

Comparative Tribological Study of NiTi Diffusion Coated Titanium with Pure Titanium

G. Khosravi

University of Tehran

M. Heydarzadeh Sohi (✉ mhsohi@ut.ac.ir)

University of Tehran

HM. Ghasemi

University of Tehran

N. Jalalian Karazmoudeh

Iran University of Science and Technology

Research Article

Keywords: Cp titanium, Diffusion surface treatment, NiTi intermetallic, Wear, Friction coefficient

Posted Date: November 12th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1054373/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Dry tribological behaviors of commercial pure (Cp) titanium and Cp titanium diffusion coated with equiatomic NiTi intermetallic layer were studied and compared at room temperature. Wear tests were performed by a pin on disk tribometer using 52100 steel pins, under various normal loads of 10, 20, and 40 N. worn surfaces were examined by scanning electron microscope, equipped with EDS analyzer. The wear rates of the coated materials were lower than those of the Cp titanium at all loads. This was mainly attributed to the higher hardness of the NiTi intermetallic layer compared to that of the untreated titanium. Furthermore, under an applying load of 10 N, a tribological layer was formed which could protect the surface from severe wear. The results also demonstrated a lower coefficient of friction in the treated specimens compared to those of the Cp materials.

1. Introduction

Despite the high specific strength and almost good corrosion resistance of titanium alloys [1,2], these materials exhibit poor wear resistance and high friction coefficient which restrict their application in items subjected to wearing conditions [3,4]. To overcome these deficiencies, several surface modification techniques like plasma nitriding, ion implantation, physical vapor deposition, liquid phase surface treatments, laser cladding, electroless, gas tungsten arc welding, and pulsed plasma electrolysis have been applied on these alloys [5–12]. The formation of diffusion coatings like nickel titanium compound (NiTi) has also drawn significant attention to combat wear [13-16]. NiTi intermetallic shows pseudoelasticity behavior [17,18] which is elastic responses to applied stresses, due to reversible martensitic phase transformation [19]. Recently several research groups employing various techniques to fabricate NiTi intermetallic as reliable protective layers on titanium and its alloys [20-22]. Tran et al. [15], studied the possibility of the formation of NiTi intermetallic phase via ultra-fast reaction of nickel droplet deposited by thermal spray on a titanium substrate. Waghmare et al. [21], fabricated a thick NiTi coating on Ti-6Al-4V by tungsten inert gas (TIG) surfacing method. The clad layer possessed a hardness value of more than 500 HV and the wear resistance improved up to 9.5 times compared to that of the substrate. Mokgalaka et al. [22], produced NiTi intermetallic coating on Ti-6Al-4V alloy using a laser metal deposition process. Results revealed that the presence of NiTi, NiTi₂, and NiTi₃ led to improvement in wear resistance up to 80%. Nevertheless, the aforementioned methods have limitations such as the formation of micro pores and inherent defects like cracks, expensive equipment, and operating complexity. Therefore, applying a diffusion-based treatment, which improves adhesion strength to the substrate, can overcome the defects of the previous methods [23]. The authors of the present work have reported the formation of Ni-Ti intermetallic coatings by nickel plating on commercially pure titanium followed by heat treatment [24]. A 20 μm thick layer with equi-atomic Ni-Ti composition is produced on the surface of Cp titanium via diffusion treatment. The aim of this work is to study and compare the wear behavior of commercial pure (Cp) titanium and Ni-Ti coated material. In this regard, the wear mechanisms are discussed based on the microstructural studies which provide an explanation to the enhancement of wear resistance in the coated samples in comparison with Cp titanium.

2. Materials And Methods

40 mm × 40 mm square shape specimens were cut from a 3mm pure titanium sheet. The specimens were grounded with emery paper up to 800 grid and then polished. To activate the titanium surface, the specimens were initially immersed in an aqueous solution containing copper sulfate 200 g/l, sulfuric acid 40 g/l, aluminum sulfate 24 g/l, and wetting agent 0.1% for one minute. They were then immersed in a second solution containing sodium dichromate 100 g/l, copper sulfate 5 g/l for one minute at 85 °C, and hydrofluoric acid (52%) 50 ml/l for five minutes.

The activated specimens were then electroplated with nickel using Watts bath (containing 240 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 30 g/l $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 30 ml/l H_3BO_3), at a current density of 20×10^4 mA/m² for one hour at room temperature to produce a 30 μm nickel coating. The distance between the cathode and anode during electroplating was fixed at 2 cm. After the plating process, the samples were washed with deionized water and then dried. The coated specimens were then heat treated at 900°C for 12 hours in a controlled atmosphere furnace and were consequently cooled to room temperature in the furnace.

The phase structure of the coated layers was identified by X-ray diffractometer (XRD) using Cu k_α (step size = 0.01, and time per step = 0.5) operated at 40 kV with a 30 mA emission current. Morphology and elemental composition of the coating layers and worn surfaces were studied using a scanning electron microscope (Cambridge stereo scan 440 SEM) equipped with an energy dispersive spectroscope (Philips PV 9800 EDS) employing an accelerating voltage of 30 kV. A typical microhardness profile of the coated materials was obtained at an applied load of 0.147 N for 15 s by a microhardness machine using a Vickers indenter. The hardness measurement was repeated five times for each point, and the average values were reported.

Pin-on-disk wear test machine was used to measure the room temperature dry sliding wear rate of titanium before and after coating. For this purpose, the bare and coated specimens were prepared as 30 mm diameter disks. AISI 52100 steel pins with 5 mm diameter and a hardness of approximately 740 HV were used as counterface. The schematic diagram of this test is presented in Fig. 1. Before each test, the pins and discs were ultrasonically cleaned in acetone for 6 minutes then dried and weighed with a precision of 0.1 mg. The wear tests were performed under 3 different loads (10, 20, 40N) at a sliding speed of 0.25 m/s for a sliding distance of 500 m. Weight losses of the specimens were measured using a high-precision balance. The coefficient of friction was also recorded by a computational system during the wearing process. In addition, Hommelwerk T-8000 roughness tester was used to obtain grooves depth by measuring the roughness before and after were testing.

3. Results And Discussions

The cross sectional SEM image of the diffusion coated specimen in Fig. 2 shows two distinct layers from the surface to the core of the diffused layer on the titanium substrate. Based on the EDS results presented in Table 1, it appears that the outer layer is equiatomic NiTi with 15 μm thickness, and the bottom layer

with 4.08 μm is NiTi_2 intermetallic. The X-ray diffraction pattern shown in Fig. 3 supports the EDS result which demonstrate the presence of NiTi , and NiTi_2 intermetallic in the treated layer.

