ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 22, No. 1. 2016

Cathodic Cage Plasma Nitriding of Ti6Al4V Alloy

Maciej OSSOWSKI *, Tomasz BOROWSKI, Michal TARNOWSKI, Tadeusz WIERZCHON

Warsaw University of Technology, Faculty of Materials Science and Engineering, Woloska 141 02-507 Warsaw, Poland

crossref http://dx.doi.org/10.5755/j01.ms.22.1.7343

Received 18 June 2014; accepted 12 February 2015

Glow discharge nitriding is being used increasingly more often for modifying the properties of titanium and its alloys with the aim to increase their frictional wear resistance, fatigue strength, and, in the case of medical applications, to eliminate the metallosis effect. Unlike PVD methods, ion nitriding ensures the formation of diffusive layers with very good adhesion to the substrate, but which still have some disadvanteges such as the “edge effect” or “hollow cathode effect” which hinders treatment of complex workpieces.

The paper compares nitrided layers produced on Ti6Al4V alloy using two different types of nitriding processes. The first process is conventional dc plasma nitriding (DCPN) where the samples were placed at the cathode potential, while the second one is a new method of cathodic cage plasma nitriding (CCPN) process, where the substrate is insulated from the cathode and anode. The experiments have shown that the treatment conducted in a cathodic cage can be alternative for conventional ion nitriding, especially when used for small parts with complicated shapes used in the space or medical industry.

Keywords: titanium alloys, ion nitriding, surface engineering, wear resistance, space mechanisms, medical implant.

1. INTRODUCTION

On account of their favourable properties, such as low density, a high relative strength factor and great corrosion resistance, titanium and its alloys are widely used in different branches of industry as a construction material for various types of large industrial installations and complicated and sophisticated equipment components [1, 2]. However, because of their low wear resistance in mechanical applications and due to the metallosis effect in medical implants, a series of surface treatment processes are being elaborated, which are aimed at the elimination of these shortcomings [3 – 7]. One of the processes that increases surface hardness and wear resistance is the process of producing nitrided layers on titanium and its alloys by glow discharge nitriding [7 – 9]. Unlike PVD methods, glow discharge treatment ensures the formation of diffusive layers with very good adhesion to the substrate [7, 10]. In the process, activation of the gas environment through the emission of electrons from the cathode as well as cathode sputtering at the potential drop in the space close to the cathode, allow for producing layers at considerably lower temperatures and also on materials that undergo auto-passivation i.e. titanium or stainless steels [7, 11].

The effect of cathode sputtering, that takes place during glow discharge assisted nitriding processes, accelerates formation of nitrided layer but also hinders the treatment of workpieces with complicated shapes, e.g. fine threads or ones with sharp edges or straight-through and blind holes. In those areas, the effect of sputtering is more intense, which causes the layers to have different surface topography or even a different layer thickness, while for ready made parts, unfavorable visual characteristics become apparent, which can be seen in Fig. 1 [12 – 14]. These phenomena, which are referred to as the “edge effect” and “hollow cathode effect”, may be marginalised by a proper choice of technological parameters, however in the case of some workpieces this may prove insufficient [15, 16].

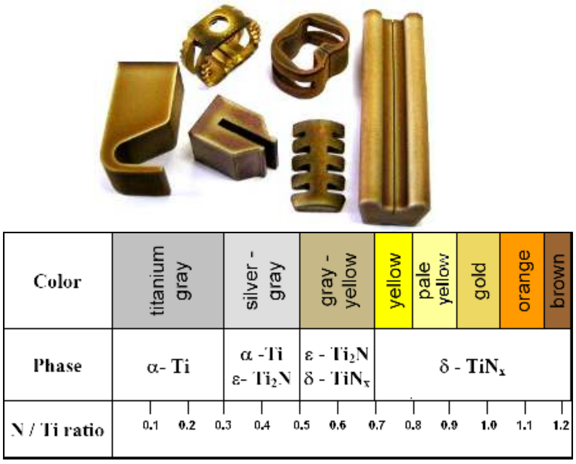


Fig. 1. Elements of titanium implants after standard plasma nitriding and a dependence diagram between titanium nitride colour and nitride stoichiometry [17]

