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Influence of Duplex Treatment on Structural and Tribological Properties of Commercially Pure Titanium

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Abstract: Titanium and its alloys are widely used in many fields, including aerospace and the chemical and biomedical industries. This is due to their mechanical properties, excellent corrosion resistance, and biocompatibility although they do have poor wear resistance. In this study, a duplex layer was successfully formed on the commercially pure titanium surface by duplex treatments (plasma nitriding and physical vapor deposition (PVD)). In the initial treatment, plasma nitriding was performed on the pure titanium samples and in the second treatment, the nitrided samples were coated with CrN by PVD. The friction and wear properties of the duplex-treated samples were investigated for tribological applications. Surface morphology and microstructure of the duplex-treated samples were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). In addition, the tribological properties were investigated using pin-on-disc tribometer. A compound layer composed of ε-Ti_2N and δ-TiN phases and a diffusion layer formed under the compound layer were obtained on the surface of pure titanium after the nitriding treatments. CrN coated on the nitrided surface provided an increase in the surface hardness and in the wear resistance.

Keywords: titanium, plasma nitriding, CrN coating, duplex treatment, wear

Introduction

Pure titanium is a material that has a very good corrosion resistance and biocompatibility [1–4], although its use as a biomaterial is limited due to its low values of tolerance and wear resistance [5]. There have been extensive studies to enhance these negative aspects of pure titanium so that it can serve a greater use in engineering and biomedical practices [6–9]. The results of these studies meant that the Ti-6Al-4V alloy was obtained through adding Al and V elements to pure titanium. This was the first titanium alloy that was ever produced and its aim at development was for use in the aviation and aerospace industry. Because of its function as a biomaterial [10–12], it was commonly used in medical practices. However, recent studies have revealed that Al and V elements within the Ti-6Al-4V alloy have harmful effects on the human body. The aluminum contained in the alloy causes allergenic effects on the body and affects the neurological system, causing Alzheimer's disease. Vanadium may cause toxic effects in the body and very severe disorders such as cancer in long-term uses [13–15]. The new Ti-6Al-7Nb and Ti-5Al-2.5Fe $\alpha+\beta$ type alloys were developed using niobium and iron instead of this alloy element due to vanadium's negative impacts [16, 17]. These alloys have similar attributes to the Ti-6Al-4V alloy in terms of mechanical and tribological behavior. However, the aluminum content in these alloys means that the problem in question for biomedical practices remains [18].

This flaw in pure titanium, which results in inadequate levels of tolerance for biomedical practices and harmful effects of the elements included in the titanium alloys, have led the way for researchers to conduct different studies on the subject. High tolerance values of materials with small grain size attract the attention of researchers to minimizing the grain size of the engineering materials. The grain size of many materials has been minimized through extreme plastic deformation techniques and the tolerance values have been increased. The extreme plastic deformation techniques applied on copper and its alloys, nickel and its alloys, magnesium and its alloys, aluminum and its alloys yielded successful results [19–21]. The extreme plastic deformation techniques were also applied to pure titanium, and the mechanic properties of pure titanium were increased [7, 22, 23]. Despite the increasing tolerance values of pure titanium, no improvement was observed in its wear resistance [24]. This is because the oxide layer that forms on the surface of titanium impacts the wear resistance of pure titanium negatively in applications with friction and contact.

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In this study, surface treatments were applied to enhance the weak tribological properties of pure titanium. The surfaces of pure titanium samples were coated by plasma nitriding, then the nitrided surfaces were CrN coated and applied with a duplex surface treatment. The tribological properties of the surfaces of the coated and uncoated samples were determined under atmosphere conditions. The surface hardness, tribological behaviors, and structural properties were investigated through different methods, these were: a micro-hardness tester device, a pin-on-disc wear tester, and SEM/XRD, respectively.

Materials and methods

Commercially pure titanium (Grade-2) was used as the initial material, its chemical composition is given in Table 1. Prior to the application of surface treatments, sample measuring 15 mm (width) × 15 mm (height) × 5 mm (thickness) were machined from pure titanium substrate, polished and then cleaned in a mixture of distilled water and ethanol.

Table 1: Chemical composition of pure titanium (wt. %).

