the number of diffused atoms. The higher the temperature of the substrate, the distance between atoms will widen and make it easier for diffused TiN atoms or compounds to be more profound.

Conversely, when the substrate temperature gets lower, the atomic distance becomes denser and hard to diffuses so that TiN compounds formed accumulate on the substrate surface. In the used DC sputtering machines, temperature control is not available, so the temperature at each substrate surface point cannot be known. The inequality of layer thickness is likely to be influenced by temperature differences at each substrate surface point. The illustration of uneven layer thickness is shown in Figure 9.

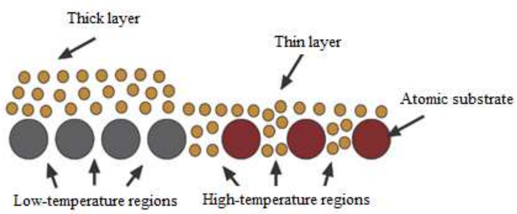
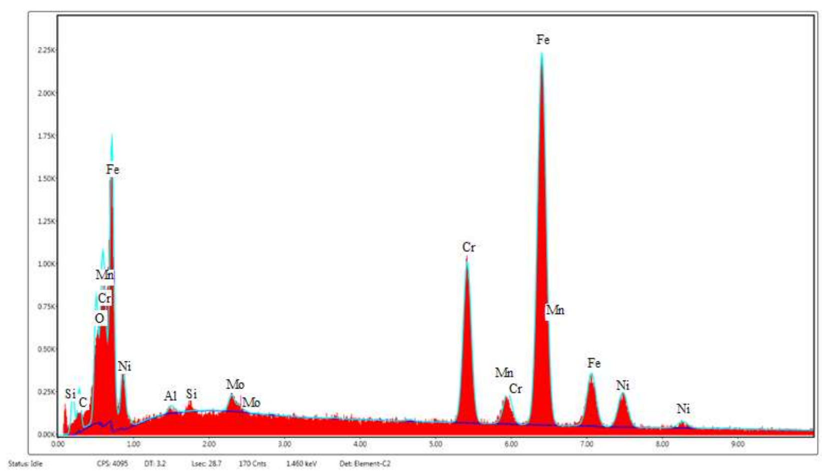


Figure 9. Mechanisms for uneven coating formation.

The process of the occurrence of plasma is strongly influenced by breakdown voltage, which plays a role in the ionization of gases in plasma reactors. The pressure influences the breakdown voltage in the reactor and the electrode distance. In this study, the reactor pressure is fixed, and the electrode distance is fixed. Inequality of layer thickness is probably caused by plasma formed less than optimal because the breakdown voltage has not been done on the DC sputtering machine used.

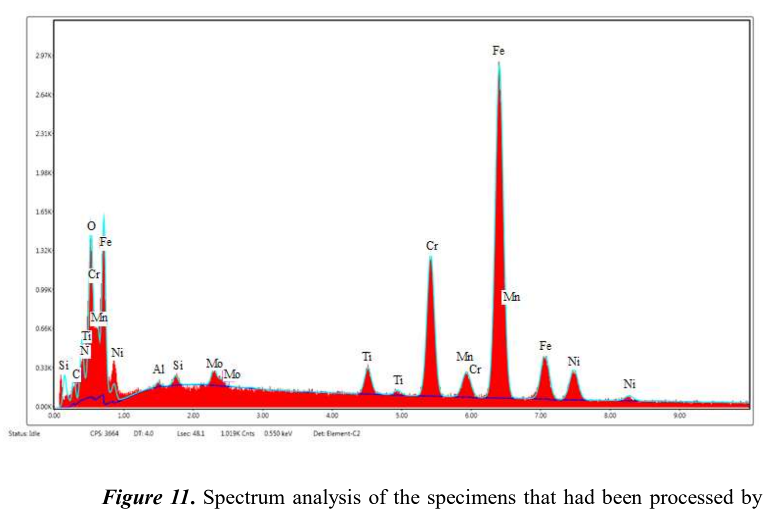
EDS testing is carried out to determine the constituent elements of the raw materials and the specimens that had been processed by the DC sputtering process. Spectrum analysis using EDS is shown in Figure 10 and Figure 11.

The test results show the presence of high carbon content in raw materials and DC sputtering specimens. This is possible that carbon content presence in specimens because of the presence of carbon elements attached to the surface of the specimen during sample preparation before SEM-EDS testing. While the oxygen content is possible due to corrosion that arises because the substrate is not stored under vacuum. In the specimens resulting from the DC sputtering process also found the addition of new elements N and Ti.



Element	Weight %	Atomic %	K Ratio
C K	3.5	13.99	0.0104
O K	1.09	3.26	0.0062
Mo L	1.16	0.58	0.0092
Cr K	15.94	14.7	0.1905
Mn K	1.63	1.42	0.0169
Fe K	66.09	56.75	0.6579
Ni K	9.9	8.09	0.0945

Figure 10. Spectrum analysis of raw material elements.



Element	Weight %	Atomic %	K Ratio
C K	2.07	7.41	0.0063
N K	3.06	9.39	0.0125
O K	4.9	13.16	0.0248
Mo L	1.11	0.5	0.0088
Ti K	1.83	1.64	0.0206
Cr K	14.67	12.12	0.1709
Mn K	1.56	1.22	0.016
Fe K	61.43	47.28	0.6019
Ni K	8.87	6.49	0.0838

Figure 11. Spectrum analysis of the specimens that had been processed by the DC sputtering process.