It is possible to eliminate the effect of cathode sputtering by using an active screen, which is also referred as plasma nitriding or floating potential nitriding. The cathode here is in the form of an active screen, which is also called the cathodic cage, and which enables the free flow of reactive gases around the processed workpieces. They are isolated from the voltage applied to the screen and are in contact with the generated low-temperature plasma. In this case, the heating of the processed components is ensured mainly as a result of convection. Currently, the research and the scope of application of this method focuses on materials that are more commonly processed by means of nitriding processes i.e. austenitic

---

*Corresponding author. Tel.: +48-22-2348708; fax: +48-22-2348701.
E-mail address: *ossomac@wp.pl* (M. Ossowski)

steels or high-speed steels. The results obtained show that this method allows for the formation of diffusion layers of a uniform thickness, maintaining strict dimensional tolerances and of a pre-determined surface topography [18 – 23].

The paper presents results of examinations of surface layers produced in conventional dc plasma nitriding (DCPN) and cathodic cage plasma nitriding (CCPN) on polished Ti6Al4V titanium alloy with a high surface smoothness. A high smoothness of the surface is important for titanium parts used in e.g. medical equipment, implants or mechanical parts.

2. EXPERIMENTAL

The examination was made on Ti6Al4V (ASTM Grade 5) titanium alloy, which is one of the most common used titanium alloys. Cylindrical samples φ 14.5mm h = 1.5 mm in size were used. They underwent grinding and mechanical polishing in a diamond suspension with silicon oxide of a grain size of 0.04 μm before process commencement.

Both direct current plasma nitriding (DCPN) and cathodic cage plasma nitriding (CCPN) were carried out in an atmosphere of 100 % N_2 at temperature 800 °C for 8 hours. All the other technological parameters were identical in both cases. Cathodic cage plasma nitriding was carried out with the use of an active screen made of titanium Grade 2. The test samples were placed inside the screen and they were isolated from the cathode potential by means of ceramic isolators (Fig. 2).

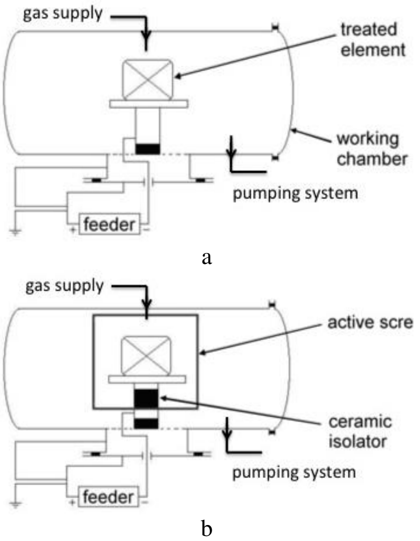


Fig. 2. Schematic view of device for: a – dc plasma nitriding (DCPN); b – cathodic cage plasma nitriding (CCPN)

An examination of the microstructure, surface morphology and chemical composition of the formed layers was made using a Hitachi S-3500N scanning electron microscope equipped with an EDS Thermo NORAN detector, whereas surface topography was examined using a Wyko NT9300 scanning optical profilometer. In order to determine the homogeneity of the produced layers, inspections were performed both in the centre and at a distance of 50 – 100 μm from the sample's edge.

An X-ray diffraction analysis of the phase composition was performed using a Brucker D-8 Advance X-ray diffractometer equipped with a CuKα radiation tube.

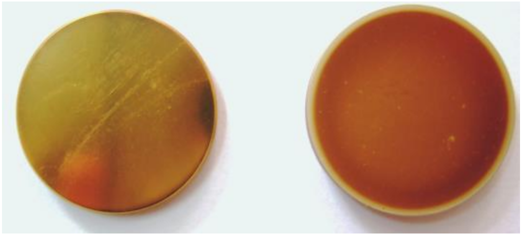
Surface microhardness was measured at the centre of the samples by means of a Zwick ZHV 10 hardness tester under a load of 100 and 50 g.

Wear resistance tests were performed using the "three roller + taper" method, which is a modified "four ball" method. In this test, three rollers constitute the investigated samples, while the taper is the couterspecim made of AISI1045 steel (hardened to 30HRC). Synthetic LUX10 engine oil was used as a lubricant.

