Dicle University Journal of Engineering (DUJE)

web: http://dergipark.gov.tr/dumf

Research Article

Investigation of wear behavior of Ti-6Al-4V and AISI 316 L biomaterials with ball on disc test device

Harun AKKUŞ^{1,*}, Tahsin KAMIŞ², Hayrettin DÜZCÜKOĞLU³

¹ Technical Sciences Vocational School, Amasya University, Amasya, Turkey, ORCID iD: 0000-0002-9033-309X

² Technology Faculty, Selçuk University, Konya, Turkey, ORCID iD: 0000-0003-2894-1809

³ Technology Faculty, Selçuk University, Konya, Turkey, ORCID iD: 0000-0002-7016-6888

ARTICLE INFO	ABSTRACT
Article history:	
Received 7 September 2019 Received in revised form 9 December 2019 Accepted 27 January 2020 <u>Available online 15 June 2020</u> <u>Keywords:</u> Biomaterials, Ti-6AI-4V, AISI 316 , coating, wear, temperature, SEM, ball on disc	Ti-6Al-4V material is generally used in biomaterial applications. However, this material is difficult to supply and an expensive material. Instead of Ti-6Al-4V material; It is investigated whether the use of 316 L material as an alternative is easier and more economical. In this study, Ti-6Al-4V and AISI 316 L test specimens made of the material subjected to the test under the same conditions wear performance were investigated using the ball on disc experimental setup. The experiments were carried out in three replicates in a dry and liquid medium. As a result, in the experiments; AISI 316 L samples are coated with PVD method compared to other samples in wear rates and abrasive wear marks on the surface of the samples were found to decrease. In studies using sodium hyaluronate fluid, it was found that the rate of abrasion and wear traces decreased compared to the dry environment. It was determined that 316 L samples coated with PVD method showed better wear performance compared to uncoated Ti-6Al-4V material. Considering the density differences of Ti6Al4V and 316L materials, 316L can be used instead of Ti6Al4V material.

Introduction

mühendislik derg

Due to their crystal structure and strong metallic bonds, metal and metal alloys with superior mechanical properties are used as biomaterials. It is used as a joint prosthesis and bone replacement material in orthopedic applications, while it is also used as an artificial heart, catheter, valve, heart valve in face and jaw surgery, such as an implant, or in cardiovascular surgery [1]. In order to use the metals as biomaterials, factors such as compatibility with tissues, wear and corrosion behaviors, surface properties, side effects and cost are investigated [2].

Wear and corrosion are an important problem in biomaterials. It is not possible to completely eliminate this problem. The aim is to slow down the speed of this damage mechanism [3]. In recent years, surface coating processes have increased interest in increasing the tribological properties of 316 L stainless steel and Ti-6Al-4V alloy used as biomaterials [4-7].

Some researchers have described the term biocompatibility as surface and structural compatibility. Surface compatibility is that a biomaterial is physically, chemically and biologically compatible with body tissues. Structural compatibility is the optimum fit of the material to the mechanical behavior of body tissues [8, 9]. The biocompatibility of metal prostheses is related to their corrosion in the body (in vivo) [10].

Ti-6Al-4V is a titanium alloy which is the raw material of most of the implants used in the field of medical orthopedics and neurosurgery. It is preferred for Ti-6Al-4V implant production because it is more resistant to corrosion than stainless steel in pure uncoated condition,

because of its flexibility and compatibility with human body [11-13].

316 L stainless steel material is used as an implant because of its high resistance to intergranular and stressed corrosion cracking. This material was used as test material for the purpose of improving the resistance properties due to the inability to apply hardening with normal heat treatment applications [14-18].

Biomaterials should not be reduced while corrosion resistance is improved while coating high corrosion resistance that makes these materials superior [19, 20].

In this study, test samples made of Ti-6Al-4V and AISI 316 L materials were tested under the same conditions and their wear performances were investigated by ball on disc test setup.

Material and Method

Purpose of experimental study

In our study, we aim to investigate the wear behavior of AISI 316 L stainless steel material which is more advantageous in terms of ease of procurement, and easier to process, which can eliminate these disadvantages in comparison to the disadvantages of Ti-6Al-4V material supply and economically high costs.