CONCLUSION

Based on the research on the effect of the ratio of gas mixtures to mechanical properties and crystal structure on 316L stainless steel biomaterials with sputtering techniques it can be concluded that the TiN layer deposited on 316L stainless steel specimens was evidenced by the emergence of TiN phase peaks on layer of 111, 200, 202, 311 and 222 in XRD testing with cubic crystals. The optimum conditions were achieved at Ar: N_2 ratio = 70:30. The highest hardness in order of 232.02 VHN, while before being coated, the hardness is 133.61 VHN, or there is an increasing hardness by factor 1.73, while the wear resistance reduces from 11.6×10^{-8} mm^2/kg to 1.17×10^{-8} mm^2/kg or there is reducing in wear resistance by factor 9.9. The thickness of the TiN layer on the surface of the test specimen was around 733 nm. The study showed that it was possible to deposited a titanium nitride (TiN) thin film on the surface of stainless steel 316L. The TiN thin film was successfully carried out to increase the hardness and to reduce the wear resistance.

REFERENCES

[1]. J. Park and R. S. Lakes, *Biomaterials: an introduction*. Springer Science & Business Media, 2007.

[2]. Callister, William D. and D. G. Rethwisch, "*Materials Science and Engineering: An Introduction*," p. 992, 2009.

[3]. R. E. Smallman. and R. J. Bishop, "Metalurgi Fisik Modern & Rekayasa Material," *Int. J. Adolesc. Youth*, vol. 3, no. 1, pp. 27–39, 2016.

[4]. Sudjatmoko, L.Susita R.M., Wijoadi, and B. Siswanto, "Corrosion Resistance Improvement of Aisi 316L Stainless Steel Using Nitrogen Ion Implantation," Ganendra *J. Nuclear Sci Tech.*, vol. 16, no. 2, pp. 67–76, 2013.

[5]. Q. Chen and G. A. Thouas, "Metallic implant biomaterials," *Mater. Sci. Eng. R Reports*, vol. 87, pp. 1–57, 2015.

[6]. X. H. Zheng, J. P. Tu, B. Gu, and S. B. Hu, "Preparation and Tribological Behavior of TiN/a-C Composite Films Deposited by DC Magnetron Sputtering," *Wear*, vol. 265, no. 1–2, pp. 261–265, 2008.

[7]. B. H. Priyambodo *et al.*, "The Influence of TiN-Sputtering on Hardness and Corrosion Rate of AISI 304 for Biomaterials Application The Influence of TiN-Sputtering on Hardness and Corrosion Rate of AISI 304 for Biomaterials Application," *J. Corros. Sci. Eng.*, vol. 20, December, 2018.

[8]. M. Yazici, H. Kovaci, A. F. Yetim, and A. Çelik, "Structural, mechanical and tribological properties of Ti and TiN coatings on 316L stainless steel," *Ceram. Int.*, vol. 44, no. 12, pp. 14195–14201, 2018.

[9]. A. Kinbara, "Sputtering/ : Encylopedia of Apllied Phsyics," *Phys. Today*, vol. 47, no. 12, pp. 60–62, 2008.

[10]. T. Sujitno, A. Santoso, Wiryoadi, Sayono, B. Siswanto, and L. Susita, "Optimasi parameter proses sputtering pada deposisi lapis tipis titanium nitrida (TiN) pada bahan aluminium," in *Prosiding Pertemuan dan Presentasi. Penelitian Dasar IImu Pengetahuan dan Teknologi Nuklir P3TM-BATAN*, 2002, pp. 156–165.

[11]. W. Andriyanti, H. S. Prama, and D. Priyantoro, "Deposisi Lapisan Tipis Titanium Nitrida Pada Stainless Steel 316 Menggunakan Metode DC Sputtering", in *Prosiding Pertemuan dan Presentasi Ilmiah Penelitian Dasar Ilmu Pengetahuan dan Teknologi Nuklir*, Nov. 2017, pp. 155–160 .

[12]. American Society for Testing and Materials, "ASTM A240: Standard Specification for Chromium and Chromium-Nickel Stainless Steel Plate , Sheet , and Strip for Pressure Vessels and for General Applications," *ASTM Int.*, vol. 1, p. 12, 2004.

[13]. Wirjoadi, B. Siswanto, and Sudjatmoko, "Pengaruh Suhu Deposisi Lapisan Tipis TiN Terhadap Sifat Mekanik Metal Hasil Plasma Sputtering," in *Prosiding PPI - PDIPTN 2010 Pusat Teknologi Akselerator dan Proses Bahan - BATAN*, 2010, pp. 138–146.

[14]. H. O. Pierson, "Interstitial Nitrides: Properties and General Characteristics," in *Handbook of Refractory Carbides and Nitrides*, William Andrew, 1996, pp. 181–208.

[15]. A. Zhecheva, W. Sha, S. Malinov, and A. Long, "Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods," *Surf. Coatings Technol.*, vol. 200, no. 7, pp. 2192–2207, 2005.

[16]. S. Mahieu, D. Depla, and R. De Gryse, "Characterization of The Hardness and The Substrate Fluxes During Reactive Magnetron Sputtering of TiN," *Surf. Coatings Technol.*, vol. 202, no. 11, pp. 2314–2318, 2008.

[17]. J. Freixas *et al.*, "Sputtered titanium nitride: a bifunctional material for Li-ion microbatteries." *J. Electrochem. Soc.*, vol. 162, no. 4, pp. A493-A500, 2015.

[18]. I. Aziz, "Nitridasi Baja Tahan Karat SS 316L untuk Biomaterial." B.A. minithesis, *Sekolah Tinggi Teknologi Nasional*, Yogyakarta, 2014.