Table 1
EDS analysis of the layers a and b in Fig. 1, formed after Ni plating followed by heat treatment

Layer	Ni (at%)	Ti (at%)
a	49.8	50.2
b	33.9	66.1

The hardness profile along the top of the fabricated layer toward the CP titanium substrate in the treated material is shown in Fig.4. The outer layer (NiTi layer) hardness is 280 HV, and then it drops with a steep hardness gradient in the diffusion zone at a hardness level of about 200 HV. Finally, the other decrease in hardness level to about 180HV is attributed to the Cp Titanium.

The wear rates of the Cp titanium before and after diffusion treatment as a function of load for a sliding distance of 500 m are shown in Fig. 5a. As can be seen in this figure, there is a significant increase in wear rate with the load increasing for both materials. Nevertheless, the wear rates of the treated material under all applied loads are much lower than those of Cp titanium. The wear rates of the counterface pins are shown in Fig. 5b. It is obvious that under three different loads the wear rate of the pins against the bare samples are significantly lower than those used for treated specimens. This could be a result of the lower hardness of the untreated material in comparison with the surface treated ones. Besides, increasing the load up to 40 N reduces the wear rate of the pin against Cp titanium to zero. It is believed that applying high loads results in temperature rise that in turn deteriorates the mechanical strength of the bare titanium and consequently the wear rate of the counterface pin is reduced to zero [25].

In order to eliminate the effect of the sliding distance, the specific wear rate of disks was calculated by dividing the wear rate to the applying load. Fig. 6 shows the specific wear rates of the Cp and diffusion coated specimen as a function of load. The figure reflects a dramatic increase in wear resistance after the aforementioned surface treatment.

Fig.7 shows a typical depth profile of the worn surface of the diffusion coated specimen achieved after 500 m sliding under 40N load. It appears that the intermetallic layer has been totally removed because according to Fig.2, the thickness of the layer was less than 20 μm ; therefore, to evaluate the wear mechanism before losing the intermetallic layer, the sliding distance decreased to 200m for this particular specimen.

Figure 8 shows the SEM images of the worn surfaces of diffusion coated and Cp titanium achieved after wearing under 10, 20, and 40 N. The respected EDS analysis of the worn surfaces of the diffusion treated specimens are also demonstrated in this figure. The EDS results are in favor of the formation of tribological layers on the coated specimens in the wearing course of the treated material. These layers are

mainly contained nickel, titanium, iron, and oxygen. With respect to the image of the treated sample after abrasion under 10 N (Figure 8.a), it becomes apparent that the tribological layers in area A are thicker than those of area B, because the amount of iron and oxygen in area A are higher than those of the area B. Furthermore, cross sectional image in Fig. 9 also confirms the formation of the tribological layer with perfect bonding on the surface of the coated specimen during wear under an applied load of 10 N. It appears that the rate of the formation of oxides is higher than their removal. This can protect the surface from severe wear and results in the reduction of the wear rate as can be seen in Figure 5a. The remarkable wear rate of the pin against the diffusion treated sample under 10 N load (Fig. 5b) also confirms the existence of a hard tribological layer.

The SEM images of the worn surfaces of the Cp titanium produced under an applied load of 10N are also shown in Fig. 8a. The relevant EDS analyses of these worn surfaces reveal that the chemical composition of the region marked as A in this figure consists of 86.5% titanium, 12.5% iron, and 1% oxygen. These results demonstrate that a Ti-based tribological oxide layer was formed on the surface in regions like A. In addition, as is shown in figure 8a some cracks are formed on this tribological layer. It seems that the rate of the formation of the tribological layer is lower than its removal, so this layer could not protect the surface.

The micrograph and the EDS analysis of the worn surface of the coated specimen under 20N are shown in Fig. 8b. These results reveal that a mixture of titanium, nickel, and iron oxides as a tribological layer is formed in the region marked as C. The EDS analyses of region D and some broken regions indicate that the tribological layer is broken and removed. Therefore, the wear rate of the coated specimen under 20 N applied load is more than that of the 10 N. Furthermore, as can be seen in the SEM image of the worn surface of Cp Ti under 20N load, there is no oxide layer to protect the surface, and plastic deformation is the main wear mechanism which leads to increase of the wear rate under 20 N load in comparison with the diffusion treated specimen.

The micrograph and the EDS analysis of the worn surface of the coated material under 40 N (Fig. 8c) show that the mixed oxide layer yet remains on the surface in regions like E. This figure also illustrates the formation of debris that were able to aggravate abrasion and as a result, no protection layer was left on the surface in the region marked as F, which led to a higher wear rate as compared to those of similar specimens under lower forces (as shown in Fig. 6a). In addition, with due attention to the micrograph of the worn surface of Cp Ti under 40 N in Fig. 8c, it becomes clear that there is not any tribological layer to protect the surface. The plastic deformation and possible fatigue cracks are the main wear mechanisms in this specimen. Fig. 10 shows the cross section of the worn Cp Ti sample under an applied load of 40 N. It can be seen that holes and cracks are formed in depth below the surface and eventually result in the formation of debris with a delamination mechanism. In fact, by increasing the amount of the applied force, the surface temperature increases due to the heat generated by friction, and as stated in a previous research [25], the yield strength of titanium decreases by increasing temperature and as a consequence, the plastic deformation becomes more severe.

Fig 11 presents the friction coefficient of treated and bare specimens versus sliding distance under 10, 20, and 40N loads. These figures both confirm the transition of wear mechanism by increasing the applied forces. As can be seen, under 10N load (Fig.11a) both the treated and the bare materials possess the lowest friction coefficient fluctuations, which indicates a low adhesion between these samples and the counter facing pins during the wear test. This confirms the presence of the tribological layer on the surface of the samples because the formation of this layer reduces the adhesion and friction coefficient by reducing metal-on-metal contact. By increasing the applied load up to 20N (Fig.11b) some fluctuations are noticed. This is because the adhesion has increased after 200m, which can be attributed to an increase in the metal-on-metal contact and subsequent failure of the oxide layer. Further rising in load value (Fig.11c) and consequently increasing the temperature on the surface during the course of wear, results in the surface oxide layer failure. Therefore, the wear mechanism changes, and the plastic deformation becomes the dominant mechanism of wear according to Fig.8c. Rising the load value causes an increase in the hardness of NiTi intermetallic phases that is due to the transformation of austenite to martensite [26]. However, hardening does not seem to have a significant effect on the reduction of the wear rate, because the thickness of the treated surface layer decreases by increasing the sliding distance, and the effect of titanium substrate increases. The comparison between treated and bare materials reveals lower friction coefficients in all treated samples compared to those of the untreated ones.