Substrate	N	O	C	Fe	H	Ti
Commercially pure titanium (Grade 2)	0.006	0.15	0.008	0.041	0.002	The rest

The duplex surface treatment was then applied to these prepared samples. In the first section of the duplex treatment, the pure titanium samples were treated by plasma nitriding. Prior to the plasma nitriding treatment, the samples were cleaned with hydrogen sputtering at a pressure of 5 mbar over 15 min in order to remove any foreign matters on the surfaces of the samples, then the plasma nitriding treatment was performed with a mixture of 75 % N_2 + 25 % H_2 under 5 mbar pressure at 600 °C and 700 °C over 4 h. In the second section of the duplex treatment, the samples were coated with CrN by physical vapor deposition (PVD) at the Barlok PVD Coating Company (Istanbul, Turkey). The deposition process was characterized by the following parameters: substrate bias DC 100 V, target materials Ti and CrN, gas flow 40 %, working pressure 2.20–002 PTR, glow gas values 2.0 ps Ar and 1.6 ps H, working temperature 300–350 °C, deposition time 60 min, glow stages 20 min 240 V pulse 20 min 280 V, gas rate 70–75 ps (N), glow time 40 min, preheating time 60 min.

For phase identifications, XRD measurements were performed using a Cu Kα (λ = 1.5405 Å) source diffractometer (Rigaku diffractometer) with 2θ range from 20 ° to 80 °. The surface morphologies after the surface treatments were investigated using a scanning electron microscope (SEM) Quanta FEG 250. The surface roughness was measured with a profilometer device (Mahr surface profilometer). The hardness measurements of untreated and treated samples were performed using a Vickers microhardness tester operated at $HV_{0.05}$. The wear and friction tests were performed on a pin-on-disc tester (Turkyus PODTW&RWT), using a 6 mm diameter Al_2O_3 ball as the pin. The coefficients of friction were taken automatically by this device during the experiments. Friction and wear tests were conducted under laboratory conditions at a temperature of 23 ± 1 °C and relative humidity of about 47 ± 5 %. The tests were performed under a normal load of 2 N at a sliding speed of 62.8 $mm.s^{-1}$ for a sliding distance of 141 m. To calculate the wear volume loss, the wear track profiles were recorded by a profilometer and then calculated by the superimposed profiles. The wear rate was obtained using the equation, $V = W/FL$; where V is the wear rate (μm^3/Nm), W is the wear volume (μm^3), F is the normal load (N) and L is the sliding distance (m). Worn surfaces of the samples in all conditions were examined using an SEM.

Results and discussion

XRD analyses

Figure 1 shows the XRD patterns of the untreated and treated pure titanium samples. The XRD results indicated that α-Ti peaks appeared in the spectra from the untreated sample because the pure titanium (Grade-2) has an alpha-titanium alloy [8].

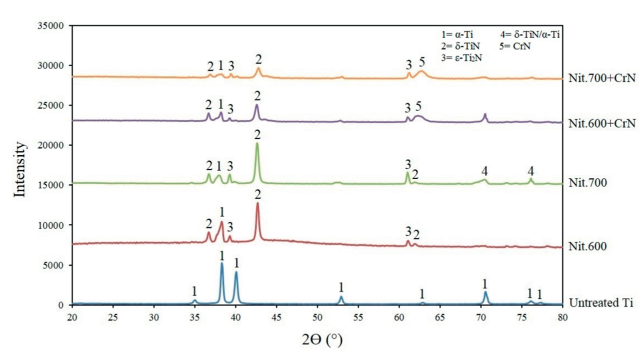

Figure 1: XRD results of the untreated and treated pure titanium samples.

For the first treatment, the samples were plasma nitrided for 4 h at 600 °C (Nit.600) and 700 °C (Nit.700). In the literature, the formation of a nitrided surface considered to be a complex treatment can be explained with a simplified physical model as follows:

This model, which can be applied to the temperatures below the β transformation point is based on the diffusion rules. The layer formed as a result of the nitrogen atoms diffused into titanium forming interstitial solution in the α-Ti structure during the plasma nitriding is called a “diffusion layer”. The formation of the interstitial solution by the nitrogen atoms continues as long as the α-Ti structure continues its ability to solve nitrogen. If a nitrogen density occurs higher than a value that the α phase can solve, ε-Ti_2N phase appears on the nitrogen-enriched α-Ti structure. Similarly, if the nitrogen density is higher than the necessary value for the formation of the ε-Ti_2N phase, ε-Ti_2N phase transforms into δ-TiN phase. The most important parameters beside the nitrogen density are the treatment temperature and duration [25].

