EFFECTS OF NITROGEN ION IMPLANTATION ON HARDNESS AND WEAR RESISTANCE OF THE Ti-6Al-4V ALLOY

PENGARUH IMPLANTASI ION NITROGEN PADA KEKERASAN DAN KETAHANAN AUS PADUAN Ti-6Al-4V

Sudjatmoko, Lely Susita R.M., Wirjoadi, Bambang Siswanto
Center for Accelerator Science and Technology, BATAN
Jl. Babarsari P.O. Box 6101 Ykbb, Yogyakarta 55281
e-mail: djatmoko@batan.go.id

Received 18 July 2014, received in revised form 11 December 2014, accepted 16 December 2014

ABSTRACT

EFFECT OF NITROGEN ION IMPLANTATION ON HARDNESS AND WEAR RESISTANCE OF THE Ti-6Al-4V ALLOY. *The nitrogen ion implantation technique was chosen for improving surface hardness and the wear resistance properties of the Ti-6Al-4V alloy. An optimum nitrogen ion dose of 5×10^{16} ion/cm^2 and ion energies of 70, 80 and 100 keV were used in this study. Microstructure, chemical composition and surface morphology studied using the technique of Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray (EDX) and X-ray Diffraction (XRD). Analysis of the SEM-EDX micrographs and XRD diffraction patterns indicate that implanted layer on the surface of the Ti-6Al-4V alloy sample showed the presence of Ti_2N and TiN phases which very hard and excellent wear resistance properties. Micro-hardness was measured by Vickers method, and the wear resistance was determined using the wear test equipment that work based on the amount of samples material lost during wear time. The results of measurements clearly indicate that implanted layer on surface of the Ti-6Al-4V alloy sample produced an optimum enhancement of hardness properties and wear resistance, and it occurs at ion energy of 80 keV and ion dose of 5×10^{16} ion/cm^2. It is obtained that the hardness of implanted layer was increased by a factor of 2.1; whereas the wear resistance increased up to a factor of 27 compared to the standard sample. The increase in hardness and wear resistance of implanted layer are mainly due to the formation of Ti_2N and TiN phases.*

Keywords*: nitrogen ion implantation, micro-hardness, wear resistance, Ti_2N and TiN phases*

ABSTRAK

PENGARUH IMPLANTASI ION NITROGEN PADA KEKERASAN DAN KETAHANAN AUS PADUAN Ti-6Al-4V. *Teknik implantasi ion nitrogen dipilih untuk meningkatkan sifat kekerasan permukaan dan ketahanan aus paduan Ti-6Al-4V. Dalam penelitian ini digunakan dosis ion nitrogen optimum 5×10^{16} ion/cm^2 dan dengan energi ion 70, 80 dan 100 keV. Struktur-mikro, komposisi kimia dan morfologi permukaan dipelajari dengan menggunakan teknik* Scanning Electron Microscope *(SEM) yang digabungkan dengan* Energy Dispersive X-*ray (EDX) dan* X-*ray* Diffraction *(XRD). Analisis mikrograf SEM-EDX dan pola difraksi XRD menunjukkan bahwa lapisan yang terimplantasi pada permukaan cuplikan paduan Ti-6Al-4V menunjukkan adanya fase Ti_2N dan TiN yang sangat keras dan sifat ketahanan aus yang sangat baik. Kekerasan mikro diukur dengan metode Vickers, dan ketahanan aus ditentukan dengan menggunakan alat uji keausan yang bekerja berdasarkan jumlah bahan cuplikan yang hilang selama waktu pengausan. Hasil pengukuran jelas menunjukkan bahwa lapisan yang terimplantasi pada permukaan cuplikan paduan Ti-6Al-4V menghasilkan peningkatan optimum sifat kekerasan dan ketahanan aus, dan hal itu terjadi pada energi ion 80 keV dan dosis ion 5×10^{16} ion/cm^2. Diperoleh bahwa kekerasan lapisan yang terimplantasi meningkat dengan faktor 2,1; sedangkan ketahanan aus meningkat hingga faktor 27 dibandingkan dengan cuplikan standar. Peningkatan kekerasan dan ketahanan aus lapisan yang terimplantasi terutama karena terjadinya pembentukan fase Ti_2N dan TiN.*