4. Conclusions

Commercial pure (Cp) titanium was surface treated with equiatomic NiTi intermetallic layer via electroplating and subsequent heat treating. Morphological and dry tribological tests were conducted to evaluate the behavior of diffusion coated and Cp titanium and the results summarized as follows:

1. XRD analysis revealed the formation of NiTi and NiTi₂ phases on the surface of the diffusion treated materials. The hardness profile along the top of the fabricated layer toward the CP titanium substrate showed a steep drop.
2. SEM observation represented the formation of a tribological oxide layer on the surface of the treated sample under 10 N load in the course of wear. Applying higher forces led to aggravate abrasion and consequent removing of the oxide layer.
3. The wear rate of both Cp titanium and diffusion treated samples increased significantly by rising of the load, but there was a dramatic increase in wear resistance after the aforementioned surface treatment.
4. Studying the worn surface of Cp titanium revealed that there was a non-continuous oxide layer under 10 N load, and by further increasing the load plastic deformation mechanism prevailed which led to increased wear rates.
5. Under 10 N load, treated material showed the lowest friction of coefficient fluctuations, but by further rising of the load, the amplitude of these fluctuations increased.

Declarations

Author contributions

G. Khosravi contributed to the methodology and study design, conducted the experiments, performed data analysis, and wrote the initial draft version of the manuscript. M. Heydarzadeh Sohi contributed to the study design, critically reviewed the manuscript, and supervised the study. HM. Ghasemi contributed to the study design, data interpretation, and supervised the study. N. Jalalian Karazmoudeh checked data and analysis and prepared figures.

Corresponding author:

Correspondence to M. Heydarzadeh Sohi

Competing interests

The authors declare no competing interests.

References

- [1] Liu, X., Chu, P. K., Ding, C. Surface modification of titanium, titanium alloys, and related materials for biomedical applications. *Mater. Sci. Eng. R.* **47**, 49–121 (2004).
- [2] Cui, C., Hu, B. M., Zhao, L., Liu, S. Titanium alloy production technology, market prospects and industry development. *Mater. Des.* **32**, 1684–1691 (2011).
- [3] Nishimoto, A., Nishi, C. Carbide layer coating on titanium by spark plasma sintering technique. *Surf. Coatings Technol.* **353**, 324–328 (2018).
- [4] Mohazzab, B. F., Jaleh, B., Fattah-alhosseini, A., Mahmoudi, F., Momeni, A. Laser surface treatment of pure titanium: Microstructural analysis, wear properties, and corrosion behavior of titanium carbide coatings in Hank's physiological solution. *Surfaces and Interfaces.* **20**, 100597; 10.1016/j.surfin.2020.100597 (2020).
- [5] Nolan, D., Huang, S. W., Leskovsek, V., Braun, S. Sliding wear of titanium nitride thin films deposited on Ti-6Al-4V alloy by PVD and plasma nitriding processes. *Surf. Coatings Technol.* **200**, 5698–5705 (2006).
- [6] Oliveira, A. C., Oliveira, R. M., Reis, D. A. P., Carreri, F. C. Effect of nitrogen high temperature plasma based ion implantation on the creep behavior of Ti-6Al-4V alloy. *Appl. Surf. Sci.* **311**, 239–244 (2014).
- [7] Ding, Z., Zhou, Q., Wang, Y., Ding, Z., Tang, Y., He, Q. Microstructure and properties of monolayer, bilayer and multilayer Ta₂O₅-based coatings on biomedical Ti-6Al-4V alloy by magnetron sputtering. *Ceram. Int.* **47**, 1133–1144 (2021).
- [8] Ghorbani, H., Sohi, M. H., Torkamany, M. J., Mehrjou, B. Liquid Phase Surface Treatment of Ti-6Al-4V Titanium Alloy by Pulsed Nd:YAG Laser. *J. Mater. Eng. Perform.* **24**, 3634–3642 (2015).

- [9] Yang, Y. L., Zhang, D., Yan, W., Zheng, Y. Microstructure and wear properties of TiCN/Ti coatings on titanium alloy by laser cladding. *Opt. Lasers Eng.* **48**,119–124 (2010).
- [10] Dabalà, M., Brunelli, K., Frattini, R., Magrini, M. Surface hardening of Ti – 6Al – 4V alloy by diffusion treatment of electroless Ni – B coatings. *Surf. Eng.* **20**,103–107 (2004).
- [11] Lin, Y. C., Lin, Y. C. Elucidation of microstructure and wear behaviors of Ti-6Al-4V cladding using tungsten boride powder by the GTAW method. *J. Coatings Technol. Res.* **8**,247–253 (2011).
- [12] Aliofkhazraei, M., Rouhaghdam, A. S., Denshmaslak, A., Jafarian, H. R., Sabouri, M. Study of bipolar pulsed nanocrystalline plasma electrolytic carbonitriding on nanostructure of compound layer for CP-Ti. *J. Coatings Technol. Res.* **5**,497–503 (2008).
- [13] Swain, B., Mallick, P., Bhuyan, S. K., Mohapatra, S. S., Mishra, S. C., Behera, A. Mechanical Properties of NiTi Plasma Spray Coating. *J. Therm. Spray Technol.* **29**,741–755 (2020).
- [14] Wang, L., Xing, S., Liu, H., Jiang, C., Ji, V. Improved wear properties of Ni–Ti nanocomposite coating with tailored spatial microstructures by extra adding CeO₂ nanoparticles. *Surf. Coatings Technol.* **399**,126119; 10.1016/j.surfcoat.2020.126119(2020).
- [15] Bram, M., Ahmad-Khanlou, A., Buchkremer, H. P., Stöver, D. Vacuum plasma spraying of NiTi protection layers. *Mater. Lett.* **57**,647–651 (2002).
- [16] Stella, J. *et al.* Cavitation erosion of plasma-sprayed NiTi coatings. *Wear.* **260**,1020–1027 (2006).
- [17] Momeni, S., Biskupek, J., Tillmann, W. Tailoring microstructure, mechanical and tribological properties of NiTi thin films by controlling in-situ annealing temperature. *Thin Solid Films.* **628**,13–21 (2017).
- [18] Swain, B., Bajpai, S., Behera, A. Microstructural evolution of NITINOL and their species formed by atmospheric plasma spraying. *Surf. Topogr.: Metrol. Prop.* **7**,1-14 (2019).
- [19] Sharma, N., Gupta, K., Davim, J. P. On wire spark erosion machining induced surface integrity of Ni_{55.8}Ti shape memory alloys. *Arch. Civil Mech. Eng.* **19**,680-693 (2019).
- [20] Tran, A. T. T., Goutier, S., Vardelle, A., Hyland, M. M. Microsecond-scale formation of NiTi intermetallics in thermal spray coatings. *Surf. Coatings Technol.* **321**,425–437 (2017).
- [21] Waghmare, D. T., Kumar, P. C., Prasad, R., Masanta, M. NiTi coating on Ti-6Al-4V alloy by TIG cladding process for improvement of wear resistance: Microstructure evolution and mechanical performances. *J. Mater. Process. Technol.* **262**,551–561 (2018).
- [22] Mokgalaka, M. N., Pityana, S. L., Popoola, P. A. L., Mathebula, T. NiTi Intermetallic Surface Coatings by Laser Metal Deposition for Improving Wear Properties of Ti-6Al-4V Substrates. *Adv. Mater. Sci. Eng.*

2014,1–8 (2014).

