СРПСКИ АРХИВ
ЗА ЦЕЛОКУПНО ЛЕКАРСТВО
SERBIAN ARCHIVES
OF MEDICINE

Address: 1 Kraljice Natalije Street, Belgrade 11000, Serbia
☏ +381 11 4092 776, Fax: +381 11 3348 653
E-mail: office@srpskiarhiv.rs, Web address: www.srpskiarhiv.rs

Paper Accepted*

ISSN Online 2406-0895

Current Topic / Актуелна тема

Slađana Laketić[1], Marko Rakin[2], Aleksandra Čairović[3], Vesna Maksimović[1], Ivana Cvijović-Alagić[1,†]

Laser surface modification of metallic implant materials

Ласерска површинска модификација металних имплантних материјала

[1]University of Belgrade, Vinča Institute of Nuclear Sciences, Belgrade, Serbia;
[2]University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia;
[3]University of Belgrade, School of Dental Medicine, Belgrade, Serbia

Received: November 26, 2018
Accepted: May 17, 2019
Online First: May 24, 2019
DOI: https://doi.org/10.2298/SARH181126054L

†Correspondence to:
Ivana CVIJOVIĆ-ALAGIĆ
Vinča Institute of Nuclear Sciences, University of Belgrade, Mike Petrovića-Alasa 12–14, 11001 Belgrade, Serbia
E-mail: **ivanac@vinca.rs**

Laser surface modification of metallic implant materials

Ласерска површинска модификација металних имплантних материјала

SUMMARY
Metallic biomaterials are the most commonly used as hard-tissue replacements because of their favorable mechanical features and excellent biocompatibility. Paper aims to present an overview of the diverse surface modification techniques, with the special emphasis on the laser surface modification method, as well as diverse characterization techniques used for investigation of the surface modification process impact on the metallic implant materials properties. Moreover, the effect of laser radiation on the surface and mechanical characteristics, as well as on the structure of metallic bioimplants, is presented. The study of the high-intensity laser radiation influence on the metallic materials surface includes primarily investigations of the surface morphology modifications and the specific surface structures formation since their presence enables enhanced osseointegration.
Keywords: metallic implant materials; laser radiation; surface modification; osseointegration

САЖЕТАК
Метални биоматеријали се најчешће користе за израду импланата чврстих структурних делова људског тела због својих добрих механичких карактеристика и одличне биокомпатибилности. Циљ рада је да се прегледно представе различите технике површинске модификације имплантних материјала са посебним освртом на методу ласерске модификације површине, као и многобројне карактеризационе методе за испитивање утицаја процеса површинске модификације на својства металних имплантних материјала. Осим тога, представљен је и разматран утицај ласерског зрачења на површинске и механичке карактеристике, као и на структуру металних биоимпланата. Испитивање утицаја ласерског зрачења високог интензитета на површину металних материјала првенствено обухвата испитивање морфолошких површинских промена и формирања специфичних површинских структура, које доприносе побољшању осеоинтеграције металних импланата.
Кључне речи: метални имплантни материјали; ласерско зрачење; површнска модификација; осеоинтеграција

INTRODUCTION

Biometallics are metallic materials used in contact with cells, tissues or body fluids of the human body with the purpose to replace or upgrade structural components of the human organism as compensation for the hard-tissue damages which may occur due to aging, illnesses or accidents [1, 2].

Metallic implant biomaterials have been in use since the 19th century in a wide range of dental, orthopedic, cardiovascular and other medical applications [1]. Stainless steels, cobalt-chromium alloys, and titanium-based materials are the main biocompatible metallic materials used in biomedical engineering [1–6]. Due to their excellent electrical and thermal conductivity, mechanical properties, and corrosion resistance, metallic biomaterials have been and will continue to be an essential part of medical devices in the future [2]. However, biometallics show some undesirable characteristics and because of that their further development is of prime importance [1, 6].

Biometallics must meet certain criteria in order to be used in biomedicine (see Figure 1) [1, 6].