Kata kunci*: implantasi ion nitrogen, kekerasan-mikro, ketahanan aus, fase Ti_2N dan TiN*

INTRODUCTION

Materials used for implant applications should have good mechanical strength, high chemical stability, excellent corrosion resistance and biocompatibility (1-3). Ti-6Al-4V alloy has many desirable features, such as biocompatibility, high corrosion and wear resistance, suitable mechanical properties, and so on; thus it has been widely used in aeronautical and biomedical applications (4-6). The materials used as implants are expected to be highly non toxic and should not cause any inflammatory or allergic reactions in the human body. The success of the biomaterials is mainly depend on the reaction of the human body to the implant, and the measure of the biocompatibility of a material (7). The low wear and corrosion resistance of the implants in the body fluid results in the release of non compatible metal ions by the implants into the body. The released ions are found to cause allergic and toxic reactions. The low wear resistance also results in implant loosening and wear debris are found to cause several reactions in the tissue in which they are deposited. The mechanical properties decide the type of material that will be selected for a specific application. Some of the most important properties are hardness, tensile strength, modulus and elongation.

Ti-6Al-4V alloy is the most biocompatible among biomaterials and has in recent years gained increased usage in total joint replacements because of it combination of excellent fatigue strength, good corrosion resistance, low density and elastic modulus, and chemical stability properties (8,9,10). Its excellent corrosion resistance is attributed to the formation of a passive titanium oxide film. This protection layer is formed by the contact of metal surface with air, avoids further oxidation of the bulk, thus providing alloy passivity and biocompatibility (5). However, despite the many favorable characteristics of Ti-6Al-4V alloy, the main weaknesses of titanium alloys are their poor friction and surface wear resistance, or unsatisfactory tribological properties (11-13). Excluding the wear problem, the Ti-6Al-4V alloy possesses excellent corrosion resistance in many environments including saline solutions, that similar to corporeal fluids. However, problems arise when localized wear starts, causing intense corrosion. Numerous efforts have been reported that the poor friction and surface wear resistance of titanium alloys can be improved by surface modification technologies, such as nitrogen ion implantation, thermal oxidation or hard coatings (11-14).

Nitrogen ion implantation has been successfully done in biomaterial surface modifications, such as in improving the wear resistance of Ti-6Al-4V alloy for biomedical engineering. Ion implantation serves as a powerful tool of surface modification of biomaterials though it is similar to the coating process, it does not involve the addition of a layer on the surface of sample. Ion implantation is the process which involves the introduction of a controlled amount of atoms of any element into the surface of any material with a beam of high velocity ions, without modifying the surface finishing or the bulk properties of the underlying material and thermodynamic constraints independency (9,15,16). It has several advantages with other modification methods such as possibility of introducing any elements into any solids target, low temperature treatment, hence without dimensional change of treated compounds (8), no interface discontinuity as in film deposition, possibility of new structures in non equilibrium and new metallurgical phases (9).

In this work, nitrogen ions were implanted into the Ti-6Al-4V alloy to enhance the surface hardness properties and wear resistance. The main purpose of this work was to investigate the effect of nitrogen ion energy and its ion dose on the surface properties of the Ti-6Al-4V alloy. In this study, surface microstructure, chemical composition and morphology of the samples were also studied using SEM-EDX and XRD respectively. The hardness of samples was studied using Vickers micro hardness tester, and wear resistance is determined based on the wear rate of the material or the amount of material lost from the surface of the samples during wear time.