[23] Rampin, I., Brunelli, K., Dabalà, M., Magrini, M. Effect of diffusion of Ni and B on the microstructure and hardness of Ti Cp.*J. Alloys Compd.* **481**, 246–253 (2009).

[24] Khosravi, G., Sohi, M. H., Ghasemi, H. M., Vafadar, A. K. Characterisation of Ni-Ti intermetallic coatings formed on Cp titanium by diffusion treatment.*Int. J. Surf. Sci. Eng.* **9**,43–54 (2015).

[25] Nemat-Nasser, S., Guo, W. G., Cheng, J. Y. Mechanical properties and deformation mechanisms of a commercially pure titanium.*Acta Mater.* **47**,3705–3720 (1999).

[26] Hiraga, H., Inoue, T., Shimura, H., Matsunawa, A. Cavitation erosion resistant coating of NiTi made by laser plasma hybrid spraying.*wear.* **231**,272–278 (1999).

Figures

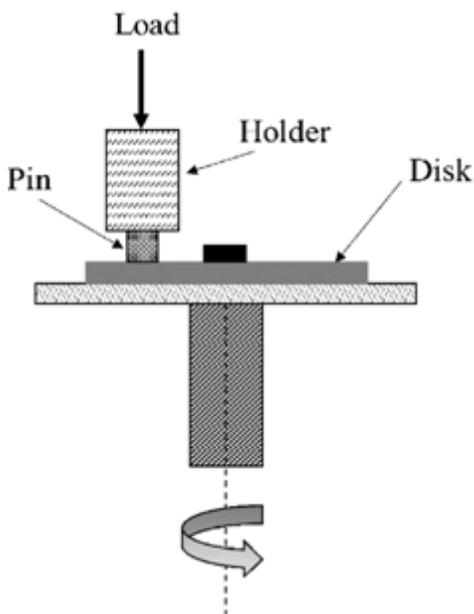


Figure 1

Schematic of Pin-on-disk tribometer

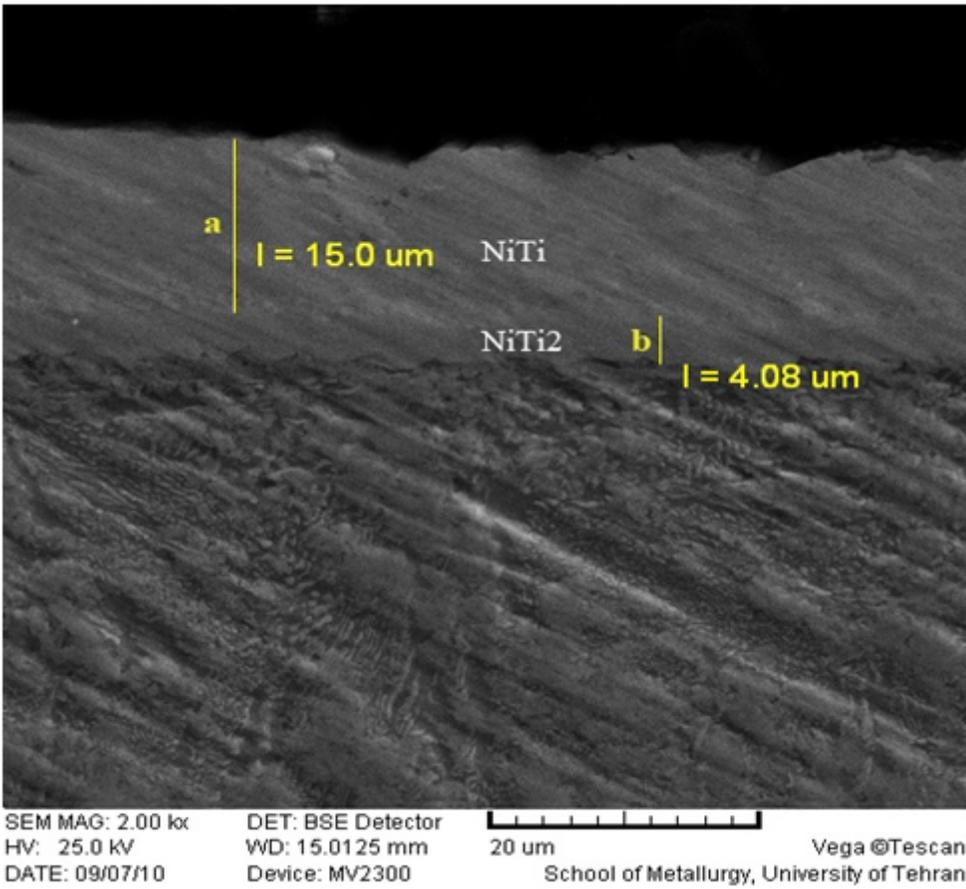


Figure 2

Cross sectional SEM image of the nickel plated specimen after 12 h heat treatment at 900°C