The parameter values we have determined in our study are given in Table 1.

Table	1. Exp	erimental	conditions.
-------	---------------	-----------	-------------

Experimental conditions	Definitions					
Experiment device	Ball on disc					
Experiment materials	AISI 316 L, Ti-6Al-4V, Nitrided AISI 316 L, TiN coated AISI 316 L, CrN / TiN coated AISI 316 L					
Experiment speeds (m/s)	1-1,5-2					
Experiment force (N)	7,5-10					
Experiment distance (m)	500					
Experiment medium	Dry-Liquid (Sodyum hyaluronat)					
Experiment ball diameter (mm)	10					
Experiment ball material	100Cr6					

	Wear rate,
Experiment measurements	Temperature change,
-	SEM images

The discs to be used in the experiments were subjected to the required measurements and polishing was carried out using 200-400-600-1000 grains. Samples whose polishing was completed were subjected to plasma nitration process. The test samples were subjected to plasma nitration for 12 hours at a temperature of 600 °C in 40% nitrogen and 60% ammonia medium. Plasma nitration process was applied to the parts using 1000 grit sandpaper. After polishing, one of the discs was coated with TiN by applying 450 °C temperature and 10^{-5} Torr vacuum, and one was coated with CrN/TiN by applying 475 °C temperature and 10^{-5} Torr vacuum.

Hardness measurements

Hardness measurements of PVD coated and uncoated discs made of plasma nitration were performed in Mht-2 micro hardness tester as shown in Figure 1. Microhardness measurements were measured as HV by applying a 100 g load for 15 seconds with a diamond tip. The hardness values measured in Table 2 are given.

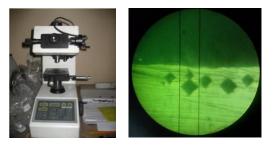


Figure 1. Mht-2 microhardness measuring devices.

Table 2. The measured hardness value	es.
--------------------------------------	-----

Material	Hardness value
AISI 316 L	320 HV_1
Ti-6Al-4V	$350 HV_1$
Nitrided 316L	1014 HV _{0,1}
TiN coated 316 L	2500 HV _{0,1}
CrN/TiN coated 316 L	2850 HV _{0,1}
Ball	64-66 HRc

The PVD coated disc was cut as shown in Figure 2 to measure the thickness of the samples.



Figure 2. Example of disc cut to measure thickness.

Preparation of samples for the experiment

After the test samples and abrasive balls were cleaned with ethanol, they were dried for 15 minutes in the drying oven as shown in Figure 3 and pre-test weights were determined with a 10⁻⁴ g weight scale. The weighed samples were subjected to abrasion in the ball-disc test apparatus under dry and sodium hyaluronate fluid conditions. After the test, the samples were cleaned and weighed by ethanol and the wear losses were determined. Wear rates were calculated depending on the wear losses. Wear tests were carried out at room temperature and under normal atmosphere. The abrasion marks on the disc were examined at 100x, 250x and 400x magnification. All experiments were repeated three times and averaged.



Figure 3. a) Drying oven, b) Weighing machine.

The ball on disc test device is driven by a 2.2 kW and 1400 rpm motor and the disc is rotated. The device consists of a 2.2 kW AC motor, 2.2 kW speed adjuster, a disk, support arm, clamp mechanism, table, slide mechanism, weighting apparatus, variable weights, load cell data transfer card. Squirrel data logger with versatile, general purpose, 8 analog inputs is used for

friction coefficient and temperature measurement. Using the Squirrel View interface program, 10 values are read and recorded per second. Figure 4 shows the ball-disc test device.

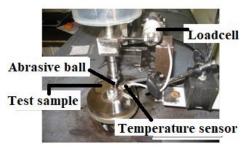


Figure 4. Ball on disc test device.

After the work in dry environment was finished, 0.5 liters of sodium hyaluronate liquid was added to the system by adding the tank seen in Figure 5 and the experiments in the liquid medium were also carried out.