Corrosion resistance was investigated by means of the potentiodynamic method in a 0.5 M NaCl solution at a temperature of 22 °C with the use of the Autolab PGSTAT 100 device, while the polarisation speed was 0.2 – 1 mV/s.

3. EXAMINATION RESULTS

The surface layers produced on the Ti6Al4V titanium alloy in the CCPN process have a uniform glossy shine and a golden colour on the whole surface of the examined samples. After the conventional DCPN process, the same differences in appearance across the sample were observed. On the edge of the cylindrical sample, the bright yellow ring was noticeable, while the centre of the sample had a uniform dark gold colour (Fig. 3).



CCPN DCPN

Fig. 3. Mechanically polished Ti6Al4V samples after CCPN and DCPN processes

The thickness of the titanium nitride layer formed in the DCPN process was about 2.0 μm, which was about 50 % higher than for layers produced in CCPN (about 1.3 μm). Measurements of layer thickness on the edge and in the centre of the samples didn't show significant differences, but the most noticeable changes were observed for the dc plasma nitriding sample where a layer produced on the edge was about 0.2 μm thicker than that in centre. The microstructure of the layers produced both using CCPN and DCPN are shown in Fig. 4.

An analysis of the phase composition showed the presence of TiN and Ti_2N type titanium nitrides as well as αTi phase with changed lattice parameter in both the layers (Fig. 5), which is connected with the diffusive character of the produced layers and a decrease of nitrogen content from the surface of the titanium alloy towards the substrate. On the basis of the phase analysis and the comparison of diffraction patterns it may be stated that the higher thickness of the DCPN layer is connected mainly with a higher content of the Ti_2N phase. Significant differences resulting from the applied nitriding methods are observed in the values of the surface roughness parameters of the produced nitrided layers (Table 1).

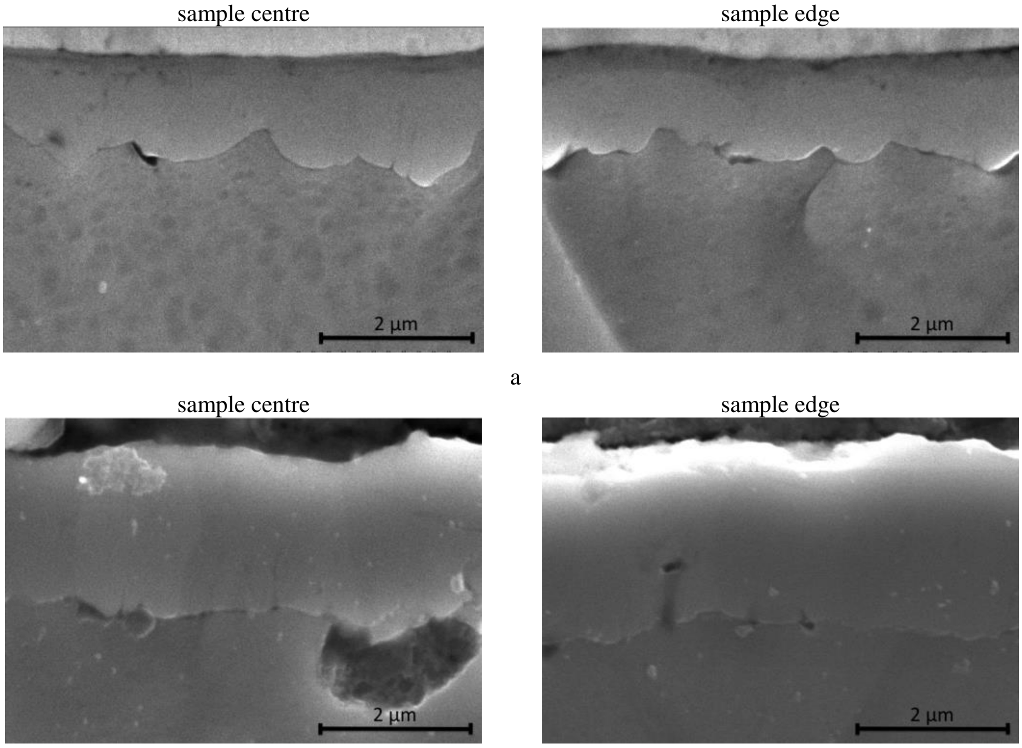


Fig. 4. Microstructure of nitrided layers produced on Ti6Al4V titanium alloy in CCPN) (a) and DCPN (b) processes