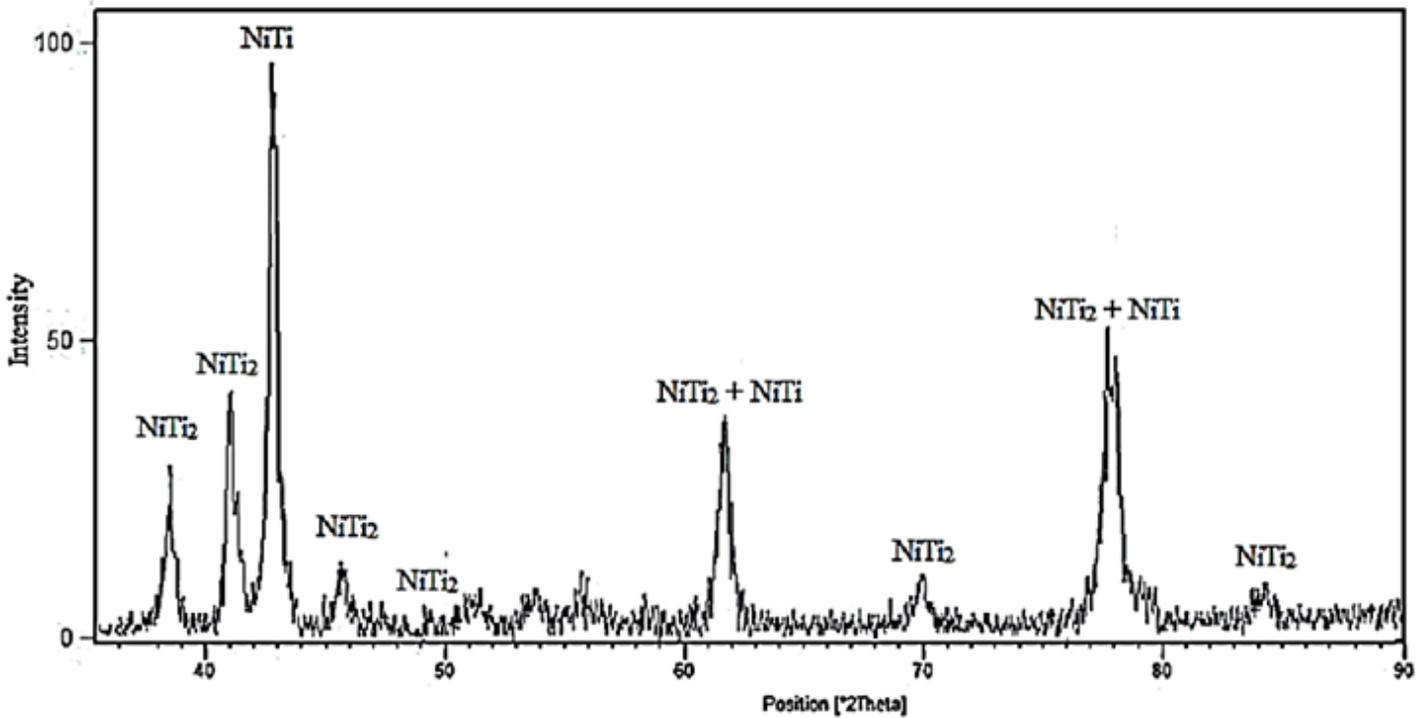


Figure 3

XRD pattern of Ni plated CP titanium after 12 h heat treatment at 900°C

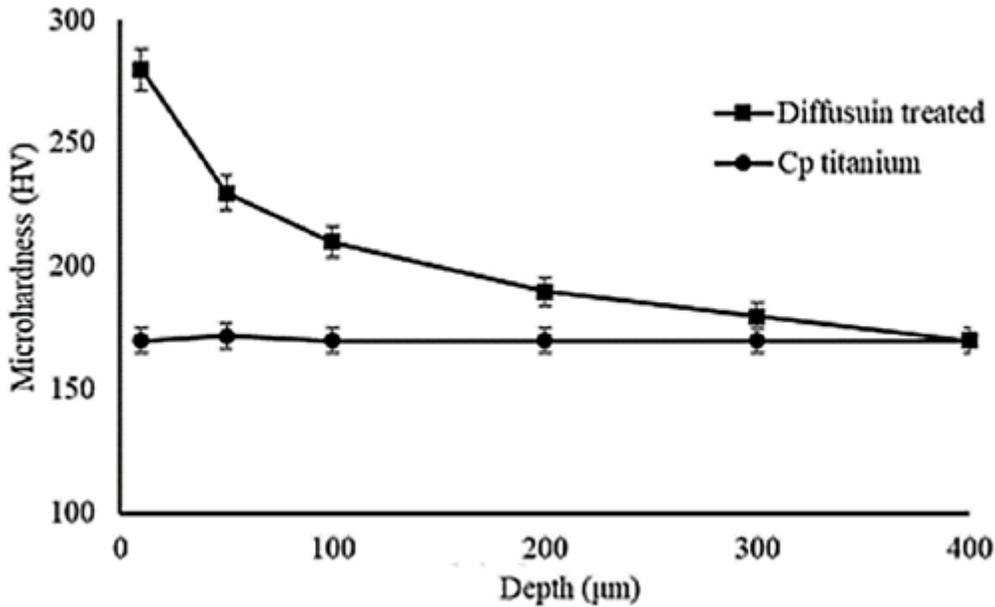


Figure 4

Micro hardness profile along the cross-section of Cp titanium and the diffusion coated material

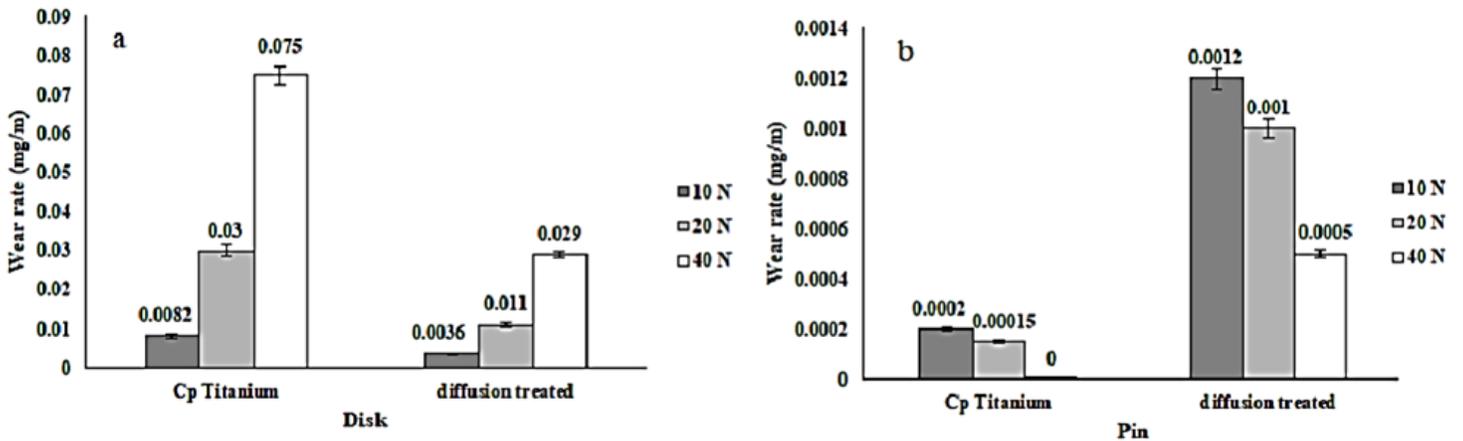


Figure 5

Variation of wear rates versus loads for a) Cp titanium and diffusion treated materials, and b) counterface pins