High osseointegration ability is the essential requirement which all biometallics must fulfill [1]. Osseointegration is a process of the direct interface formation between an implant and a bone, without a negative effect on the surrounding soft tissues [5]. The inability of the implant surface to connect with the adjacent bone and surrounding tissues will cause the formation of fibrous tissue around the implant, and in turn, promote prosthesis release [7]. Therefore, it is necessary for an implant to have an appropriate surface morphology, *i.e.* surface chemistry, surface roughness, and surface topography, which will ensure its good integration. Accordingly, the implant surface modification is desirable in order to achieve improved biomechanical-bi-functional balance [8].

LASER SURFACE MODIFICATION

Surface modifications are used to improve implant biocompatibility and bioactivity, as well as to ensure proper osseointegration and aim to change the surface physicochemical properties in order to improve bone healing and load transfer [7]. This can be achieved by altering the surface topography or by modifying surface chemistry.

Possibilities of changing/processing the surface of different biometallics using laser radiation are numerous and consequently various modern surface treatment techniques, such as ion implantation or coating, have lost their precedence in favor of laser processing [7, 8, 9]. Nowadays lasers find widespread applications in the medical device industry.

A laser represents a source of light radiation that emits a coherent photon beam, and as a source is stable in frequency, wavelength, and power [9]. In relation to other light sources, laser radiation is monochromatic, spatially oriented, intense and coherent. All emitted photons of a laser beam, unlike photons in spontaneously emitted radiation, are completely identical, *i.e.* have the same direction and phase.

The interaction of laser radiation and metallic targets depends on the characteristics of the laser radiation source, as well as on structural, optical and thermodynamic characteristics of the target, focusing method, and type and pressure of the surrounding atmosphere [10]. Laser radiation that falls on the surface is partially absorbed and partially reflected. Absorbed radiation causes heating, melting, and evaporation of the material.

A very important parameter describing the breakthrough of radiation in the material is the depth of absorption or optical breakthrough of light (Figure 2) [10]. By selecting radiation with a low absorption depth, local changes in surface properties can be obtained without changing the volume (interior) of the material.

There are two mechanisms of the surface particles removal using laser: 1) laser-induced desorption (without any visible mesoscopic changes in the surface composition and structure) and 2) laser ablation (visible changes in the surface structure and composition) [11]. Laser-induced desorption and laser ablation are not completely separated, independent phenomena. Therefore, desorption and ablation should be observed as two phases in the process of laser interaction with the material surface [11].

Lasers provide the direction of a large amount of energy to a limited target area in order to achieve the desired material modification [7, 9, 10]. During the interaction of electromagnetic radiation with a solid target, the following changes can occur: radiation damage in the crystal lattice, structural changes leading to amorphisation of the target and recrystallization in the collision zone, changes in the chemical composition of the target, and changes in the target surface topography caused by erosion and redeposition.

The laser radiation induced target surface changes depend on the characteristics of the laser beam, the number of accumulated impulses, the optical and thermophysical properties of the material, and the irradiation conditions (Figure 3) [7, 10].

If plasma is generated during the interaction of laser radiation with the material, it can significantly affect the intensity by which the radiation is acting on the surface and thus affect the formation of the crater [12]. The interaction of incident laser radiation and plasma can be expected during use of a nanosecond and picosecond radiation, while in the case of ablation with femtosecond radiation this interaction is absent.

LASER MODIFICATIONS OF IMPLANT MATERIALS

The surface morphological changes due to the action/interaction of the laser with the surface of the implant material can be examined using various techniques, such as light optical microscopy (LOM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and profilometry [7, 13]. First information on the surface morphological changes is obtained by LOM and SEM, while EDS allows an estimate of the surface elemental composition. Topographic changes and specific surface geometry of the areas modified by the laser irradiation are analyzed by contact and non-contact profilometry.

Torres et al. [8] showed that in the case of the Ti-6Al-4V alloy laser treatment in combination with different chemical and thermo-chemical treatments (etching and chemical oxidation) can enhance the surface bioactivity due to the formation of a stable titanium oxide layer. The laser modified surfaces manifested a rough surface covered with submicro- and nanopores.