METHODOLOGY

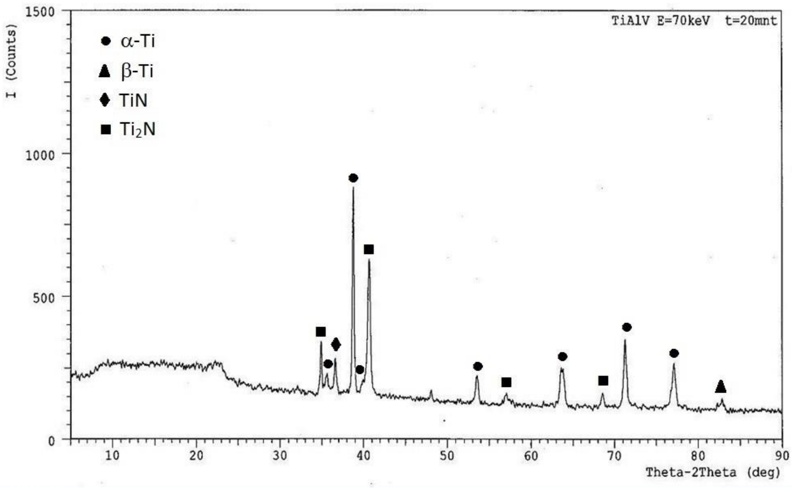
In a set of planned experiments the ion implantation on the Ti-6Al-4V alloy was performed using the ion implantation accelerator of the CAST (Centre for Accelerator Science and Technology) - BATAN, Yogyakarta. The substrate sample was the Ti-6Al-4V alloy with $\alpha + \beta$ phase microstructure. This sample has been prepared as plates of $(10 \times 10 \times 2)\ mm^3$ size, and then were mechanically polished using polishing machine with a series of waterproof abrasive papers up to 1,200 grit followed by a final mirror polished using a diamond paste. The polished samples were rinsed using deionized water and then degreased by acetone with an ultrasonic cleaner before their surface modification.

Nitrogen ion implantation was performed at the CAST laboratory using the 150 keV/1 mA ion implantation accelerator. The Ti-6Al-4V samples were implanted with optimum ion doses of 5×10^{16} ions/cm^2 at a different ion energy of 70, 80 and 100 keV, respectively. Microstructure and chemical composition of the samples were analyzed using the analytical techniques of scanning electron microscopy (SEM) equipped with energy dispersive x-ray (EDX). X-ray diffraction analysis (Cu-Kα radiation) was performed in order to identify the phases present in the surface layers. Micro-hardness measurement of the samples was carried out using Vickers micro hardness tester, whereas the wear resistance was determined based on the wear rate of the material or the amount of material lost from the samples surface per wear time.

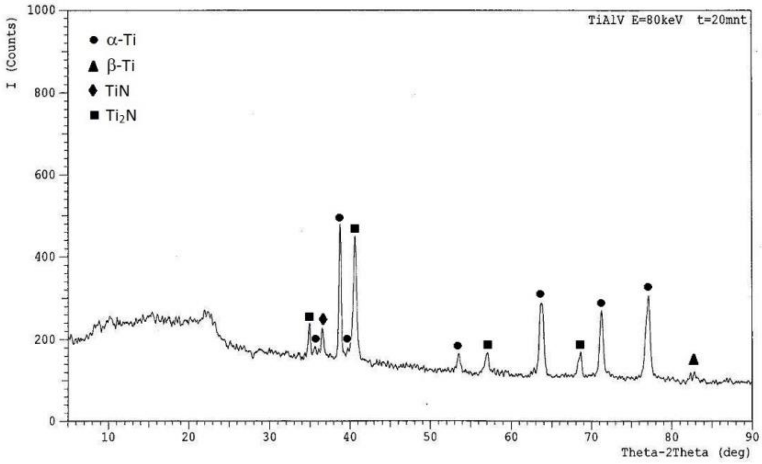
RESULTS AND DISCUSSION

The crystal structure and the phase composition of the modified samples were examined by using the XRD method. This method can provide direct evidence of inter metallic compounds formed in implanted surface area. The X-ray diffraction patterns in Figure 1 shows that alpha structural phase of the titanium alloy (α-Ti) and the beta structural phase (β-Ti) are observed in all samples, and the phases of Ti_2N and TiN are also observed. These α-Ti phase and β-Ti phase are observed in all samples because in this study Ti-6Al-4V α-β alloys were used. During ion implantation take place, the implanted nitrogen ions were placed in the interstitial sites, and a solid solution of nitrogen was formed in the titanium matrix; a part of the interstitial nitrogen ions was arranged into the structure, and Ti_2N as well as TiN phases arose. According to Figure 1(a) and (b) at the ion energy of 70 and 80 keV, the Ti_2N(101), Ti_2N(210), Ti_2N(105), Ti_2N(320) and TiN(111) crystalline phases are formed on surface of the Ti-6Al-4V samples after nitrogen ion implantation. Further increases of nitrogen ion energy to 100 keV, produce formation TiN(200) beside the Ti_2N and TiN crystalline phases previously formed on the ion energy 70 and 80 keV. These high hardness nitrides were contributed a supporting to heavy loading and an improvement of wear resistance. Similar results were obtained by A. Shokouhy et al. [(14)], they have introduced nitrogen ion implantation at ion energy of 90 keV with different ion dose on Ti-6Al-4V alloy; also S. Kadam et al.[(9)] has implanted nitrogen ions at ion energy of 60 keV with different ion dose on the commercially pure Ti.