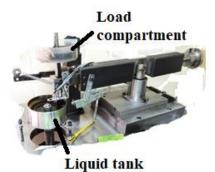


Figure 5. Ball-disk test device; Working with sodium hyaluronate fluid.

Scanning Electron Microscope(SEM) images

Appropriate samples were cut in the cutting machine to take images from the section and measure the thickness of the coating. The surfaces of the horizontal sander were cleaned and etched with pure alcohol and then examined by a metal microscope at a magnification of 600X (Figure 6). Then, images and coating thicknesses from the section were made by SEM. In Figure 6, the hardness thicknesses were found to be 10 μ m on the nitrided disc, 2.5 μ m on the TiN coated disc and 4 μ m on the CrN/TiN coated disc.

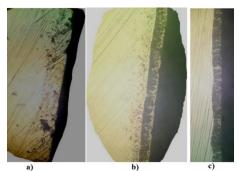


Figure 6. SEM image a) TiN coated, b) Nitrided, c) CrN/TiN coated.

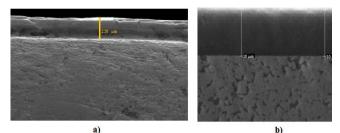


Figure 7. SEM image a) TiN coated, b) Nitrided, c) CrN/TiN coated.

Experimental Results

Wear quantities for ball and disc

Table 3 shows the wear rates on discs that are subject to wear with a 100Cr6 bearing ball. When we examine the table, it is seen that the highest abrasion rate in the uncoated 316 L sample was the highest abrasion rate. The highest hardness value of CrN/TiN coated 316 L sample was observed. When we examine Table 3, it is seen that the highest abrasion value of the most abrasion was observed in the uncoated 316 L sample with the lowest hardness value (320 HV), and the highest hardness value of CrN/TiN coated 316 L sample was observed. Again in nitrided and TiN coated samples, it is seen that the abrasions are very low compared to both the uncoated 316 L and the uncoated Ti-6Al-4V material. The reason for the improvement of the abrasion resistance is the formation of many hard phases together with the coating, the reduction of the particle size, the high dislocation density and the interlocking of the dislocations [21]. When the amount of abrasion in the coated samples is examined, it is seen that, according to the uncoated 316 L sample, approximately 50% less wear is observed in the nitrided samples, 70% in the TiN coated samples and 85% in the CrN/TiN coated samples. Again, compared to the uncoated Ti-6Al-4V sample, it is seen that the nitrided 316 L sample provides about 18% -20%, the TiN-coated 316 L sample gives about 35% -40% and the CrN/TiN coated sample gives about 60-65% advantage. Table 3 shows that the amount of wear occurring on the discs is between 20% and 50% lower than the dry environment.

The highest abrasion rate is seen in the uncoated 316 L samples in the coated samples with the thickness of the coating is observed to decrease the wear rate. This reduction in the wear rate can be explained by the resistance of the hard layer against abrasion. Again, the increase of the coating thickness interlocked with the hard layers and reduced the wear resistance, which resulted in the lowest wear rate of CrN/TiN coating [16].

Table 3. For disk; shear rate and abrasion rates according to the applied force. [Wear rate X 10^{-6}
$(mm^3N^{-1}m^{-1})].$

	1 m/s				1,5 m/s				2 m/s			
Experimental samples	7,5 N		1	10 N		7,5 N		7,5 N		10 N		,5 N
	Dry	Liquid	Dry	Liquid	Dry	Liquid	Dry	Liquid	Dry	Liquid	Dry	Liquid
AISI 316 L	33	25	36	29	35	28	38	30	38	32	40	30
Ti-6Al-4V	23	17	27	22	20	15	21	17	20	15	22	16
Nitrided 316L	14	10	15	11	10	7	11	8	10	8	10	9
TiN coated 316 L	10	7	12	8	9	5	10	6	8	6	9	7
CrN / TiN coated 316 L	7	4	8	4	7	2	8	3	4	2	6	2

As the effect of the force is increased in Table 4. the abrasion rate in the ball increases for all shear speeds and for all discs. This is due to the increase of the load and the increase of the contact surface of the two materials. The wear rate increased steadily with the uncoated 316 L sample as the slip speed increased, but increased for a while, but then decreased for other samples. This is due to the fact that the materials with high chemical stability do not adhere to the surface of the abraded material and have a lubricity characteristic. The highest abrasion on the ball is the highest measured (2850 HV) CrN/TiN coating, and as the hardness of the discs, the amount of wear on the ball decreases. Again in the same table, the amount of abrasion in all tests has decreased with the effect of film formed by liquid. It is seen that the liquid has an advantage between 25% and 35% in terms of the amount of wear of the ball.