After the plasma nitriding is applied at the appropriate treatment temperatures and for the necessary duration, the ε-Ti_2N/δ-TiN structure appears on the surface of titanium, this structure is called the “compound layer”. As a result, a diffusion layer composed of the interstitial nitrogen-enriched α-Ti structure and a compound layer composed of ε-Ti_2N and δ-TiN phases on this layer is obtained [26]. The formation of the ε-Ti_2N and δ-TiN phases as a result of plasma nitriding the pure titanium and its alloys is directly associated both with the treatment duration and the treatment temperature. It is emphasized in the literature that a steady δ-TiN phase occurs at 600 °C and above [27, 28]. The density of the peaks which belongs to the α-Ti phase coming from the base material decreases with the increasing treatment temperature. This proves that the density of the ε-Ti_2N and δ-TiN phases forms the compound layer. The results obtained in this study comply with the current studies in the literature [28–32]. When nitrided specimens were coated with CrN (Nit.600 + CrN and Nit.700 + CrN), it was detected that the density of the peaks coming from the nitrided surface decreased. The CrN phase appeared at about $2\theta = 62.5°$ [33].

SEM analyses

The SEM micrograph of the cross section of the duplex-treated pure titanium substrates are given in Figure 2. It can be seen in the figure that the CrN film appears uniformly. The thickness of the CrN film is about 4–5 µm (Table 2). It was also found that a compound layer and a diffusion layer appeared after the nitriding treatment. A clear and continuous compound layer formation was seen on the plasma nitrided samples (Table 2).

Images of surface morphology of untreated and treated pure titanium are given in Figure 3. The metallic grey color of the pure titanium samples turned golden after

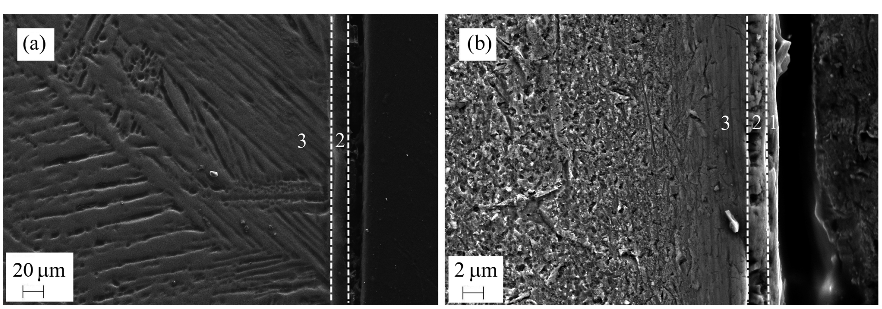

Figure 2: Cross-section SEM micrographs of (a) Nit.700 sample and (b) Nit.700 + CrN sample: (1) CrN film, (2) compound layer, and (3) diffusion layer.

Table 2: The values of compound layer thickness, diffusion layer thickness, surface roughness, surface hardness, wear rate, and CrN film thickness.

Specimen (pure titanium)	Surface hardness ($HV_{0.05}$)	Surface roughness (Ra)	Wear rate (mm^3/Nm)	Compound layer (µm)	Diffusion layer (µm)	CrN film (µm)
Untreated	213 ± 10	0.10	3.52×10^{-4}	–	–	–
Nit.600	714 ± 25	0.24	1.46×10^{-5}	4–6	75–85	–
Nit.600 + CrN	1,077 ± 6	0.23	1.38×10^{-5}	4–6	75–85	4–5
Nit.700	900 ± 26	0.25	6.73×10^{-6}	8–10	155–165	–
Nit.700 + CrN	1,616 ± 11	0.24	5.88×10^{-6}	8–10	155–165	4–5