If the energy density is close to the threshold of damage, during the metallic material laser radiation on the surface of the target material formation of the structures in the form of periodically repeated parallel waves can be expected [14]. These structures are designated by the term laser-induced surface periodic surface structures, LIPSS. An important requirement for the emergence of LIPSS is the surface roughness that allows the intersection of the incident beam so that the polarized light, normal to the surface, can initiate electronic oscillations.

It is obvious from Figure 4 that the accumulation of a large number of impulses on the target, at a constant energy density and with different lasers, leads to an increase in the ablation depth and surface traces formation [13]. Zhang et al. [7] noticed that the laser beam radiation performance in a single-pulse and multiple-pulse mode results in a different damage depth. Ablation results in the formation of the prominent crater and the removal of the dissolved material onto the surface.

Comparing the specific surface features obtained during irradiation of Ti implant in gaseous (air) and liquid (water) medium, Trtica et al. [14] concluded that the liquid medium is a better choice for laser surface treatment since it results in better surface roughness (Figure 5). Also, the appearance of LIPSS is observed on the surface in both environments. In water environment LIPSS are recorded after low-impulse, while in air atmosphere after the high-impulse interaction. It was found that during irradiation in air in the central part of the laser beam oxygen is absent, while its concentration is relatively high in the presence of water. Water also shows a high oxidation capacity that stimulates the bioactivity of the surface.

Trtica et al. [15] observed that irradiation treatment of Ti at high intensities contributes to the formation of large craters after a few pulses, and as the number of impulses increases the creation of the surface craters with a periodic structure can be expected. These properties enhance the Ti implants biointegration potential. Also, wavelength increase results in more visible surface damage.

Laser modification improves the surface roughness [14, 15, 16]. In the air and oxygen atmosphere, the resulting surface structures correspond to the smooth, periodic dome structures. In the presence of increased oxygen concentration, an oxide surface layer is formed. In a nitrogen atmosphere, the obtained surface structure is non-compact and porous. The surface structure formed in the helium atmosphere is completely different and the presence of micropores can be noticed.

Hermann et al. [16] noticed that the presence of plasma protects the titanium surface from radiation and that the further heating of the material can be achieved through the plasma itself. In the atmosphere of helium, a better transfer of energy to the material is achieved.

LASER EFFECT ON THE IMPLANT TRIBO-MECHANICAL PROPERTIES

Wear occurs during the relative movement of the joint parts that are in contact with one another and results in the component damage [5]. The type and severity of the wear damage depend on many interaction factors and can be accompanied with processes such as corrosion, which in turn leads to the increased material loss and in extreme cases fast metallic implant failures.

Laser surface modifications can enhance wear resistance and friction properties of the implant [17]. Chen et al. [17] showed that the surface treated with high laser power shows higher hardness and wear resistance than the untreated and surface treated by low laser power.

One of the laser modification methods, used to improve mechanical properties, corrosion resistance, biocompatibility and wear resistance, is laser cladding [18]. Laser cladding enables the formation of the protective coating on the alloy substrate surface. Also, laser alloying, laser-heat treatment and laser overlaying are methods which can be used in order to enhance the implant material hardness, wear and corrosion resistance [19].

The low hardness values and poor tribological characteristics of the metallic implant materials can be improved by laser powder deposition [18]. Comparing the Ti-6Al-4V substrate characteristics with the characteristics of the Ti-Al intermetallic coating formed on the Ti-6Al-4V alloy surface (Figure 6), Liu et al. [20] noticed that intermetallic coating displays lower friction coefficients due to the higher hardness values since the biometallics hardness and wear resistance are greatly influenced by each other [17–20].