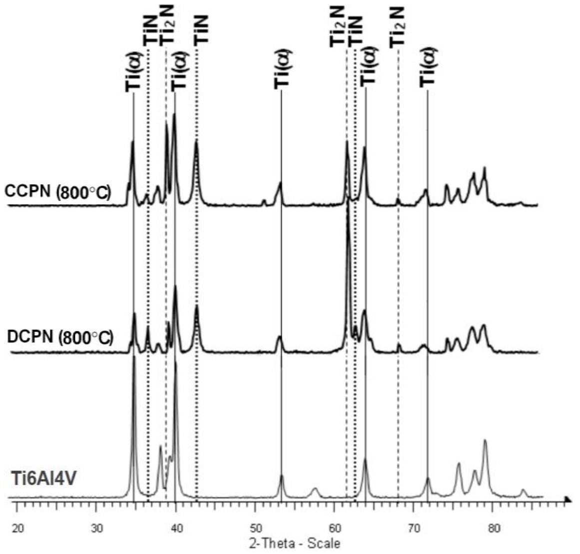


Fig. 5. XRD patterns of nitrided layers produced on Ti6Al4V titanium alloy in cathodic cage plasma nitriding (CCPN) and dc plasma nitriding (DCPN) processes

Roughness measurements showed a considerably smaller increase of R_a and R_q parameters for layers produced in th CCPN process than in conventional DCPN. When compared to the sample in the initial state (mechanically polished titanium alloy) the R_a parameter value was only two times greater for samples made in the CCPN process and up to ten times greater for the sample after conventional DCPN.

Moreover, the increase in the surface roughness value after DCPN nitriding was different in the centre and edge of the sample, unlike in the CCPN process. A comparison of surface morphology after nitriding processes at the centre and the edge of nitrided samples confirmed no differences in the layer produced using a cathodic cage (Fig. 6 a), while such differences are observed in the case of layers produced in conventional DCPN (Fig. 6 b).

Table 1. Roughness parameters of mechanically polished titanium alloy and nitrided layers produced on Ti6Al4V titanium alloy in CCPN and DCPN processes

Parameter, µm	Region	Ti6Al4V	CCPN	DCPN
R_a	centre	0.031	0.103	0.369
	edge	0.049	0.102	0.468
R_q	centre	0.040	0.135	0.479
	edge	0.054	0.134	0.636
R_z	centre	0.434	2.24	4.94
	edge	0.681	2.44	10.86
R_t	centre	0.493	1.70	6.38
	edge	0.773	1.73	18.31

Both R_z and R_t parameter values for the DCPN process are more then two times higher on the edge than in the centre. It means that the growth mechanism of nitrides in these two areas is different. Because all the technological parameters ware constant, this is the effect of cathodic sputtering which is more intensive on the corners.

A chemical composition analysis made on the surface by an EDS spectrometer shows significant homogeneity of the nitride layers produced in CCPN and heterogeneity of layers produced in DCPN.

Nitrogen content at the edge of the DCPN layer is more than 15% lower than in the centre of the tested sample (Table 2), which can suggest a different share in the volume of TiN and Ti_2N titanium nitrides or their different stoichiometry, which is connected with the different colours observed on the sample. Differences observed in the thickness, phase composition and surface parameters of the produced nitrided layers lead to differences in their properties.