It is seen that the abrasion rate increases as the abrasion force increases in all coatings. It is seen that the coated discs are more erosive than the uncoated discs and the most abrasion is carried out by the CrN / TiN coated 316 L sample. This is believed to result from increased surface hardness of the discs. It is seen that sodium hyaluronate fluid added to the medium reduces the wear rate on the balls according to the dry environment due to the film layer formed between the disc and the ball.

Table 4. For ball; shear rate and abrasion rates according to the applied force. [Wear rate X 10^{-6} (mm³N⁻¹m⁻¹)].

	1 m/s					1,5 m/s				2 m/s			
Experimental samples	7,5 N		1	10 N		7,5 N		10 N		7,5 N		10 N	
	Dry	Liquid	Dry	Liquid	Dry	Liquid	Dry	Liquid	Dry	Liquid	Dry	Liquid	
AISI 316 L	4	3	7	5	4	3	5	3	2	1	3	1	
Ti-6Al-4V	5	4	8	6	5	3	6	4	3	2	3	2	
Nitrided 316L	8	6	10	7	6	5	8	5	6	5	6	4	
TiN coated 316 L	11	8	12	9	8	5	9	5	8	6	10	7	
CrN/TiN coated 316 L	14	10	16	12	9	7	12	10	11	9	13	10	

Examination of temperature change

The temperature values recorded by the computer system and measured instantly by the help of sensors in the ball on disc system were compared according to the sliding distance.

For the shear rate of 1 m/s in Figure 8, for the shear rate of 1.5 m/s in Figure 9 and for the shear rate of 2 m/s in Figure 10; The effects of the coatings on the dry and liquid medium temperature are shown under 7.5 N load. It is observed that the surface temperature decreases with the coatings. This is related to reduced surface roughness and reduced abrasive wear resulting in reduced particles. In addition, the temperature distribution of TiN coatings has also been found to reduce the temperature.

Average temperature for the shear rate of 1 m/s; in uncoated 316 L sample, dry medium 27,15 °C, in liquid medium 21,25 °C, in nitrated 316 L sample, in dry medium 25,3 °C, in liquid medium 20,85 °C and in CrN/TiN coated 316 L sample in dry medium 24.10 °C in liquid medium and 20.65 °C. In the light of this information, the temperature of CrN/TiN coating was found to decrease by 11%, while sodium hyaluronate fluid added to the environment decreased the temperature by 18% -22%.

Average temperature for the shear rate of 1.5 m/s; Uncoated 316 L sample, dry medium 26,15 °C, liquid medium 20,10 °C, nitrated 316 L sample, dry medium 25,45 °C, liquid medium 23,15 °C and CrN/TiN coated 316 L sample, dry medium 24, 35 °C and 23.45 °C in liquid medium. In the light of this information, it is seen that CrN/TiN coating reduces the temperature by 9% and the addition of sodium hyaluronate liquid by 15-20%.

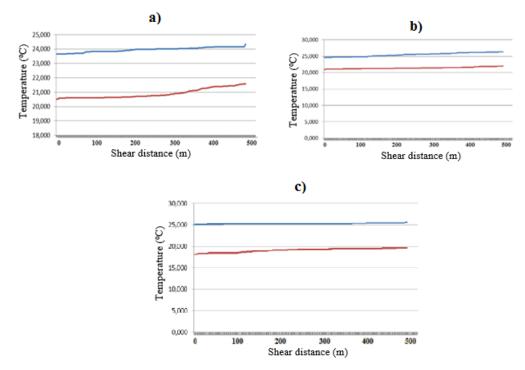


Figure 8. Effect of the sliding distance on the dry and liquid wear environment under 7.5 N load at a shear rate of 1 m/s; a) Uncoated 316 L b) nitrided 316 L, c) CrN/TiN coated 316 L (_______ : Dry, ______ : Liquid).

