**Relationship between phase composition and wear resistance of titanium alloys**

I V Ivanov¹, A Thoemmes, K I Emurlaev, E I Tkachenko and E A Rudenya
Department of Material Science in Mechanical Engineering
Novosibirsk State Technical University, 20 Prospekt K. Marksa, Novosibirsk, Russia

E-mail: i.ivanov@corp.nstu.ru

**Abstract.** The wide use of titanium alloys is often due to their unique properties. Availability of a wide variety of mechanical, physical and chemical properties is associated with a large number of polymorphic modifications of titanium alloys. During the last decade, the metastable omega phase piques the largest interest among all titanium modifications. This study attempts to explain the different wear behavior of some titanium alloys with different Nb content during dry friction impact.

1. Introduction

An ideal metallic biomaterial should provide perfect biocompatibility, excellent corrosion resistance, high strength and a low Young’s modulus which is close to the Young’s modulus of human bone (4 – 30 GPa) [1-5]. The nowadays most commonly used metallic alloys for biomedical application are Cr-Co based alloys, stainless steels and titanium and its alloys [6,7]. From the beforementioned alloys titanium and its alloys are, due to their low Young’s modulus the most promising candidates. Ti-6Al-4V, an alloy originally invented for aerospace application, possess a Young’s modulus of 110 GPa, whereas Cr-Co alloys and stainless-steel show values minimum twice higher (240 and 210 GPa) [8, 9]. The significant mismatch between the Young’s moduli of the metallic biomaterials can be the reason for the so called “stress shielding effect”, which could lead to the loosening of the implant [10]. It should be mentioned that several generations of biomedical Ti alloys have been already developed and Ti-6Al-4V is in use as metallic biomaterial since decades. However, due to several reasons it is no longer considered as the perfect biomaterial. First, aluminium can be the reason for Alzheimer’s or Parkinson’s diseases [11], while vanadium is known as considerably toxic element for human body [12]. Thus, Ti alloys of new generation are currently of great interest. These alloys should possess in addition to a lower Young’s modulus, better biocompatibility and an improved wear resistance. Especially the possibilities to enhance the wear resistance captured the interest of several research groups working on different Ti alloy systems (TMZF [13, 14], TNTZ [15, 16] and Ti-Nb [17]). Because the mechanical properties are mainly influenced by the alloying elements and the resulting phases a special focus should be given to the possibility to control the phase composition of the alloys. Several phases may be formed in Ti alloys. Namely equilibrium hcp α- and bcc β phase and metastable phases like hexagonal α’, ω and orthorhombic α”. Depending on the processing route and the alloy composition the formation of metastable hexagonal ω phase is also possible [18, 19]. Most of

¹ To whom any correspondence should be addressed.
the abovementioned alloys consists, due to the high content of β isomorphous stabilizers, mainly of β phase, which is known to show a low Young’s modulus and acceptable wear resistance. Due to the low alloying concentration when stable β phase is observed and the absence of a miscibility gap the Ti-Nb possess a model character for new low modulus Ti-based metallic materials for biomedical application. Only a few data are available on the wear resistance of Ti-Nb alloys with different metastable phases. It can be suggested that the reason for this is the low modulus of Ti-Nb alloys consisting mainly of β phase. Therefore, this paper aims to research the influence of different phases (α, β and ω phase) on the wear resistance of some titanium alloys.

2. Experimental procedure

Biocompatible titanium alloys cp-Ti; Ti30Nb and Ti45Nb were prepared from commercially pure (c.p.) Ti and Nb by using the BUEHLER ArcMelter melting furnace. The melting processes were conducted in argon atmosphere (800 mbar) with pre-flushing. Cylindrical specimens with a diameter 10 mm and a height of 20 mm were cut from the obtained ingots. After the cutting, the samples were mechanically ground by using a 1000 grit SiC sandpaper. The final polishing was performed using a suspension consisting of 73% (vol.) colloidal SiO2 oxide, 18% (vol.) H2O2 (solution 40%) and 9% (vol.) Kroll's Solution (Kroll's Reagent). The Kroll solution consisted of 92% (vol.) H2O, 6% (vol.) HNO3, 2% (vol.) HF. After polishing cylinders have been annealed at 900°C in vacuum during 1 h.

To carry out wear experiments a friction apparatus was developed at the Materials Science department of NSTU. That allowed to varying the load and rotation speed of the material under study and found optimal conditions for wearing experiments. In order to minimize abrasion of the counterbody during the experiment, tungsten-carbide alloy (WC-Co) indenter was used. Table 1 presents some technical details of the experiment.

| Rotation rate, rpm | Linear friction velocity, mm/s | Apparent contact area, mm² |
|--------------------|-------------------------------|---------------------------|
| 10                 | 4.7                           | 3                         |

| Real contact area, mm² | Indention load, kg | Contact pressure, MPa |
|------------------------|--------------------|-----------------------|
| 2                      | 17.35              | 86.75                 |

The surface of the alloys after friction were investigated by using ZYGO New View 7300 optical surface profilometer with 5X objective. Obtained data processing was carried out by using Python programming language.