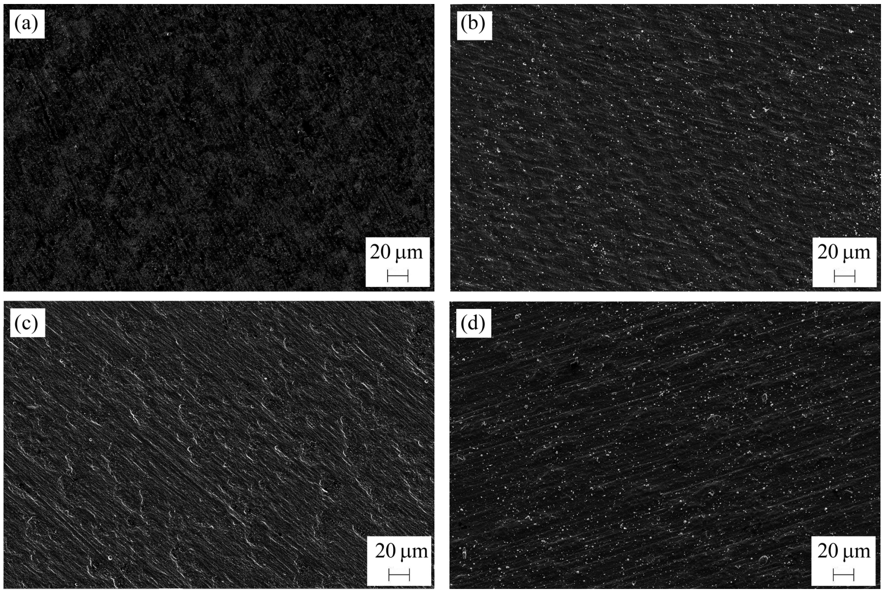

Figure 3: Surface morphology of the treated specimens: (a) Nit.600, (b) Nit.600 + CrN, (c) Nit.700, and (d) Nit.700 + CrN.

the plasma nitriding process [34, 35]. When the surface of the plasma nitrided pure titanium is examined, it is seen that the nitrided layer was composed of a structure of δ-TiN and ε-Ti_2N phases according to the data obtained from the XRD analyses (Figure 3(a) and 3(c)). As the temperature increased, the δ-TiN phase saw a columnar expansion and tended to form clusters, [36] this structure appeared as a result of the material exposed to more ion bombardment along with the increasing temperature [37]. This structure formed especially as a result of the plasma nitriding at 700 °C (Nit.700). The microstructure of the CrN layers consists of densely-packed fibrous grains and is similar to the so-called T zone in Thornton's growth model of PVD coatings [38, 39].

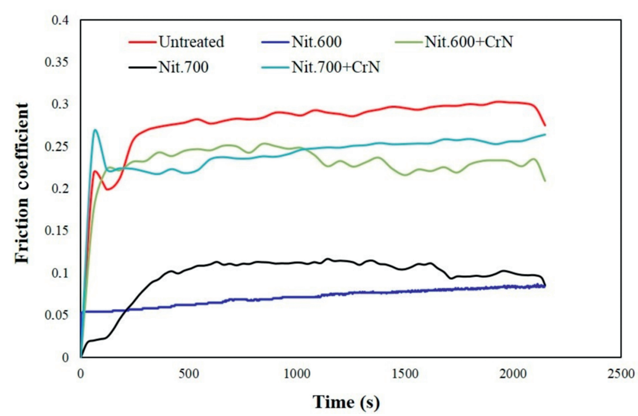

Figure 4: Friction test results of the untreated, plasma nitrided, and duplex-treated pure titanium samples.

Tribological properties

Friction test results of the untreated, plasma nitrided, and duplex treated samples are given in Figure 4. After the surface treatments, the average friction coefficient of pure titanium decreased, the average friction coefficient of the untreated specimen is 0.28. The lowest average friction coefficient was 0.073, and this value was found in the Nit.600 specimen. The highest average friction coefficient was observed in the Nit.700 + CrN among the treated specimens. After the duplex surface treatments, higher average friction coefficient values were measured in nitrided specimens.