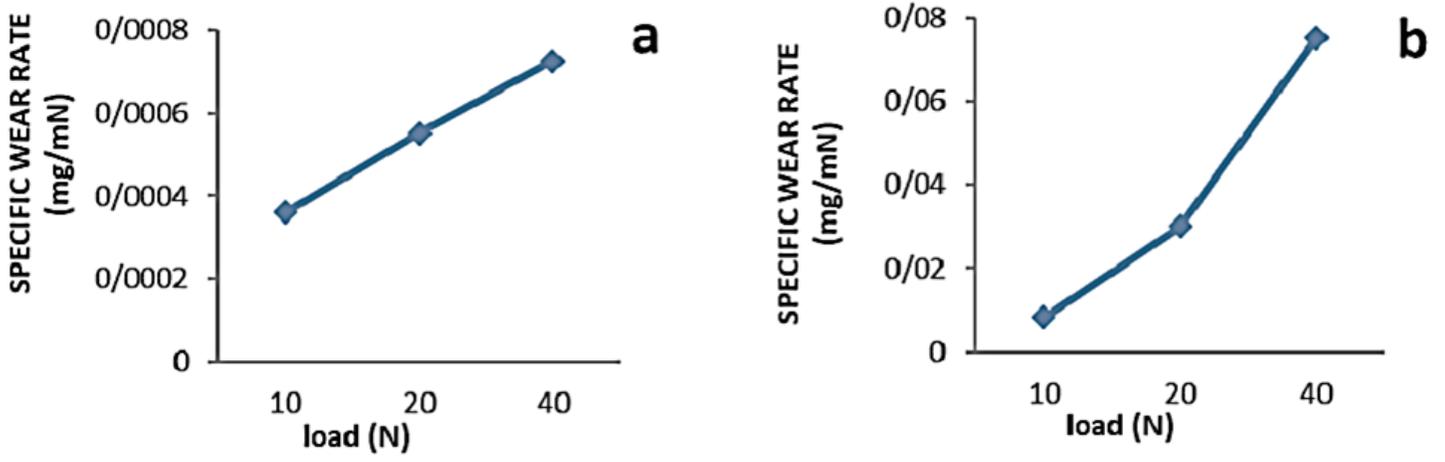


Figure 6

Variation of specific wear rates as a function of loads for a) diffusion treated and b) Cp titanium samples

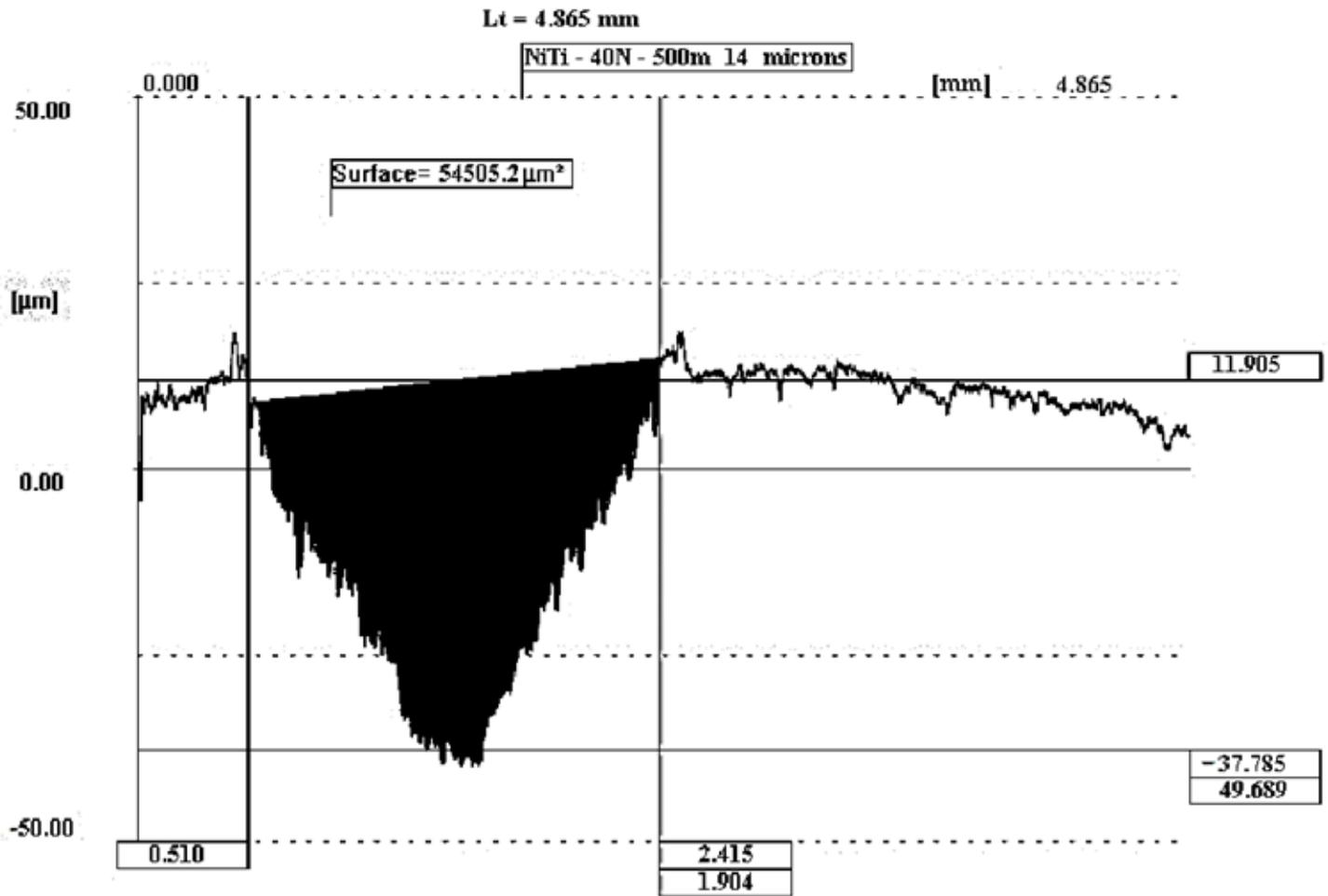


Figure 7

Depth profile of the worn surface of the treated specimen after 500 m sliding under 40N load