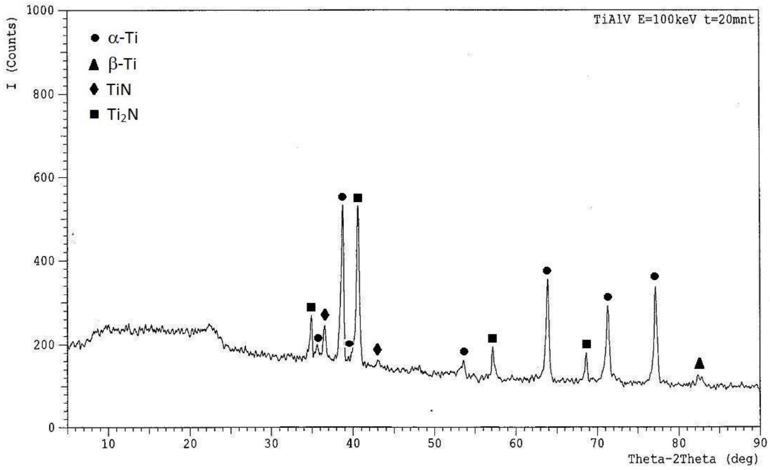
SEM micrographs of cross-section Ti-6Al-4V samples after nitrogen ion implantation at ion energy of 80 keV and optimum ion dose of 5×10^{16} ion/cm^2 shown in Figure 2. On the surface of Ti-6Al-4V samples have been formed the compound layer which consisting of Ti_2N and TiN phases, while underneath the compound layer is a diffusion zone comprising an interstitial solution of nitrogen in the α - β titanium phase. As it has been known that a compound layer consisting of Ti_2N and TiN phases have very hard properties.



(a)



(b)



(c)

Figure 1. Diffraction patterns of the ion implanted Ti-6Al-4V sample on an ion dose of 5×10^{16} ion/cm^2 for variation of ion energies: (a) 70 keV, (b) 80 keV and (c) 100 keV.