The initial surface phase content was analyzed by synchrotron radiation. Experiments were carried out at the beamline P07 (The High Energy Materials Science) at Deutsches Elektronen-Synchrotron (DESY). The used wavelength was 0.014 nm. A 16-inch 2D PerkinElmer XRD 1621 scintillation detector with resolution of 2048 × 2048 pixels was used to record the diffraction patterns. The obtained diffraction patterns were azimuthally integrated by means of the pyFAI open-source software package [18]. The microhardness was evaluated with a WOLPERT Group 402 MVD Vickers hardness tester under a load of 0.98 N and a dwell time of 10 s.

3. Results and Discussion

It’s believed that the main reason for the low wear resistance of titanium alloys is the adhesion of some sections of the material surface and the counterbody. This process is the main reason for the appearance of debris, which upon further frictional impact can lead to active wear as abrasive. In
addition, it is believed that the cause of the adhesion can be repassivation of the surface [13]. Also, in some works it is reported that the frictional resistance of titanium alloys can significantly depend on their phase composition [19].

Results of synchrotron X-ray phase analysis of the studied materials are shown in Figure 1. It can be seen that cp-Ti and Ti45Nb are single-phase materials consisting of hexagonal α- and cubic β-phases, respectively. However, Ti30Nb is characterized by a complex phase composition. This material besides α- and β-, includes hexagonal ω-phase.

![Figure 1. XRD phase analysis a – Ti; b – Ti30Nb; c – Ti45Nb.](image)

Among the stable phases (α and β - phase) as well as among the metastable phases (α’, α” and ω - phase) in titanium alloys it is well known that the ω phases shows the most significant influence on physical and mechanical properties. Namely the ω phase increase markedly the Young’s modulus, bending strength as well as the microhardness of the alloy by restricting dislocation movement [20] A high volume fraction of ω phase causes embrittlement [21]. According to the surface profile analysis after 250 cycles of friction (Figure 2), the state of the surface after impact directly depends on the phase composition of the alloy. It can be seen that the entire surface of α-titanium has undergone significant wear. Both grooves (blue) and areas of the most deformed material located above the median plane (red) of the surface are visible on the surface.

![Figure 2. Surface profile analysis after 250 cycles of friction.](image)
The results of the adhesion process — tearing off and shearing of the surface layers of the material with the formation of debris are clearly visible on the β-titanium surface. According to the surface roughness analysis (Table 2), the value of $R_a$, (arithmetical mean of the absolute values of profile high in a sampling surface) reaches a maximum in the Ti45Nb sample among all investigated materials. Krishnan H. et al. [19] attribute this behavior of β-titanium to the fact that, during friction the β phase is not strengthened. Detailed study of this behavior requires in-situ experiments of structure changing of the surface layers.

| Table 2. Roughness parameters of titanium alloys after 250 and 500 cycles of friction. |
|----------------------------------------|-----------------|-----------------|-----------------|
| 250 cycles                            | Ti              | Ti30Nb          | Ti45Nb          |
| Ra                                    | 3.08            | 3.36            | 4.5             |
| Rz                                    | 18.33           | 13.46           | 24.32           |
| 500 cycles                            | Ti              | Ti30Nb          | Ti45Nb          |
| Ra                                    | 3.64            | 2.27            | 11.52           |
| Rz                                    | 18.14           | 11.75           | 59.72           |

However, in the case of Ti30Nb the delaminated surface areas were not observed. It can be seen that in the process of friction the indenter contacted the material mainly in only one region 0.3-0.6 mm wide. It is likely that this behavior is associated with increased mechanical properties of the ω-phase. As mentioned before, this phase is the hardest and strongest among all the phases of titanium. Table 3 shows the microhardness of the investigated alloys. It can be seen that the presence of the ω-phase significantly increases the microhardness of the material. Thus, the presence of one wide groove can be explained by the increased microhardness of Ti30Nb compared to Ti and Ti45Nb. It is likely that during the initial stages of the friction, the counterbody contacted only a very small area of the material and due to the high hardness did not penetrate significantly deeper into the material. As a result, the wear of Ti30Nb occurred much slower than Ti and Ti45Nb. This assumption is confirmed by the study the surface after 500 friction cycles (Figure 3).