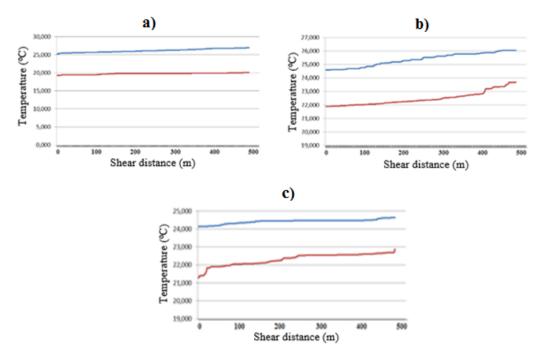


Figure 9. Effect of the sliding distance on the dry and liquid wear environment under 7.5 N load at a shear rate of 1.5 m/s; a) Uncoated 316 L b) nitrided 316 L, c) CrN/TiN coated 316 L (______ : Dry, _____ : Liquid).

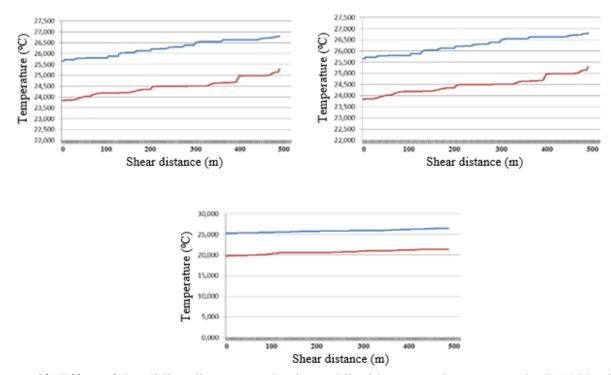
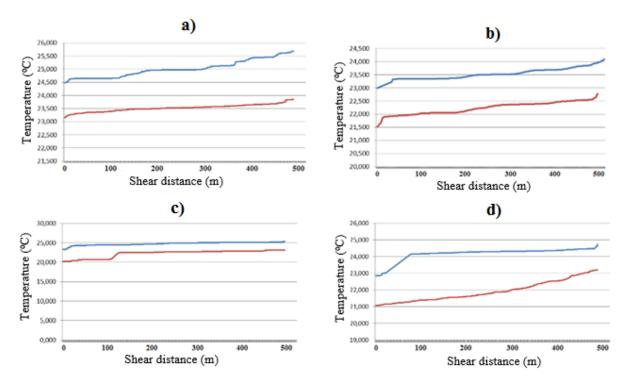
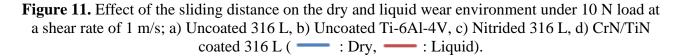


Figure 10. Effect of the sliding distance on the dry and liquid wear environment under 7.5 N load at a shear rate of 2 m/s; a) Uncoated 316 L b) nitrided 316 L, c) CrN/TiN coated 316 L (—— : Dry, —— : Liquid).

Average temperature at a shear rate of 2 m/s; in uncoated 316 L sample, 26.8 °C in dry medium, 24.10 °C in liquid medium, nitrated 316 L sample, 26.2 °C in dry medium, 316 L sample in liquid medium 24.5 °C and CrN/TiN coated, in

dry medium 26 oC and 21 °C in liquid medium. In the light of this information, it is seen that CrN/TiN coating reduces the temperature by 9% and the addition of sodium hyaluronate liquid by 15% - 20%.