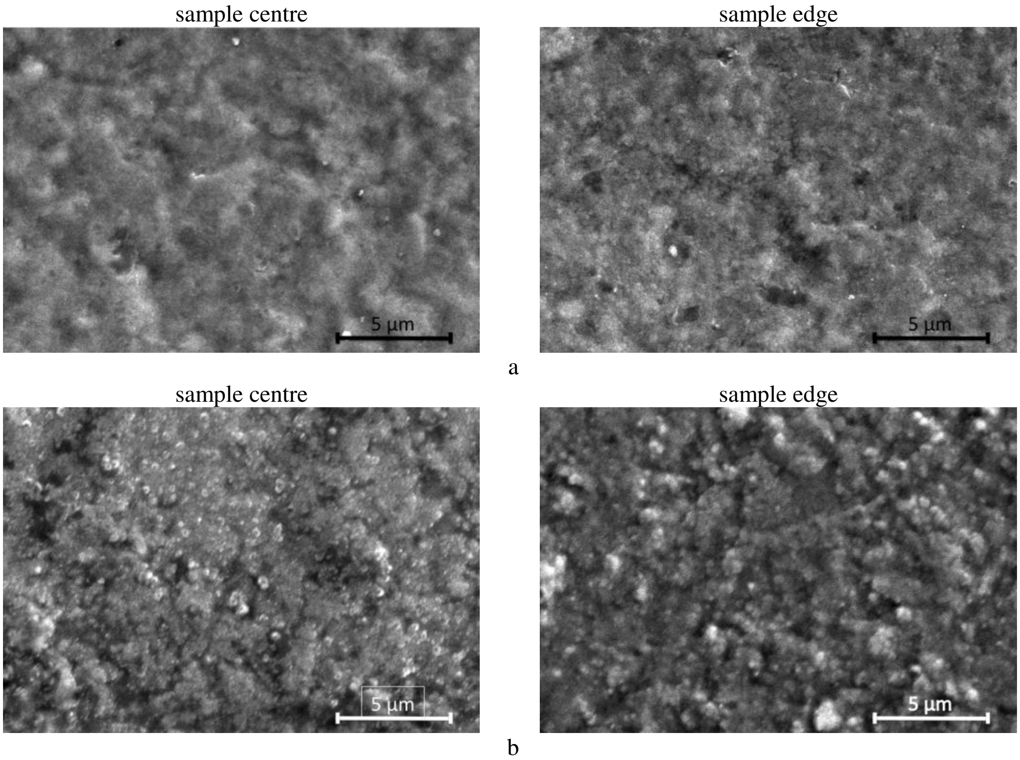


Fig. 6. Surface morphology of nitrided layers produced on Ti6Al4V titanium alloy in CCPN (a) and DCPN) (b) processes

Table 2. Chemical composition of nitrided layers produced on Ti6Al4V titanium alloy in CCPN and DCPN processes

Elements	Region	CCPN, at.%	DCPN, at.%
N	centre	30.3	33.8
	edge	30.3	28.5
Ti	centre	67.1	64.5
	edge	66.1	69.6
Al	centre	1.4	0.4
	edge	2.3	0.5
V	centre	1.2	1.3
	edge	1.3	1.4

The nitrided layers resulted in an increase of surface hardness of the Ti6Al4V titanium alloy. In the case of the CCPN process, the hardness grew nearly three times from 310HV0.1 to 880HV0.1. A much greater hardness of 1110HV0.1 was obtained in the DCPN process (Fig. 7) which is the effect of a greater thickness of the layer produced in this method. Measurements taken under a lower load show another difference between the two layers, more specifically in their near surface region. The hardness of the near-surface region for the DCPL layer is more then 30% higher then for the CCPN layer despite the fact that, as the previous investigation of phase composition and microstructure has shown, both layers are $TiN+Ti_2N+\alpha Ti(N)$ type diffusive layers and the volume of TiN nitrides is almost the same. A defected TiN nitride structure produced in DCPN process, where the volume of defects is related to cathodic sputtering intensity and ion energy, is responsible for this phenomenon of such big differences in hardness betwen these two layers.

Wear resistance tests confirmed a higher hardness and thickness of DCPN layers which had the lowest volume of wear, but CCPN layers still show great improvement over the untreated Ti6Al4V alloy and a higher wear volume then DCPN layers applied 50 minutes after the test.

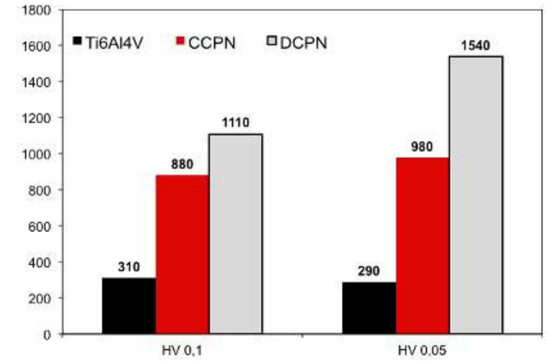


Fig. 7. Surface microhardness of nitrided layers produced on Ti6Al4V titanium alloy in (CCPN) and (DCPN) processes