The alloy microstructural characteristics, such as phase composition and grain size, greatly affect and determine alloy mechanical properties [5, 21]. There are numerous laser irradiation methods which can contribute to the achievement of excellent implant mechanical properties [21]. One of those methods is laser surface remelting (LSM). Using this method, grain refinement can be obtained in the remelting zone. Diagrams presented in Fig. 7 show a great improvement in mechanical properties achieved by laser treatment [21]. The LSM increases the elastic modulus and hence metallic material stiffness and hardness, throughout the material microstructural transformations. From Figure 7 one can observe that the hardness value is the highest in the remelting zone and the lowest in the metal substrate zone. This also applies to the elastic modulus.

CONCLUSION

When developing new materials for biomedical applications, most attention is devoted to implant material biocompatibility, non-toxicity, and osseointegration. The desirable characteristics of the bioimplants can be achieved by surface modifications. Laser surface modification is one of the methods by which the enhancement of mechanical, physical and tribological characteristics can be obtained. Excellent surface roughness, high hardness value, outstanding biocompatibility, and implant surface bioactivity, non-toxicity, excellent corrosion and wear resistance, low friction coefficients and porosity can be achieved. The interaction of laser impulses with the metallic implant material surfaces causes changes in their surface morphology, optical characteristics, chemical composition, etc. according to the selected parameters of the laser (beam). Surface periodic structures can be formed by laser modification and the appearance of these structures can influence the improvement of the implant surface characteristics and implant osseointegration.

ACKNOWLEDGMENT

This work was financially supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia through Project No. ON174004 and PhD fellowship of Slađana Laketić.

Conflict of interest: None declared.

REFERENCES

1. Cvijović-Alagić I, Rakin M. Integrity of biomedical implants of titanium alloys (first part). Structural Integrity and Life. 2008; 8(1):31-40.
2. Čairović A, Maksimović V, Radović K, Đurišić S. The effect of recasting on biological properties of Ni-Cr dental alloy. Srp Arh Celok Lek. 2016; 144:574-9.
3. Cvijović-Alagić I, Cvijović Z, Bajat J, Rakin M. Composition and processing effects on the electrochemical characteristics of biomedical titanium alloys. Corros Sci. 2014; 83:245-54.
4. Dimić I, Cvijović-Alagić I, Obradović N, Petrović J, Putić S, Rakin M, et al. In vitro biocompatibility assessment of Co-Cr-Mo dental cast alloy. J Serb Chem Soc. 2015; 80(12):1541-52.
5. Cvijović-Alagić I. (2013) Damage and fracture resistance of titanium based alloys for medical application [dissertation]. Belgrade (Serbia): University of Belgrade. Serbian.
6. Cvijović-Alagić I, Rakin M. Integrity of biomedical implants of titanium alloys (second part). Structural Integrity and Life. 2008; 8(2):121-30.
7. Zhang R, Wan Y, Ai X, Wang T, Men B. Preparation of micro-nanostructure on titanium implants and its bioactivity. T Nonferr Metal Soc. 2016;26:1019-24.
8. Torres Y, Sarria P, Gotor FJ, Gutiérrez E, Peon E, Beltrán AM, González JE. Surface modification of Ti-6Al-4V alloys manufactured by selective laser melting: Microstructural and tribo-mechanical characterization. Surf Coat Tech. 2018;348:31-40.
9. Steen WM, Mazumder J. Laser Material Processing. London (UK): Springer – Verlag; 2010.
10. Brown MS, Arnold CB. Chapter 4: Fundamentals of Laser-Material Interaction and Application to Multiscale Surface Modification. In: Sugioka K, Meunier M, Piqué A. Laser Precision Microfabrication. NY: Springer Press. 2010; p. 91-120.
11. Rykalin N, Uglov A, Zuev I, Kokora A. Laser and Electron Beam Material Processing Handbook. Moscow: Mir Publishers. 1988.
12. Poprawe R, editor. Tailored Light 2: Laser Applicaiton Technology. Berlin (Germany): Springer - Verlag. 2004.
13. Milovanović D, Petrović S, Shulepov M, Tarasenko V, Radak B, Miljanić Š, et al. Titanium alloy surface modification by excimer laser irradiation. Opt Laser Technol. 2013; 54:419-27.
14. Trtica M, Stašić J, Batani D, Benocci R, Narayanan V, Ciganović J. Laser-assisted surface modification of Ti-implant in air and water environment. Appl Surf Sci. 2018;428:669-75.
15. Trtica M, Batani D, Redaelli R, Limpouch J, Kmetik V, Ciganović J, et al. Titanium surface modification using femtosecond laser with 1013-1015 W/cm2 intensity in vacuum. Laser Part Beams. 2013; 31:29-36.
16. Hermann J, Boulmer-Leborgne C, Dubreuil B, Mihailescu IN. Influence of irradiation conditions on plasma evolution in laser-surface interaction. J Appl Phys. 1993; 74(5):3071-9.
17. Chen S, Usta AD, Eriten M. Microstructure and wear resistance of Ti6Al4V surfaces processed by pulsed laser. Surf Coat Tech. 2017; 315:220-31.
18. Ur Rahman N, de Rooij MB, Matthews DTA, Walmag G, Sinnaeve M, Römer, GRBE. Wear characterization of multilayer laser cladded high speed steels. Tribol Int. 2018; 130:52-62.
19. Rajamure RS, Vora HD, Gupta N, Karewar S, Srinivasan SG, Dahotre NB. Laser surface alloying of molybdenum on aluminum for enhanced wear resistance. Surf Coat Tech. 2014; 258:337-42.
20. Liu Y, Liu W, Ma Y, Liang C, Liu C, Zhang C, Cai Q. Microstructure and wear resistance of compositionally graded TiAl intermetallic coating on Ti6Al4V alloy fabricated by laser powder deposition. Surf Coat Tech. 2018; 353:32-40.
21. Yao Y, Li X, Wang YY, Zhao W, Li G, Liu RP. Microstructural evolution and mechanical properties of Ti–Zr beta titanium alloy after laser surface remelting. J Alloys and Compd. 2014; 583:43-7.