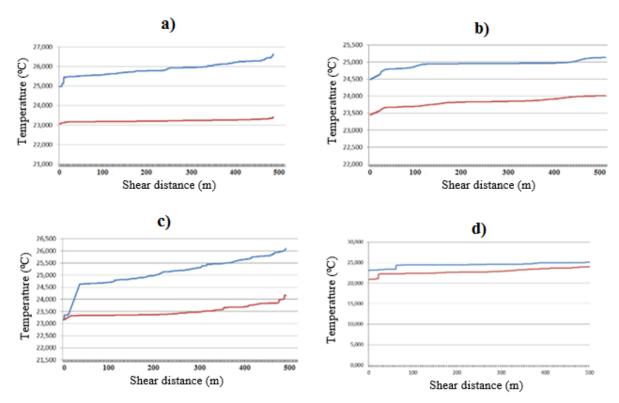


Figure 12. Effect of the sliding distance on the dry and liquid wear environment under 10 N load at a shear rate of 1,5 m/s; a) Uncoated 316 L, b) Uncoated Ti-6Al-4V, c) Nitrided 316 L, d) CrN/TiN coated 316 L (______ : Dry, _____ : Liquid).

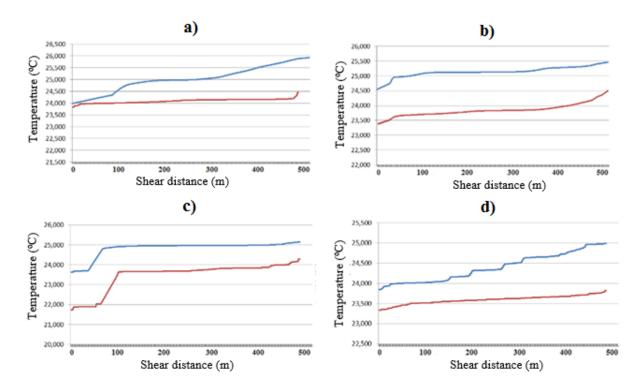


Figure 13. Effect of the sliding distance on the dry and liquid wear environment under 10 N load at a shear rate of 2 m/s; a) Uncoated 316 L, b) Uncoated Ti-6Al-4V, c) Nitrided 316 L, d) CrN/TiN coated 316 L (______ : Dry, _____ : Liquid).

When the figures were examined, it was seen that the coatings contributed to the reduction of the temperature at every load and shear rate and this contribution was between 9% and 15%. In addition, it was found that sodium hyaluronate fluid also contributed 20%-30% to lower the temperature.

SEM images reviews

Figure 14 and Figure 15 show SEM images of wear marks on discs. In Figure 14 a) it is seen

that very intense abrasive abrasions occur in the uncoated 316 L sample. It is seen that the ball has caused abrasive abrasion in the uncoated sample and formed wide wear channels. In Figure 14 b) it is seen that the abrasions of abrasive wear and wear channels in the nitrided 316 L sample decrease with increasing surface quality. As shown in Figure 14 c), abrasive wear was observed in CrN/TiN coated 316 L samples, however, the resulting damage occurred at much lower rates. As can be seen from the figures, the wear marks on the samples with decreasing surface hardness gradually decreased and the wear marks were reduced to almost none.

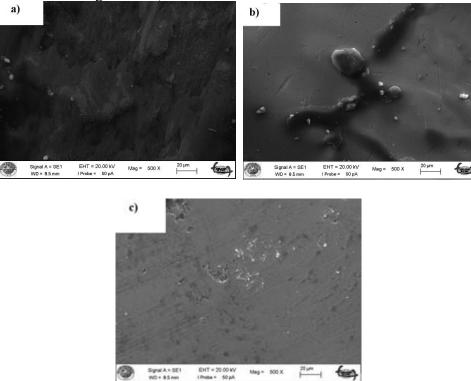


Figure 14. Wear marks on disc surfaces at 1.5 m/s shear rate and 7.5 N load; a) Uncoated 316 L, b) Nitrided 316 L, c) CrN/TiN coated 316L.

L samples, which were the most hard samples, were reduced to almost none.