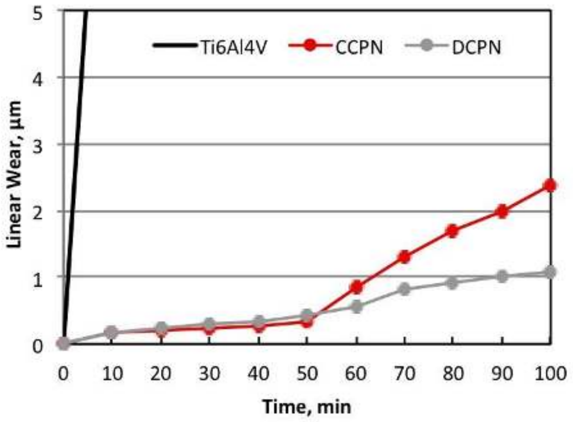
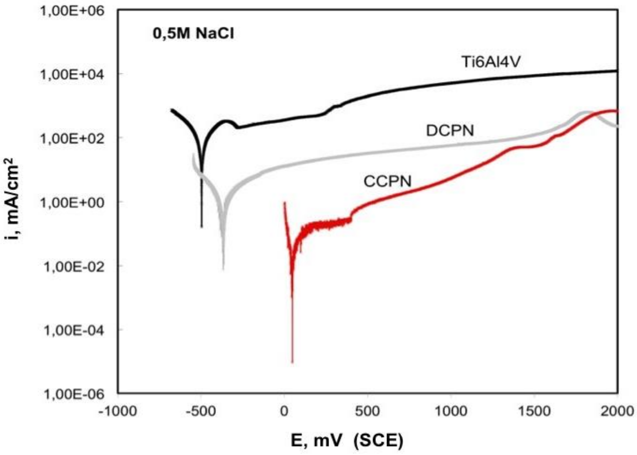


Fig. 8. Wear resistance under unit load of 400MPa of virgin state Ti6Al4V alloy and after nitriding in DCPN and CCPN processes

Corrosion examinations carried out in synthetic seawater (0.5 M NaCl solution) showed good corrosion resistance of the nitrided layers in an environment with chloride ions. Both DCPN and CCPN layers show higher corrosion potential, a lower value of polarization resistance and lower corrosion currents then untreated Ti6Al4V alloy (Fig. 9).



Sample	E_{cor}, mV	I_{cor}, $\mu A/cm^2$	R_{pol}, $k\Omega*cm^2$
Ti6Al4V	-497	758	0,337
DCPN	-366	0.806	21.5
CCPN	45	0.024	397

Fig. 9. Potentiodynamic curves and corrosion parameters of Ti6Al4V titanium alloy in initial state and after CCPN and DCPN processes obtained in corrosion tests in 0,5M NaOH solution

When considering CCPN and DCPN nitrided layers the difference of one order of magnitude in the values obtained can be observed. Corrosion parameters obtained for the sample after CCPN are significantly better then those obtained for the DCPN layer. In the opinion of the authors this may be thanks to the formation of a homogeneus, uniform, less defective TiN layer with higher smoothness in the CCPN process.

4. CONCLUSIONS

Ti6Al4V titanium alloy underwent two different nitriding processes, cathodic cage plasma nitriding (CCPN) and direct current plasma nitriding (DCPN). Nitrided layers of the $TiN+Ti_2N+\alpha Ti(N)$ type are diffusive in nature.

Basic differences were observed regarding thickness and homogeneity of the produced layers. The application of traditional dc glow discharge nitrided alloys makes it possible to produce layers of greater thickness but at the same time with a more developed surface. The lack of cathode sputtering during active screen plasma nitriding affects the homogeneity of the produced layers also on the edges of the samples.

Limitation of the influence exerted on the processed workpiece's surface topography and the possibility of maintaining its high smoothness, are the main advantages of the cathodic cage plasma nitriding process. Thus, the elaborated method of nitriding may be successfully used for the treatment of components with complicated shapes, making it possible to maintain achieve a homogenous thickness and surface topography. It can be useful especially for small parts due to the size of the active screens and area inside the screen where stable process conditions prevail.