Figures 5 and 6 illustrate the surface hardness values and the wear rates of the untreated and surface treated pure

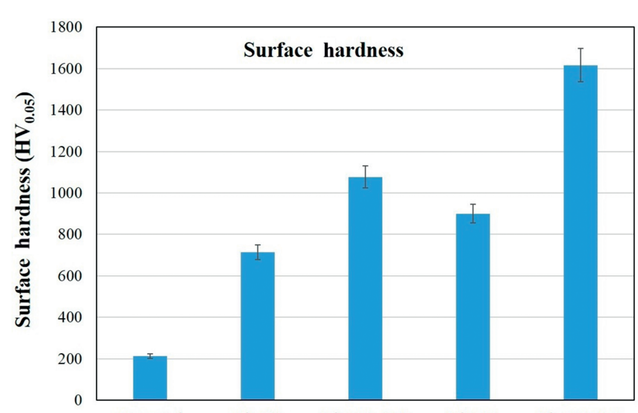

Figure 5: The graph of surface hardness values of the untreated and treated pure titanium specimens.

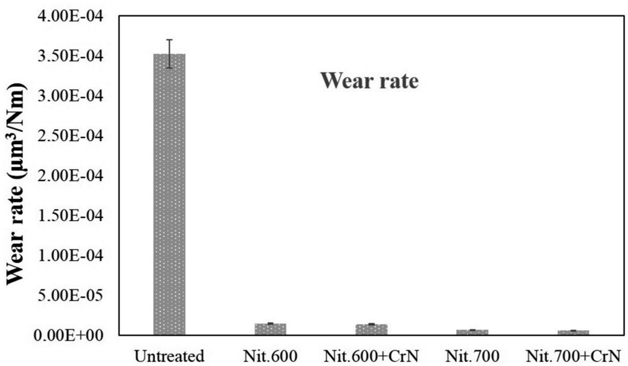

Figure 6: The graph of wear rate values of the untreated and treated pure titanium specimens.

titanium samples, respectively. In this study, the surface hardness and wear resistance of pure titanium were enhanced as a result of all these surface treatments. While the surface hardness value of the untreated specimen was 213 ± 10 $HV_{0.05}$, this increased to 714 ± 25 $HV_{0.05}$, 900 ± 26 $HV_{0.05}$, 1,077 ± 6 $HV_{0.05}$, and 1,616 ± 11 $HV_{0.05}$ after Nit.600, Nit.700, Nit.600 + CrN, and Nit.700 + CrN, respectively (Table 2). As seen in the graphic, the higher the hardness value became, the lower wear rates were achieved. The wear rate of the alloy significantly decreased with the application of the CrN film on the plasma nitrided pure titanium, this is because the load bearing ability of the coating system increased.

Figure 7 illustrates the SEM images of the wear tracks. When the untreated pure titanium wear tracks are investigated, it is seen that the wear has both abrasive and adhesive types (Figure 7(a)). Titanium is a relatively soft material, therefore, it had a plastic deformation during the wear test. Due to this deformation between pure titanium sample and pin, the contact point caused an increase in adhesive wear rate [9, 40]. The thin scratches in the wear track were created by the abrasive debris that was released as a result of a break in the thin natural oxide film on the pure titanium [9]. The best results were obtained from the duplex surface treatments in terms of wear resistance (Table 2). The plasma nitrided surfaces increased the load bearing capacity of the CrN coats and provided perfect wear resistance. The phase structure obtained on the surface after the nitriding treatment, the thickness of the diffusion layer and the compound layer are the basic causes that enhance the wear resistance of pure titanium. The rate of δ-TiN increased in the structure as the treatment temperature increased, consequently, the hardness value of the surface scaled up. Accordingly, there is a direct proportion between the increasing treatment temperature and increasing wear resistance (Table 2).

Conclusions

In this study, pure titanium specimens were successfully plasma nitrided and CrN coated. The obtained results can be summarized as follows:

- After the nitriding treatments, a compound layer composed of ε-Ti_2N and δ-TiN phases was obtained on the surface of pure titanium. A diffusion layer formed under the compound layer and this layer significantly increased the load bearing capacity of pure titanium.
- CrN coated on the nitrided layer provided an increase in the surface hardness, and therefore, in the wear resistance. The nitrided surface helped the CrN film scale up its tribological capacity.
- All these surface treatments increased the surface hardness of pure titanium about 3–8 times. The highest hardness values were achieved after the duplex surface treatments (Nit.700 + CrN).