| Table 3. Vickers microhardness of titanium alloys. |
|----------------------------------------|-----------------|-----------------|-----------------|
|                                       | Ti              | Ti30Nb          | Ti45Nb          |
| HV$_{0.1}$                            | 132±15          | 298±10          | 231±14          |
After 500 friction cycles, the surface of Ti30Nb is also the least defected compared to the other alloys under study. However, at this stage, it possesses two distinct grooves about 0.2-0.3 mm wide. In addition, it can be seen that the parameter $R_z$ (average distance between the maximum and minimum points of the surface), has decreased in comparison with the previous step. This indicates that in the process of friction, the indenter gradually sank into the material and uniformly wear the surface. There was no adhesion between Ti30Nb and the counterbody. Furthermore, formed debris do not lead to a significantly wear of Ti30Nb surface.

However, the surfaces of Ti and Ti45Nb after 500 cycles have undergone significant changes. Firstly, the profile analysis showed the presence of large surface areas located above the median plane of the material surface (red color), which are, apparently, areas of delamination shift and the result of adhesion of material and counterbody areas. Secondly, the roughness parameters $R_a$ and $R_z$ increased. Moreover, in the case of Ti45Nb, these parameters have more than doubled. In addition, a large number of wear particles were found on the surfaces of these alloys. All this indicates that the adhesion of the surface areas of these materials with areas of the counterbody leads to the appearance of wear particles acting as an abrasive, which in turn leads to a significant decrease in the wear resistance of these materials. It should be noted that there is no straight dependence between microhardness and wear resistance of titanium alloys. Ti45Nb possess higher microhardness, compare with cp-Ti but much less wear resistance.

4. Conclusions
The phase composition of titanium alloys has a significant impact on their frictional behavior. Thus, $\alpha$ and $\beta$ titanium alloys are subjected to both delamination and adhesion, while titanium with $\omega$ phase wear evenly as the indenter sinks. In addition, a significant decrease in wear resistance of $\alpha$ and $\beta$ titanium also results in the appearance of debris in the process of friction, while their presence does not have a significant effect on titanium with the $\omega$ phase. Furthermore, nonstraight relationship
between hardness and wear resistance requires *in-situ* experiments of the friction and the study of the structural changes underway.

**Acknowledgment**

The work was carried out within the framework of the C-19-15 project of a competition among young scientists on the topic "Investigation of the evolution of the structure of surface layers of titanium alloys subjected to simultaneous frictional and corrosive impacts in ex-situ and in-situ modes using synchrotron radiation" in 2019. Materials characterization was carried out at NSTU Materials Research Center.

**References**

[1] Ozaki T, Matsumoto H, Watanabe S, and Hanada S 2004 Materials Transactions 8 2776–2779
[2] Geetha M, Singh A K, Asokamani R and Gogia A K 2009 Progress in Materials 3 397–425
[3] Niinomi M, Nakai M, and Hied J 2012 Acta 11 3888–3903
[4] Ivanov I V, Thoemmes A and Kashimbetova A A 2018 KEM 769 42–47
[5] Ivanov I V, Thoemmes A, Skiba V Y, A. A. Ruktuev, and I. A. Bataev Met Sci Heat 43 42–46
[6] Niinomi M 2008 J Artif Organs 11 105–110
[7] Niinomi M 2002 Metall and Mat Trans A 33 477–486
[8] Niinomi M 1998 Materials Science and Engineering: A 243 231–236
[9] Kovalevskaya Z G 2016 Metal Working and Material Science 73 34–42
[10] Niinomi M and Nakai M 2011 International journal of biomaterials 2011 836587
[11] Eliades T, Pratsinis H, Kletsas D, Eliades G and Makou M 2004 American Journal of Orthodontics and Dentofacial Orthopedics 125 24–29
[12] Li Y, Wong C, Xiong J, Hodgson P and Wen C 2010 Journal of dental research 89 493–497
[13] Yang X and Hutchinson C R 2016 Acta biomaterialia 42 429–439
[14] Wang K K, Gustavson L J and Dumbleton J H 1996 Medical Applications of Titanium and Its Alloys: The Material and Biological Issues
[15] Li S J et al 2004 Wear 257 869–876
[16] Samuel S, Nag S, Scharf T W and Banerjee R 2008 Materials Science and Engineering: C 28 414–420
[17] Xu L, Xiao S, Tian J, Chen Y 2009 Transactions of nonferrous metals Society of China 19 639-644
[18] Ashiotis G 2015 Journal of applied crystallography 48 510-519
[19] Krishnan H 2013 The bone & joint journal 95 1011-1021
[20] Lee C M, Ju C P, Chern Lin J A 2002 Journal of Oral Rehabilitation 29 314–322
[21] Cai S, Schaffer J E, Ren Y Applied Physics Letters 106 131907