



# PHYSICAL CHEMISTRY 2016

*13<sup>th</sup> International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry*

*Proceedings  
Volume I*

**BELGRADE**  
**September 26 - 30, 2016**

**ISBN 978-86-82475-34-7**

**Title:** Physical Chemistry 2016 (Proceedings)

**Editors:** Željko Čupić and Slobodan Anić

**Published by:** Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.

**Publisher:** Society of Physical Chemists of Serbia

**For Publisher:** S. Anić, President of Society of Physical Chemists of Serbia

**Printed by:** "Jovan", Printing and Publishing Company; 200 Copies.

**Number of pages:** 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

Neither this book nor any part may be reproduced or transmitted in any form or by any means, including photocopying, or by any information storage and retrieval system, without permission in writing from the publisher.

*200 - Copy printing*



# PHYSICAL CHEMISTRY 2016

*13<sup>th</sup> International Conference on  
Fundamental and Applied Aspects of  
Physical Chemistry*

*Organized by*

*The Society of Physical Chemists of  
Serbia*

*in co-operation with*

*Institute of Catalysis Bulgarian Academy of Sciences*

*and*

*Boreskov Institute of Catalysis Siberian Branch of  
Russian Academy of Sciences*

*and*

*University of Belgrade, Serbia:*

*Faculty of Physical Chemistry  
Institute of Chemistry, Technology and Metallurgy  
Vinča Institute of Nuclear Sciences  
Faculty of Pharmacy*

*Institute of General and Physical Chemistry, Belgrade, Serbia*

### **International Organizing Committee**

**Chairman:** S. Anić (Serbia)  
**Vice-chairman:** M. Gabrovska (Bulgaria)  
A. A. Vedyagin (Russia)  
S. N. Blagojević (Serbia)  
**Members:** N. Cvjetičanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), D. Jovanović (Serbia), J. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Ostrovski (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), D. Stanisavljev (Serbia), M. Stanković (Serbia), Z. Šaponjić (Serbia), B. Šljukić (Serbia), G. Tasić (Serbia), N. Vukelić (Serbia), V. Vukojević (Sweden)

### **International Scientific Committee**

**Chairman:** Ž. Čupić (Serbia)  
**Vice-chairmans:** V. N. Parmon (Russia)  
S. Rakovsky (Bulgaria)  
B. Adnađević (Serbia)  
**Members:** S. Anić (Serbia), A. Antić-Jovanović (Serbia), G. Bačić (Serbia), R. Cervellati (Italy), G. Ćirić-Marjanović (Serbia), A. Cricenti (Italy), V. Dondur (Serbia), S. D. Furrow (USA), L. Gábor (Hungary), Vilmos Gáspár (Hungary), K. Hedrih (Serbia), M. Jeremić (Serbia), E. Kiš (Serbia), Lj. Kolar-Anić (Serbia), U. Kortz (Germany), T. Kowalska (Poland), V. Kuntić (Serbia), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), B. Novakovski (Poland), T. Parac Vogt (Belgium), M. Perić (Serbia), M. Plavšić (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech Republic), P. Ševčík (Slovakia), N. Stepanov (Russia), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia), Á. Tóth (Hungary)

### **Local Executive Committee**

**Chairman:** S. N. Blagojević  
**Vice-chairmans:** A. Ivanović-Šašić  
A. Stoiljković  
**Members:** M. Ajduković, P. Banković, N. Bošnjaković, I. N. Bujanja, D. Dimić, A. Dobrota, J. Dostanić, A. Ignjatović, S. Jovanović, Z. Jovanović, A. Jović, N. Jović-Jovičić, D. Lončarević, M. Kragović, J. Krstić, S. Maćešić, J. Maksimović, V. Marković, D. Milenković, M. Milovanović, B. Nedić-Vasiljević, M. Pagnacco, A. Pavičević, N. Potkonjak, D. Ranković, M. Ristić, B. Stanković, A. Stanojević