When Figure 15 is examined, As with Figure 14, the abrasion marks on the samples with increasing surface hardness decreased gradually and the wear marks on the CrN/TiN coated 316

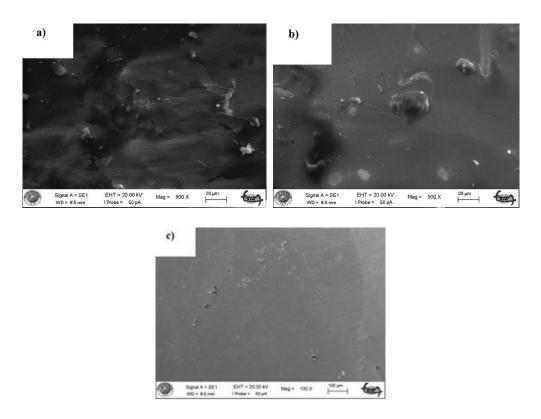
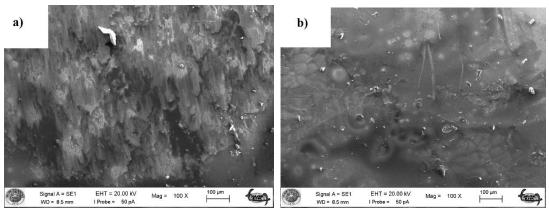


Figure 15. Wear marks on disc surfaces at 2 m/s shear rate and 7.5 N load; a) Uncoated 316 L, b) Nitrided 316 L, c) CrN/TiN coated 316L.

Figure 14 and figure 15 together with the increase in the slip rate of wear marks appear to tend to decrease. This is due to the fact that the

materials with high chemical stability do not adhere to the surface of the abraded material and show their lubricity properties.



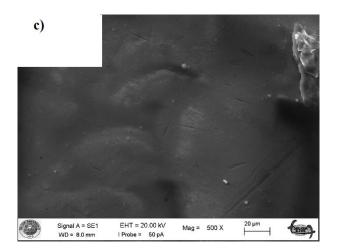


Figure 16. Wear marks on disc surfaces at 1.5 m/s shear rate and 10 N load; a) Uncoated 316 L, b) Nitrided 316 L, c) CrN/TiN coated 316L.

Figure 16 shows SEM images of abrasion traces on discs at a shear rate of 1.5 m/s and under 10 N load. As seen in the previous figures, there are also traces of deep abrasive wear in the uncoated 316 L sample. In the nitrided sample, although some abrasive abrasion is observed, it is seen that the sample is very low compared to the uncoated sample. In the CrN/TiN coated sample, it can be clearly seen that abrasive abrasions remain at the level of simple scratches. Nitrided and CrN/TiN coated samples showed that abrasive wear was reduced with increasing surface hardness.

Conclusions

In this study; The abrasion performances of CrN / TiN coated, plasma nitrided and uncoated AISI 316 L stainless steel with PVD - Cathodic Arc method were investigated under liquid friction operating conditions using dry and sodium hyaluronate fluid in the Ball-Disc test apparatus.

Ti-6Al-4V material is generally used in biomaterials applications. However, this material is difficult to supply and is also an expensive material from an economic point of view. For all these reasons, 316 L materials which be economically more suitable for supply has been used as test material. The test specimens made from Ti-6Al-4V material were also tested under the same conditions and the wear performances were compared. As a result, in the experiments performed working conditions in the Ball-Disc test apparatus;

- 1. If the 316 L samples are compared with those of other samples by wear of the PVD method, it is see the decrease the amounts and ratios of abrasion and also It has been found that the abrasive wear marks on the surface of the samples decrease.
- 2. Sodium hyaluronate liquids have been found to reduce the amount and ratio of wear when compared to dry medium.
- 3. The 316 L samples coated with the PVD method showed better wear performance than the uncoated Ti-6Al-4V material.
- 4. Considering the density differences of Ti6Al4V and 316L materials, 316L can be used instead of Ti6Al4V material.
- 5. In the following studies, it is recommended to make a comparison between Ti6Al4V and 316 L under different conditions with the tests to be performed with artificial body fluid.

References

- 1. Gümüşderelioğlu, M. Metallic biomaterials. Science and Technical Journal **2002**, July Issue, 4.
- 2. Kohn, D. H. Metals in medical applications. Current Opinion in Solid State and Materials Science **1998**, Vol. 3 (3), pp. 309-316.
- 3. Alsaran, A. Determination of structural, mechanical and tribological properties of AISI 5140 steel applied to duplex surface treatment. Ph.D. Thesis,

Ataturk University, Institute of Science and Technology, Erzurum, **2001**.