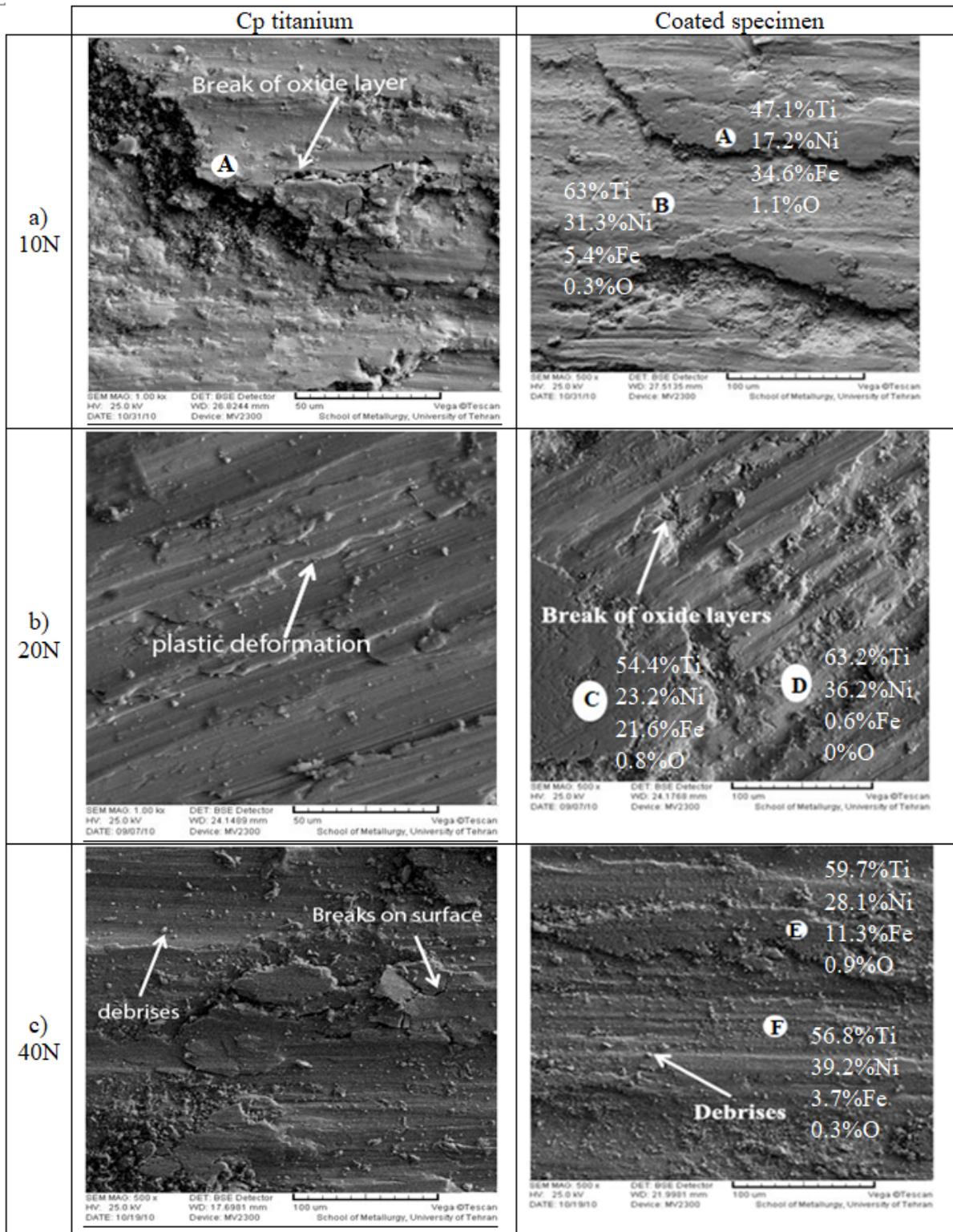


Figure 8

SEM images of the worn surfaces of Cp titanium and treated specimens under three different loads: a) 10N, b) 20N and c) 40N