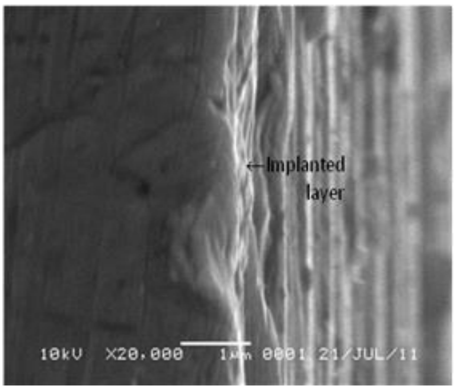
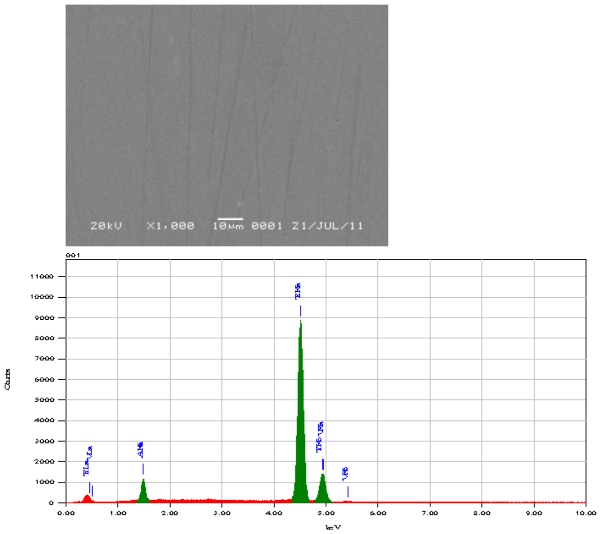
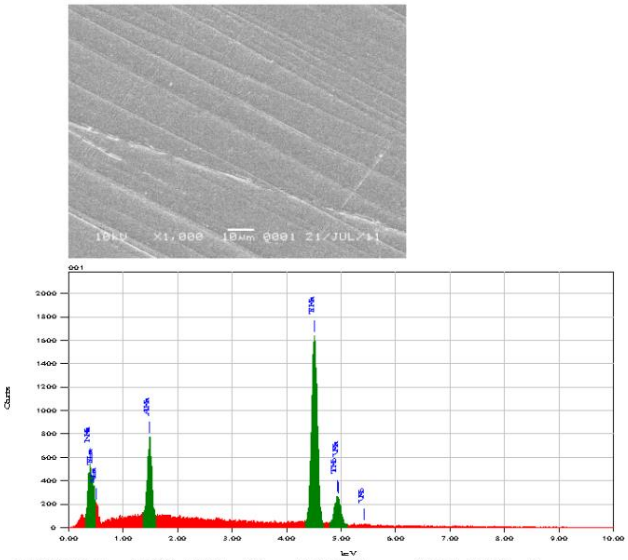


Figure 2. Cross-sectional view of the ion implanted Ti-6Al-4V sample at the ion energy of 80 keV and the optimum ion dose of 5×10^{16} ion/cm^2.



Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
Al K		1.486	4.86	0.43	8.33			2.9818	
Ti K		4.508	92.85	0.65	89.59			94.7214	
V K	*	4.949	2.29	0.83	2.08			2.2968	
Total			100.00		100.00				

(a)



Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
N K	0.392	4.57	0.04	13.56			21.8058	
Al K	1.486	5.65	0.03	8.71			12.7334	
Ti K	4.508	85.78	0.15	74.46			211.1576	
V K	4.949	4.00	0.21	3.27			9.5872	
Total		100.00		100.00				

(b)

Figure 3. SEM-EDX micrographs of the Ti-6Al-4V sample (a) before nitrogen ion implantation, (b) after nitrogen ion implantation on an ion dose of 5×10^{16} ion/cm^2 and ion energy of 80 keV.

In this study also conducted observations of the microstructure and elemental composition using SEM-EDX techniques, especially to determine the nitrogen content on the surface of Ti-6Al-4V samples after ion implantation process. Figure 3(a) shown the SEM-EDX micrograph of Ti-6Al-4V standard sample before the ion implantation process, and Figure 3(b) indicated SEM-EDX micrograph of Ti-6Al-4V sample that has been implanted with nitrogen ion at ion energy of 80 keV and optimum ion dose of 5×10^{16} ion/cm^2.

Based on Figure 3(a), on the surface of Ti-6Al-4V sample does not contain nitrogen, whereas in Figure 3(b) shows that the sample surface of Ti-6Al-4V containing of 13.56% nitrogen atom. The implanted nitrogen ions and the atoms of the Ti-6Al-4V samples are the origin of micro-structural substitution and interstitial defects, formation of vacancy and meta-stable phases, which resulted in the formation of Ti_2N and TiN phases. These structural transformations are responsible for the increase in surface hardness and consequent increase in wear resistance.

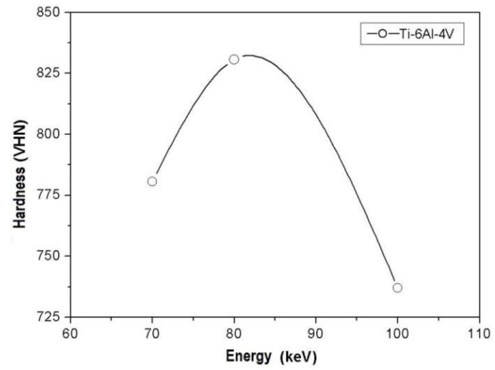


Figure 4. Hardness graph of the ion implanted Ti-6Al-4V alloy as a function of ion energy variation on the ion dose of 5×10^{16} ion/cm^2.