- Janoss, B. PVD/CVD tool coatings enhance stamping & forming of stainless steels. Metal Forming (USA) 1999, Vol. 33 (3), pp. 110-112.
- Tokaji, K.; Ogawa, T.; Shibata, H. The effect of gas nitriding on fatigue behaviour in pure titanium. International journal of fatigue **1994**, Vol. 16 (5), pp. 331-336.
- Zhao, Q.; Zhai, G.J.; Ng, D.; Zhang, X.Z.; Chen, Z.Q. Surface modification of Al 2 O 3 bioceramic by NH+ 2 ion implantation. Biomaterials **1999**, Vol. 20 (6), pp. 595-599.
- Zhecheva, A.; Sha, W.; Malinov, S.; Long, A. Enhancing the microstructure and properties of titanium alloys through nitriding and other surface engineering methods. Surface and Coatings Technology 2005, Vol. 200 (7), pp. 2192-2207.
- 8. Burg, T.; Standard, O. Materials for Biomedical Engineering. School of Materials Sciences and Engineering Universitz of New South Wales **2001**.
- 9. Çelik, İ.; Eroğlu, H. Selection application of material to be used in hip prosthesis production with analytic hierarchy process. Materialwissenschaft und Werkstofftechnik **2017**, Vol. 48(11), pp. 1125-1132.
- Tas, A.C. Synthesis of biomimetic Cahydroxyapatite powders at 37 C in synthetic body fluids. Biomaterials 2000, Vol. 21 (14), pp. 1429-1438.
- Fouquet, V.; Pichon, L.; Drouet, M.; Straboni, A. Plasma assisted nitridation of Ti-6Al-4V. Applied Surface Science 2004, Vol. 221 (1), pp. 248-258.
- 12. Lautenschlager, E.P.; Monaghan, P. Titanium and titanium alloys as dental materials. International dental journal **1993**, Vol. 43 (3), pp. 245-253.
- 13. Massiani, Y., Gravier, P., Crousier, J., Fedrizzi, L., Dapor, M.; Micheli, V.; Roux, L. Effects of ion beam implantation on the corrosion behaviour of

TiN-coated Ti-6Al-4V alloy. Surface and Coatings Technology **1992**, Vol. 52 (2), pp. 159-167.

- 14. Berríos, J.; Teer, D.; Puchi-Cabrera, E. Fatigue properties of a 316L stainless steel coated with different TiN x deposits. Surface and Coatings Technology **2001**, Vol. 148 (2), pp. 179-190.
- Borgioli, F.; Fossati, A;, Galvanetto, E.; Bacci, T. Glow-discharge nitriding of AISI 316L austenitic stainless steel: influence of treatment temperature. Surface and Coatings Technology 2005, Vol. 200 (7), pp. 2474-2480.
- Dogan, H.; Findik, F.; Morgul, O. Friction and wear behaviour of implanted AISI 316L SS and comparison with a substrate. Materials & design 2002, Vol. 23 (7), pp. 605-610.
- Fossati, A.; Borgioli, F.; Galvanetto, E.; Bacci, T. Corrosion resistance properties of glow-discharge nitrided AISI 316L austenitic stainless steel in NaCl solutions. Corrosion Science 2006, Vol. 48 (6), pp. 1513-1527.
- Sun, Y.; Bell, T. Sliding wear characteristics of low temperature plasma nitrided 316 austenitic stainless steel. Wear **1998**, Vol. 218 (1), pp. 34-42.
- Feng, H.; Lee, S.; Hsu, C.; Ho, J. Study of high cycle fatigue of PVD surface-modified austempered ductile iron. Materials chemistry and physics **1999**, Vol. 59 (2), pp. 154-161.
- Ranea, C. Wear resistance of thin coatings based on titanium. International Conference on Tribology 2002, Kayseri, pp. 15-18.
- Yi, Z.; Xiao, Z.; Ma, F.; Zhang, T.; Li, Y. Wear resistance properties of stainless steel modified with co-implantation of V+ C. Surface and Coatings Technology **2000**, Vol. 128, pp. 186-191.