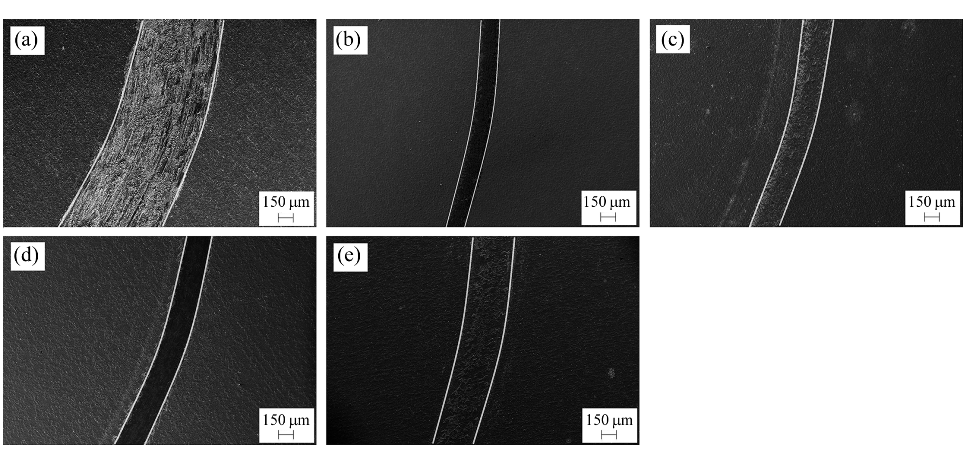

Figure 7: SEM images of the worn surfaces of the pure titanium specimens: (a) untreated, (b) Nit.600, (c) Nit.600 + CrN, (d) Nit.700, and (e) Nit.700 + CrN.

– Favorable duplex surface treatment by plasma nitriding and CrN coating is an effective method to improve the wear resistance of commercially pure titanium (grade-2), which can widen its potential applications, especially in biomedical applications.