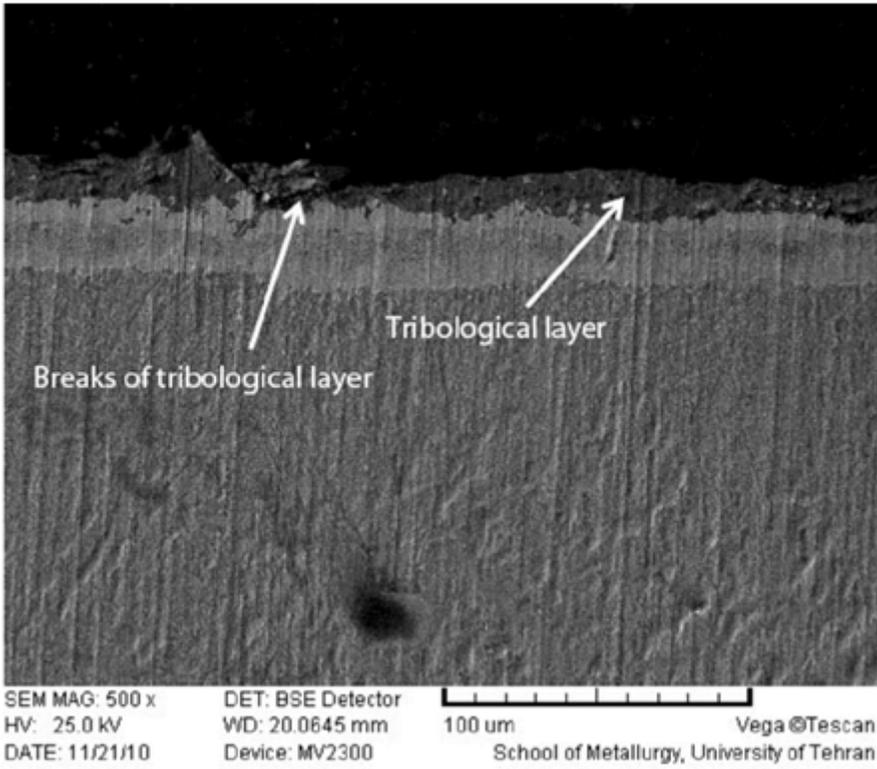


Figure 9

SEM cross sectional image of the worn treated titanium under 10N load

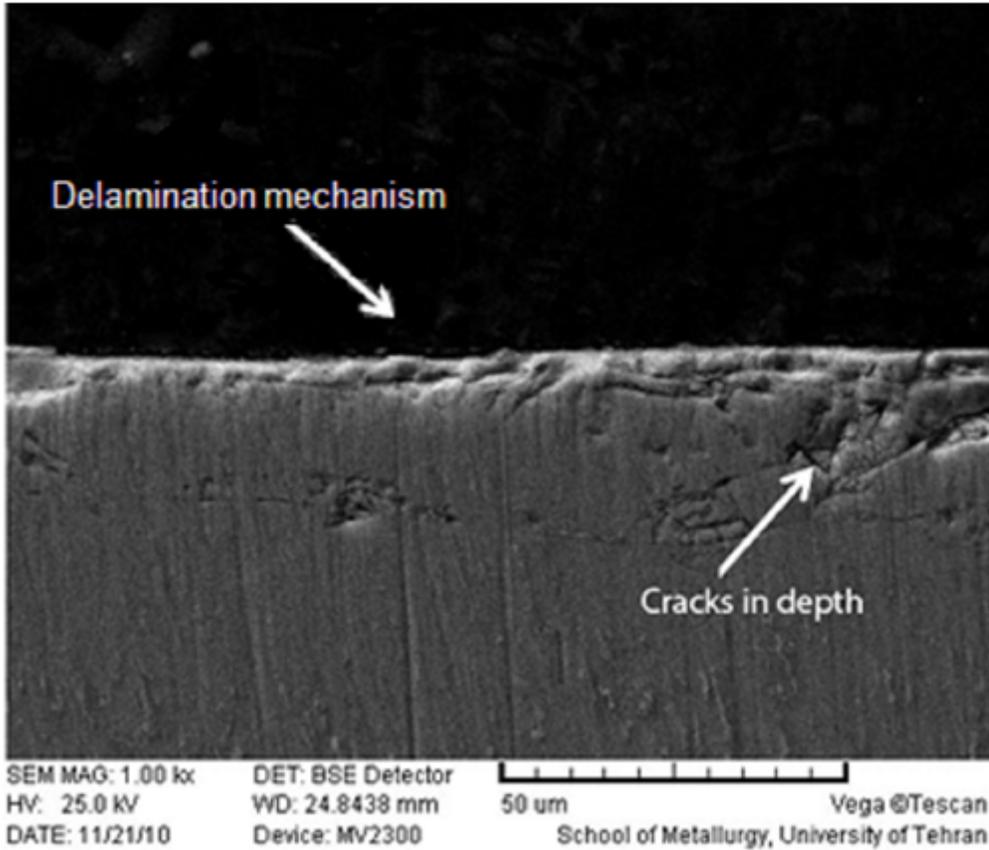


Figure 10

SEM cross sectional image of the worn Cp titanium under 40N load

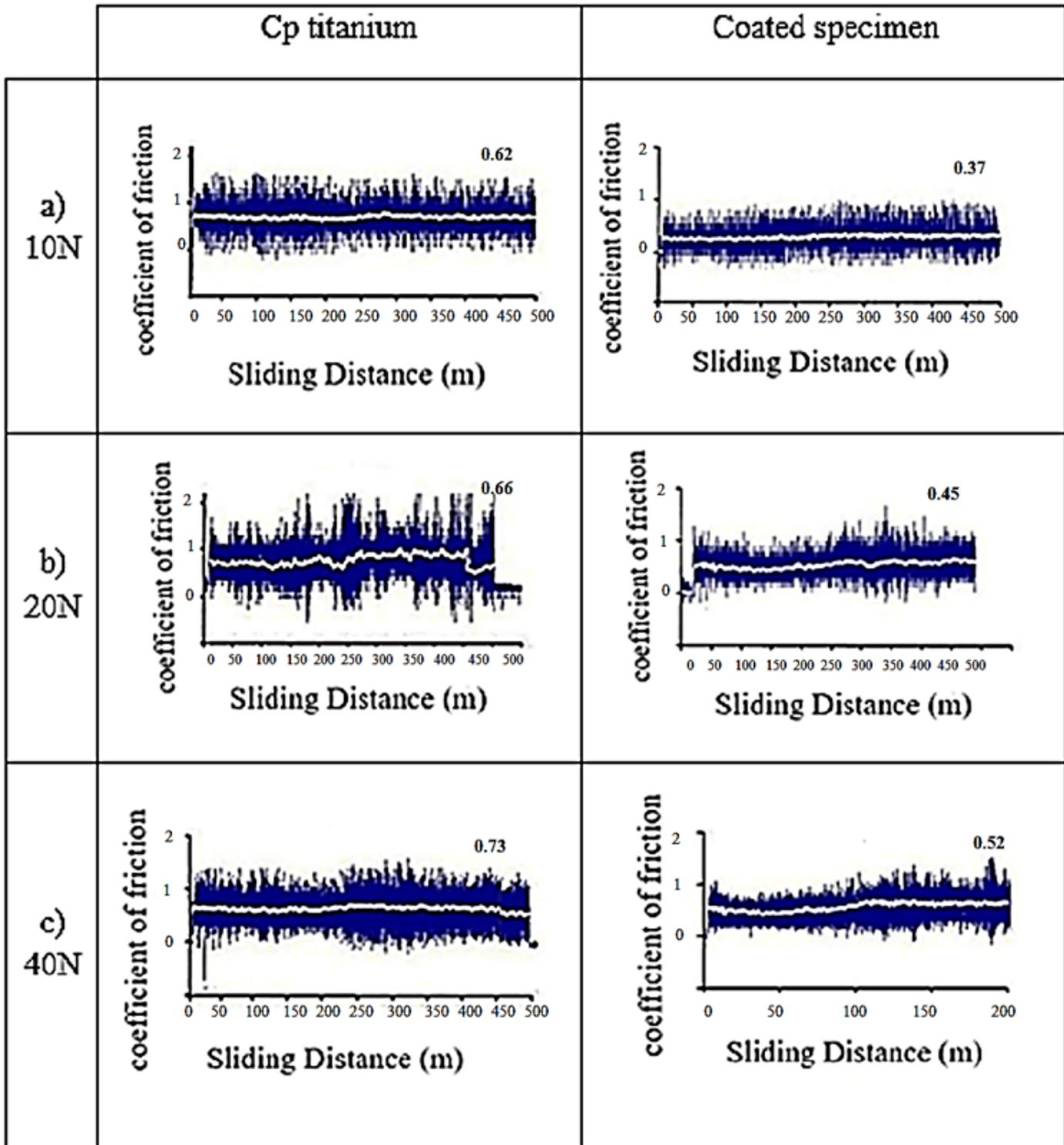


Figure 11

Friction coefficient versus sliding distance of Cp titanium and treated specimens under three different loads: a) 10N, b) 20N and c) 40N