Examples of CCPN process application can be already found in medicine where titanium elements of the ventricular heart developed by Foundation for Cardiac Surgery Development in Zabrze (Fig. 10) were nitrided for better wear resistance and antithrombogenic properties [24] or in space instruments [25] such as those designed and produced by the Polish Space Research Centre Hammering Sampling Device "CHOMIK" used to decrease the friction coefficient of titanium parts in vacuum conditions (Fig. 11) which was a part of the Russian Phobos Sample Return mission.

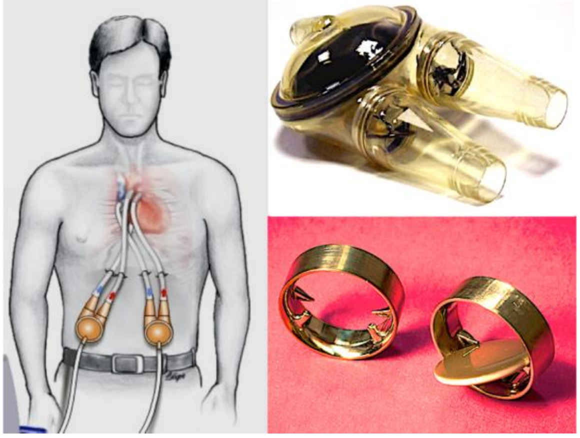


Fig. 10. Examples of Ti6Al4V parts developed in ventricular heart assist subjected to nitriding in elaborated CCPN process

These small parts with a maximum dimension of 6 centimetres was thin-walled (even below 1mm thickness) and had complicated shapes with many holes which could be impossible or very laborious to nitride in the conventional DCPN process.

Fig. 11. Examples Ti6Al4V parts developed in Hammering Sampling Device "CHOMIK" subjected to nitriding in CCPN process

On the other hand, conventional direct current plasma nitriding (DCPN) provides more possibilities to influence surface topography and morphology of the nitrided layers, has greater energy efficiency and allows for layers of greater thickness to be obtained in a shorter time on even very large parts.

As the results show, both the presented nitriding processes have their advantages and disadvantages must thus be described as complementary processes. Both nitriding methods of titanium and its alloys can be used depending on the application of the processed workpieces.

Acknowledgments

This research work was supported by the National Centre of Research and Development – project no. PBS1/A6/9/2012 and the National Center of Science – project no. 2011/01/B/ST2/07554