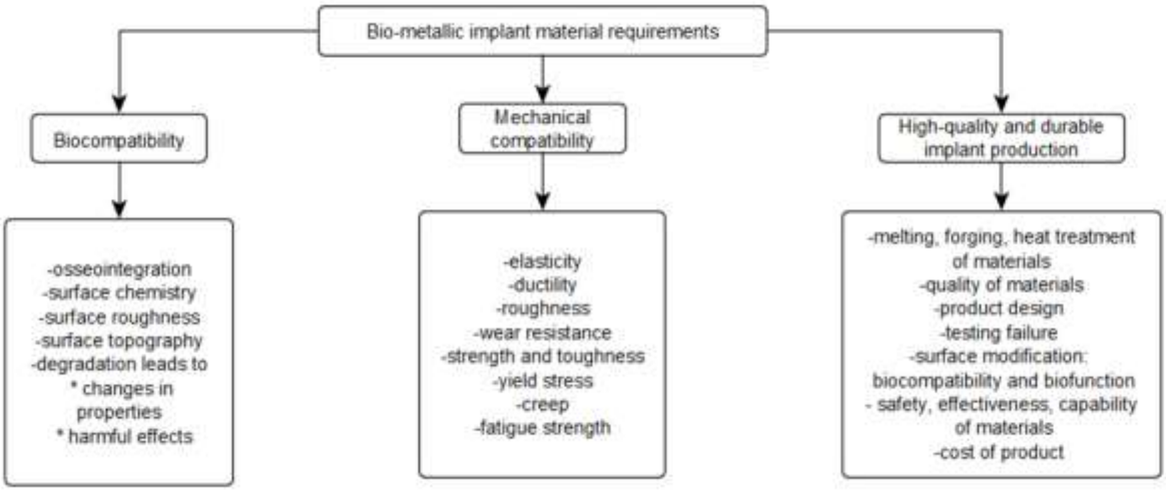


Figure 1. Implant materials requirements for biomedical applications

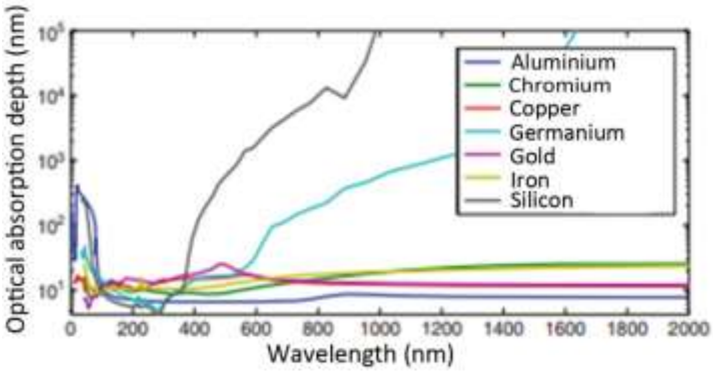


Figure 2. Optical absorption depths for diverse materials over a wide range of wavelengths [10]

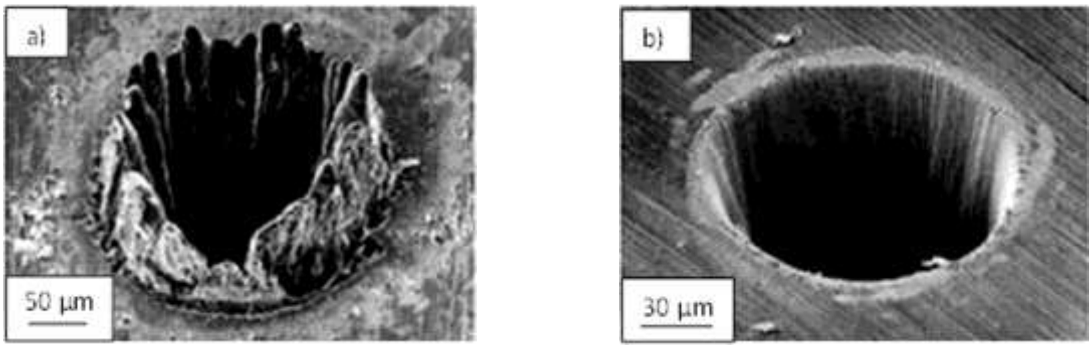