In Figure 4 is displayed the hardness graph of the implanted Ti-6Al-4V samples. Based on Figure 4 it can be seen that the optimum hardness of Ti-6Al-4V alloy sample is about 830 VHN at ion energy of 80 keV and ion dose of 5×10^{16} ion/cm^2. On the nitrogen ion energy of 70 keV, the formation of alpha structural phase (α-Ti) and beta structural phase (β-Ti) on Ti-6Al-4V is more dominant than the formation of the structural phase of Ti_2N and TiN. When the nitrogen ion energy increased to 80 keV, the formation of the structural phase of (α-Ti) and (β-Ti) are reduced and the formation of the structural phase of Ti_2N and TiN increases, so the hardness of Ti-6Al-4V achieve optimum value; and the hardness of Ti-6Al-4V decreased when the nitrogen ion energy has reached 100 keV caused by the formation of the structural phase of (α-Ti) and (β-Ti) are more dominant on the sample surface. If the implanted samples compared to the unimplanted samples, the hardness of the implanted samples is higher than that of the unimplanted sample by a factor of 2.1. Enhanced hardness behavior observed here is mainly attributed to the formation of Ti_2N and TiN phases on the surface of samples. This behavior is in agreement with Vlack et al.(12) who have done the nitrogen ion implantation with ion beam current density of 1.5 μA/cm^2 and ion energy of 90 keV on the surface of Ti-6Al-4V alloy. The hardness for the implanted layer is higher than that of the unmodified substrate by a factor of about twofold. Similar results were also obtained by Silva et al.(4), the results that obtained by using N-PIII (Nitrogen - Plasma Immersion Ion Implantation) at 800 ºC in 120 minutes implantation on Ti-6Al-4V alloy was increased by a factor of 1.9 compared to the unimplanted sample.

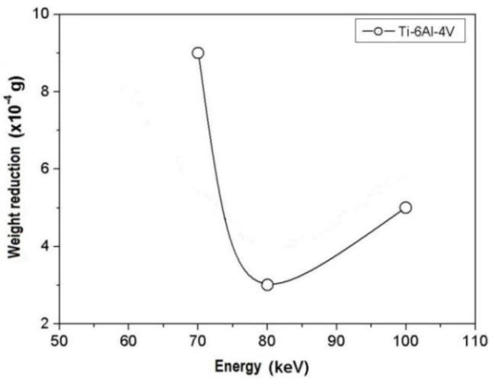


Figure 5. Weight reduction graph of the ion implanted Ti-6Al-4V sample as a function of ion energy variation on the ion dose of 5×10^{16} ion/cm^2.

Wear is the event of friction and release of metal particles from the surface caused by other metal, non-metal materials, moving liquids or gases. In this study the wear resistance is determined using the wear test equipment that work based on the amount of samples material lost, i.e. the mass per unit of wear time. Weight used to wear is 319.376 grams and the wear time for 15 minutes. If the reduction in weight of Ti-6Al-4V becomes smaller, the wear resistance of the sample will be higher, that means the hardness value of Ti-6Al-4V is very high. Figure 5 shows that on the nitrogen ion energy of 70 keV, the weight reduction of Ti-6Al-4V is high so that the value of the wear resistance is low, and the value of the wear resistance reaches optimum when the value of weight reduction of Ti-6Al-4V is a minimum on the nitrogen ion energy of 80 keV. As the nitrogen ion energy reaches 100 keV, the weight reduction of Ti-6Al-4V is increased and the value of the wear resistance is reduced. Based on Figure 5 it can be known that Ti-6Al-4V samples undergo optimum weight reduction of 0.03 mg or its wear resistance increased about 27 times compared with standard samples, which occurred at ion energy of 80 keV and ion dose of 5×10^{16} ion/cm^2. Increasing wear resistance of implanted Ti-6Al-4V samples are mainly due to the formation of Ti_2N and TiN phases on the surface of these implanted samples.