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References

[1] B. Sivakumar, R. Singh and L.C. Pathak, Mat. Sci. Eng. C-Mater., 48 (2015) 243–255.
[2] C. Martini, L. Ceschini, F. Tartertini, J.M. Paillard and J.A. Curran, Wear, 269 (2010) 747–756.
[3] A.L. Yerokhin, X. Nie, A. Leyland and A. Matthews, Surf. Coat. Tech., 130 (2000) 195–206.
[4] D. Teker, F. Muhaffel, M. Menekse, N.G. Karaguler, M. Baydogan and H. Cimenoglu, Mat. Sci. Eng. C-Mater., 48 (2015) 579–585.
[5] V. Oliviera, R.R. Chaves, R. Bertazzoli and R. Caram, Braz. J. Chem. Eng., 15 (1998) 326–333.
[6] Q. Wang, P.Z. Zhang, D.B. Wei, X.H. Chen, R.N. Wang, H.Y. Wang and K.T. Feng, Mater. Design., 52 (2013) 265–273.
[7] I. Celik, A. Alsaran and G. Purcek, Surf. Coat. Tech., 258 (2014) 842–848.
[8] İ. Çelik and M. Karakan, Kovove Materially-Metallic Materials 54 (2016) 37–43.
[9] A.F. Yetim, Surf. Coat. Tech., 205 (2010) 1757–1763.
[10] R.R. Boyer, Mat. Sci. Eng. A-Struct., 213 (1996) 103–114.
[11] J.G. Ferrero, J. Mater. Eng. Perform., 14 (2005) 691–696.
[12] İ.H. Uzun and F. Bayındır, Atatürk Ünivesitesi Diş Hekimliği Fakültesi Dergisi, 20 (2010) 213–220 (in Turkish)).
[13] K. Wang, Mat. Sci. Eng. A-Struct., 213 (1996) 134–137.
[14] Z.L. Sun, J.C. Wataha and C.T. Hanks, J. Biomed. Mater. Res., 34 (1997) 29–37.
[15] N.J. Hallab, C. Vermes, C. Messina, K.A. Roebuck, T.T. Glant and J.J. Jacobs, J. Biomed. Mater. Res., 60 (2002) 420–433.
[16] M. Long and H.J. Rack, Biomaterials, 19 (1998) 1621–1639.
[17] M. Niinomi, Metall. Mater. Trans. A, 33 (2002) 477–486.
[18] J.J. Mark and A. Waqar, Titanium and Titanium Alloy Applications in Medicine. Surface Engineered Surgical Tools and Medical Devices, Springer, New York (2007).
[19] S. Kamado, T. Ashie, Y. Ohshima and Y. Kojima, Mater. Sci. Forum, 350–3 (2000) 55–62.
[20] J. Lobos, S. Suzuki, H. Utsunomiya, H. Nakajima and M.A. Rodrigez-Perez, J. Mater. Process. Tech., 212 (2012) 2007–2011.
[21] M.W. Fu, Y.W. Tham, H.H. Hng and K.B. Lim, Mat. Sci. Eng. A-Struct., 526 (2009) 84–92.
[22] G. Purcek, G.G. Yapici, I. Karaman and H.J. Maier, Mat. Sci. Eng. A-Struct., 528 (2011) 2303–2308.
[23] D.V. Gunderov, A.V. Polyakov, I.P. Semenova, G.I. Raab, A.A. Churakova, E.I. Gimaltdinova, I. Sabirov, J. Segurado, V.D. Sitdikov, I.V. Alexandrov, N.A. Enikeev and R.Z. Valiev, Mat. Sci. Eng. A-Struct., 562 (2013) 128–136.
[24] G. Purcek, O. Saray, O. Kul, I. Karaman, G.G. Yapici, M. Haouaoui and H.J. Maier, Mat. Sci. Eng. A-Struct., 517 (2009) 97–104.
[25] S. Malinov, W. Sha and P. Markovsky, J. Alloy Compd., 348 (2003) 110–118.
[26] A. Zhecheva, W. Sha, S. Malinov and A. Long, Surf. Coat. Tech., 200 (2005) 2192–2207.
[27] B.S. Yilbas, A.Z. Sahin, A.Z. AlGarni, S.A.M. Said, Z. Ahmed, B.J. Abdulaleem and M. Sami, Surf. Coat. Tech., 80 (1996) 287–292.
[28] V. Fouquet, L. Pichon, M. Drouet and A. Straboni, Appl. Surf. Sci., 221 (2004) 248–258.
[29] S.G. Lakshmi, D. Arivuoli and B. Ganguli, Mater. Chem. Phys., 76 (2002) 187–190.
[30] M. Rahman, I. Reid, P. Duggan, D.P. Dowling, G. Hughes and M.S.J. Hashmi, Surf. Coat. Tech., 201 (2007) 4865–4872.
[31] F. Yildiz, A.F. Yetim, A. Alsaran and A. Celik, Surf. Coat. Tech., 202 (2008) 2471–2476.
[32] N.M. Lin, X.B. Huang, J.J. Zou, X.Y. Zhang, L. Qin, A.L. Fan and B. Tang, Surf. Coat. Tech., 209 (2012) 212–215.
[33] Z.K. Chang, X.S. Wan, Z.L. Pei, J. Gong and C. Sun, Surf. Coat. Tech., 205 (2011) 4690–4696.
[34] A.F. Yetim, F. Yildiz, Y. Vangolu, A. Alsaran and A. Celik, Wear, 267 (2009) 2179–2185.
[35] A.F. Yetim, A. Celik and A. Alsaran, Surf. Coat. Tech., 205 (2010) 320–324.
[36] A.F. Yetim, in: Graduate School of Natural and Applied Sciences, Atatürk University, Erzurum (2009), pp. 137.
[37] S.C. Mishra, B.B. Nayak, B.C. Mohanty and B. Mills, J. Mater. Process. Tech., 132 (2003) 143–148.
[38] P. Wiecinski, J. Smolik, H. Garbacz and K.J. Kurzydlowski, Vacuum, 107 (2014) 277–283.
[39] P. Wiecinski, J. Smolik, H. Garbacz and K.J. Kurzydlowski, Surf. Coat. Tech., 240 (2014) 23–31.
[40] O. Comakli, T. Yetim and A. Celik, Surf. Coat. Tech., 246 (2014) 34–39.