Figure 3. Craters obtained as a result of a) the femtosecond and b) the nanosecond laser radiation interaction with the surface of the steel [10]

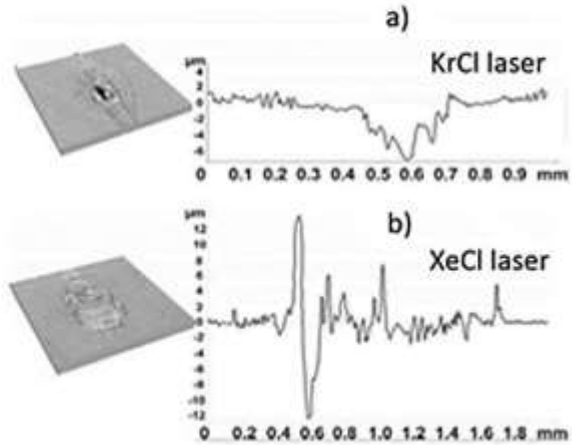
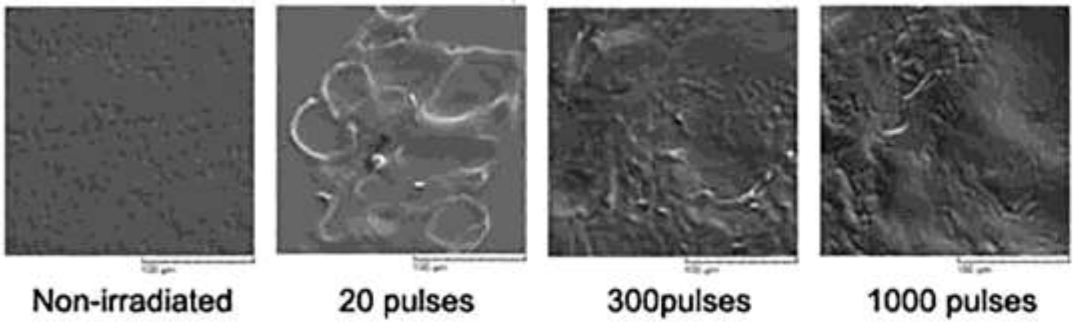
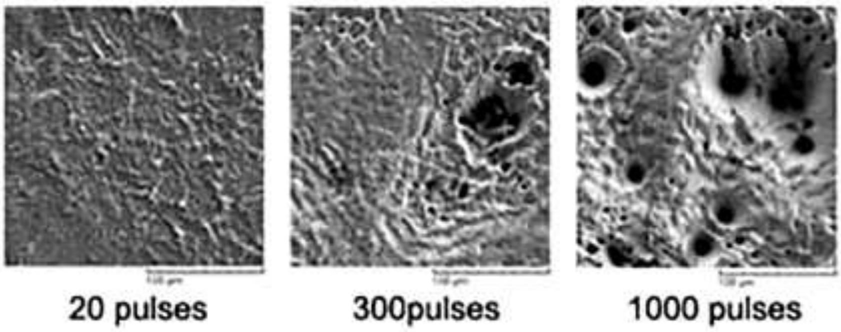