CONCLUSION

Based on the results and the above discussion the following conclusions can be given. The surface treatment of Ti-6Al-4V alloy using nitrogen ion implantation technique can produce phases of Ti_2N and TiN on the surface of the sample. These phases have properties very hard and good wear resistance. Ion implantation at a dose of 5×10^{16} ion/cm^2 and on the ion energies of 70, 80 and 100 keV, phases of Ti_2N and TiN were observed in all samples. An optimum micro hardness of the Ti-6Al-4V alloy is occurred at ion energy of 80 keV and its hardness increased by factor of 2.1 if compared to sample standard that not implanted with nitrogen ion; whereas the wear resistance increased up to a factor of 27. Based on the results of this study can be obtained that surface of the Ti-6Al-4V alloy becomes very hard and has an excellent wear resistance, so it is appropriate used as a biomedical material and many other for industries.

ACKNOWLEDGEMENTS

The research activities are fully funded by the Incentive Program of Increased Ability of Researchers and Engineers (PIPKPP) 2011, the Ministry of Research and Technology. Therefore, on this occasion the author thank to BATAN and the Ministry of Research and Technology that have funded our research activity, so this research can be implemented. The author thank also to Mr. Sunarto who has helped in the process of ion implantation.

REFERENCES

1. V.E. ANNAMALAI, S. KAVITHA, S.A. RAMJI, *The Open Materials Science Journal*, 8 (2014) 1-17
2. T.R. RAUTRAY, R. NARAYANAN, K.H. KIM, *Progress in Materials Science* 56 (2011) 1137-1177
3. G. MANIVASAGAM, D. DHINASEKARAN, A. RAJAMANICKAM, *Recent Patents on Corrosion Science*, 2 (2010) 40-54
4. L.L.G. DA SILVA, M. UEDA, M.M. SILVA, E.N. CODARO, *Surface & Coatings Technology* 201 (2007) 8136-8139
5. M.M. SILVA, M. UEDA, L. PICHON, H. REUTHER, C.M. LEPIENSKI, *Nuclear Instruments and Methods in Physics Research B* 257 (2007) 722-726
6. C. VEIGA, J.P. DAVIM, A.J.R. LOUREIRO, *Rev. Adv. Mater. Sci.* 32 (2012) 133-148
7. M. GEETHA, A.K. SINGH, R. ASOKAMANI, A.K. GOGIA, *Progress in Materials Science* 54 (2009) 397-425
8. D.K. BOAMPONG, S.M. GREEN, A. UNSWORTH, *Journal of Applied Biomaterials & Biomechanics,* 1 (2003) 164-171
9. S. KADAM, K.R. JAGDEO, M.R. NAIR, *International Journal of Engineering Research & Technology (IJERT),* Vol. 1 Issue 10 (2012) 1-7

10. H. EBRAHIMIAN, M. GHORANNEVISS, A. SHOKOUHY, M. YARI, *J. Plasma Fusion Res. SERIES,* Vol. 8 (2009) 1389-1391
11. D.M. GORDIN, D. BUSARDO, A. CIMPEAN, C. VASILESCU, D. HOCHE, S.I. DROB, V. MITRAN, M. CORNEN, T. GLORIANT, *Materials Science and Engineering*, C 33, 7 (2013) 4173-4182
12. P.VLACK, F. CERNY, Z. WEISS, S. DANIS, J. SEPITKA, Z. TOLDE, V. JECH, *Journal of Nano materials*, Vol. 2013 Article ID 475758 (2013) 1-8
13. W. LIANG, Q. MIAO, F. YING, P. ZHANG, Z. YAO, *Rev. Adv. Mater. Sci.* 33(2013) 106-110
14. A. SHOKOUHY, M. GHORANEVISS, M.M. LARIJANI, M. YARI, S.H. HAJI HOSSEINI, M. ESHGHABADI, *Journal of Fusion Energy,* Volume 30, Issue 5 (2011) 437-441
15. K.R. JAGDEO, S. KADAM, M.R. NAIR, *International Refereed Journal of Engineering and Science (IRJES),* Volume 1, Issue 4 (2012) 01-06
16. SUDJATMOKO, L. SUSITA R.M., WIRJOADI, B. SISWANTO, *Jurnal Iptek Nuklir Ganendra*, Vol. 16, No. 2 (2013) 67-75