REFERENCES

1. **Lütjering, G., Williams, J.C.** Titanium. Springer-Verlag Berlin Heidelberg, 2003. http://dx.doi.org/10.1007/978-3-540-71398-2
2. **Brunette D. M., Tengvall, P.** et al. Titanium in Medicine. Springer-Verlag, Berlin, Heidelberg, 2001. http://dx.doi.org/10.1007/978-3-642-56486-4
3. **Sennerby, L., Thompson, P., Ericson, L.E.** Early Tissue Response to Titanium Implants Inserted in Rabbit Cortical Bone *Journal of Materials Science: Materials and Medicine* 4 1993: pp. 494 – 502. http://dx.doi.org/10.1007/BF00120129
4. **Kim, K.H., Narayanan, R., Rautray, T.R.** Surface Modification of Titanium for Biomaterial Applications, Nova Science Pub Inc, 2010.
5. **Park, K.H., Heo, S.J., Koak, J.Y.** et al. Osseointegration of Anodized Titanium Implants Under Different Current Voltages: a rabbit study *Jorurnal of Oral Rehabilitation* 34 2007: pp. 517 – 527.
6. **Czarnowska, E., Wierzchon, T., Maranda-Niedbała, A., Karczmarewicz, E.** Improvement of Titanium Alloy for Biomedical Applications by Nitriding and Carbonitriding Processes Under Glow Discharge Conditions *Journal of Materials Science: Materials in Medicine* 11 2000: pp. 73 – 81. http://dx.doi.org/10.1023/A:1008980631780
7. **Bloyce, A., Morton, P.H., Bell, T.** Surface Engineering of Titanium and Titanium Alloys *ASM Handbook Surface Engineering* 5 1994: pp. 14 – 16.
8. **Wierzchoń, T.** Surface Engineering of Titanium Alloys: New Prospective Applications *Materials Science Forum* 426-432 2003: pp. 2563 – 2568.
9. **Muraleedharan, T.M., Meletis, E.I.** Surface Modification of Pure Titanium and Ti-6Al-4V by Intensified Plasma Ion Nitriding *Thin Solid Films* 221 1992: pp. 104 – 113.
10. **Raveh, A., Bussiba, A., Bettelheim, A.** Plasma Nitrided α+β Ti Alloy: Layer Characterization and Mechanical Properties Modification *Surface and Coatings Technology* 57 1993: pp. 19 – 29.
11. **Pye, D.** Practical Nitriding and Ferritic Nitrocarburizing, ASM International 2003.
12. **Alves, C.Jr.** et al. Use of Cathodic Cage in Plasma Nitriding *Surface & Coatings Technology* 201 2006: pp. 2450 – 2456. http://dx.doi.org/10.1016/j.surfcoat.2006.04.014
13. **Alves, Jr.C., Silva, E.F., Martinelli, A.E.** Effect of Workpiece Geometry on the Uniformity of Nitrided Layers *Surface and Coatings Technology* 139 2001: pp. 1 – 5. http://dx.doi.org/10.1016/S0257-8972(00)01146-4
14. **Rolinski, E., Arner, J., Sharp, G.** Negative Effects of Reactive Sputtering in an Industrial Plasma Nitriding *Journal of Materials Engineering and Performance* 14 2005: pp. 343 – 350.
15. **Axinte, M., Nejneru, C., Perju, M. C., Cimpoesu, N., Hopulele, I.** Research on Hallow Cathode Effect and Edge Effect Avoidance in Plasma Nitriding Treatment *Tehnomus* 18 (1) 2011: pp. 181 – 184.
16. **Alves, C.Jr.** et al. Nitriding of Titanium Disks and Industrial Dental Implants Using Hollow Cathode Discharge *Surface & Coatings Technology* 194 2005: pp. 196 – 202.
17. **Staskiewicz, J.** Titanium Nitride Layers – TiN – The Beginning of Hard Coatings Era, (in Polish) [online], (2010), http://www2.tu.koszalin.pl/technologiehybrydowe/opracwania.
18. **Meletis, E.I.** Intensified Plasma-assisted Processing – Science and Engineering *Surface & Coatings Technology* 149 2002: pp. 95 – 113.
19. **Skolek-Stefaniszyn, E., Kaminski, J., Sobczak, J., Wierzchon, T.** Modifying the Properties of AISI 316L Steel by Glow Discharge Assisted Low-temperature Nitriding and Oxynitriding *Vacuum* 85 2010: pp. 164 – 169.
20. **Zhao, C., Li, C.X., Dong, H., Bell, T.** Study on the Active Screen Plasma Nitriding and its Nitriding Mechanism *Surface and Coatings Technology* 201 2006: pp. 2320 – 2325. http://dx.doi.org/10.1016/j.surfcoat.2006.03.045
21. **Li, C.X., Bell, T.** Corrosion Properties of Active Screen Plasma Nitrided 316 Austenitic Stainless Steel *Corrosion Science* 46 2004: pp. 1527 – 1547. http://dx.doi.org/10.1016/j.corsci.2003.09.015
22. **Sousa, R.R.M., Araujo, F.O., Ribeiro, K.J.B.** et al. Cathodic Cage Nitriding of Samples with Different Dimensions *Materials Science and Engineering* A 465 2007: pp. 223 – 227.
23. **Wang, L., Li, Y., Wu, X.** Plasma Nitriding of Low Alloy Steels at Floating and Cathodic Potentials *Applied Surface Science* 254 2008: pp. 6595 – 6600.
24. **Gonsior, M., Borowski, T., Czarnowska, E., Sanak, M., Kustosz, R., Ossowski, M., Wierzchon, T.** Thrombogenicity of Ti(N,C,O) Diffusive Coating Layers Developed on Titanium Alloy as the Blood Contact Surface *eCM – eCells & Materials Journal* 19 (S 1) 2010.
25. **Grygorczuk, J.** et al. Advanced Mechanisms and Tribological Tests of the Hammering Sampling Device CHOMIK, conference materials at http://www.esmats.eu, ESMATS 2011.