Figure 4. Profilometric analysis of the Ti-6Al-4V alloy surface after modification using: a) KrCl and b) XeCl laser [13]



a)



b)

Figure 5. SEM analysis of the Ti implant (target) surface after irradiation with picosecond laser pulses in a) air and b) water atmosphere [14]

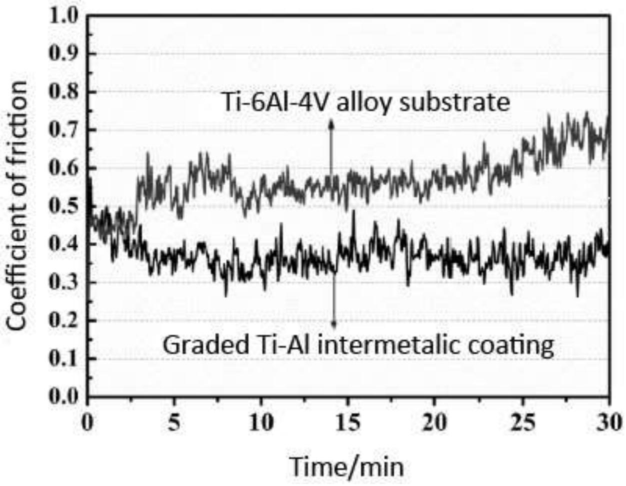
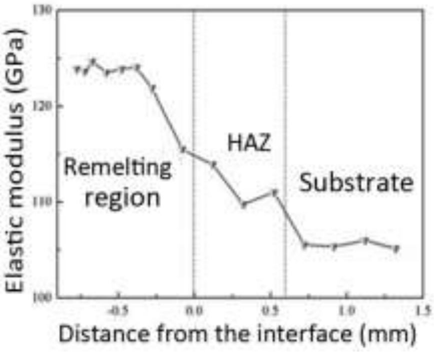
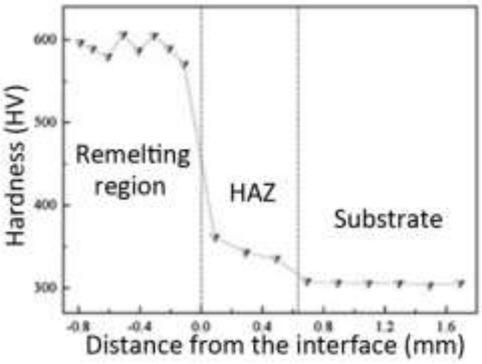


Figure 6. Friction coefficients variation for the Ti-6Al-4V substrate and Ti-Al intermetallic coating [20]



a)



b)

Figure 7. Elastic modulus a) and hardness b) of the Ti-Zr alloy in different laser-treated regions [21]