## PULSED TEA CO<sub>2</sub> LASER IRRADIATION OF TITANIUM- CONTROLLABLE GAS AMBIENCE

J. Ciganović<sup>1,2</sup>, P. Matavulj<sup>2</sup>, M. Trtica<sup>1</sup>, J. Stasić<sup>1</sup>, J. Savović<sup>1</sup>, S. Živković<sup>1</sup> and M. Momčilović<sup>1</sup>

<sup>1</sup> *University of Belgrade, Institute of Nuclear Sciences Vinca, Mike Alasa 12-14, 11001 Belgrade, Serbia. (jovanc@vinca.rs)*

<sup>2</sup> *School of Electrical Engineering, University of Belgrade, Bulevar kralja Aleksandra 73, Belgrade 11120, Serbia*

### ABSTRACT

Interaction of a TEA CO<sub>2</sub> laser, operating at 10.6 μm wavelength and pulse length of 100 ns, with titanium target (implant), in nitrogen and carbon-dioxide gas ambience was studied. The Ti-surface modifications were studied at moderate fluence (~17 J/cm<sup>2</sup>) and intensity (~60 MW/cm<sup>2</sup>) regime. The energy absorbed from the laser beam was partially converted to thermal energy, which generated a series of effects, such as melting, vaporization of the molten material, shock waves, etc. The following Ti-surface changes and phenomena were observed: (i) superficial damages in both atmospheres; (ii) creation of cone- and hill- like structures in atmosphere of N<sub>2</sub> and CO<sub>2</sub>, respectively; (iii) possible formation of TiN, Ti-oxide(s) and, Ti-carbide layers, in N<sub>2</sub> and CO<sub>2</sub> gas, respectively and, (iv) occurrence of plasma in both gas ambiences. It can be concluded that the applied laser fluence was high enough to produce effective modification of the Ti- implant target in nitrogen as well as in carbon-dioxide gas. Creation of plasma may provide sterilization effect.

### INTRODUCTION

One of possible methods for processing and surface modification of refractory metals is by lasers [1]. Generally, study of laser-refractory metal interaction is scarce in the literature. Titanium is metal which possesses extraordinary properties such as high melting point, high strength-to-weight ratio, excellent corrosion and erosion resistance, etc. Because of that, titanium has been used in a variety of fields like medicine (as implant), industry, aerospace engineering, etc. Recently, titanium and its alloys have been considered for fusion area applications.

Bio-integration of Ti-implant depends on the state of the surface [2-4]. One of possible approaches for surface morphology alternations is a laser

treatment [3-5]. In addition, formation of compounds at the surface, e.g. oxides, can have positive effect on bio-compatibility [5].

The present paper studies the effects of a pulsed TEA CO<sub>2</sub> laser emitting in the infrared (10.6 μm), at moderate fluences ~17 J/cm<sup>2</sup> and intensity of ~60 MW/cm<sup>2</sup>, on a titanium surface in controlled nitrogen and carbon-dioxide gas atmosphere. As the TEA CO<sub>2</sub> laser–titanium interaction was accompanied by the appearance of plasma, optical emission spectroscopy was applied to analyse the plasma emission.

### EXPERIMENTAL

The experimental set-up used in this study was described in details in reference [5]. It consists of the laser source, target placed in a vacuum chamber which could be filled with various gases, and plasma emission detection system (spectrometer coupled with a CCD detector). A CO<sub>2</sub> laser was a commercial version of the system developed at the VINCA Institute of Nuclear Sciences [6]. The pulse repetition rate was 1 Hz, and the laser was running under moderate fluence (~17 J/cm<sup>2</sup>) and intensity (~60 MW/cm<sup>2</sup>) regime. The optical pulse had a gain switched spike followed by a slowly decaying tail. FWHM of the spike was about 100 ns while the tail duration was ~2 μs. The laser beam was focused on the Ti-target with a ZnSe lens (focal length 13.0 cm). The angle of incidence of the laser beam with respect to the target surface was ~90°. A disk-shaped Ti samples (30 mm diameter and 5 mm thickness) were prepared by a standard metallographic procedure.

Various techniques were used for the analysis of Ti-target surface before and after the laser irradiation, e.g. optical microscopy, scanning electron microscopy and interferometric profilometric analysis. A time-integrated spatially-resolved plasma emission spectroscopy was applied for the analysis of plasma emission.

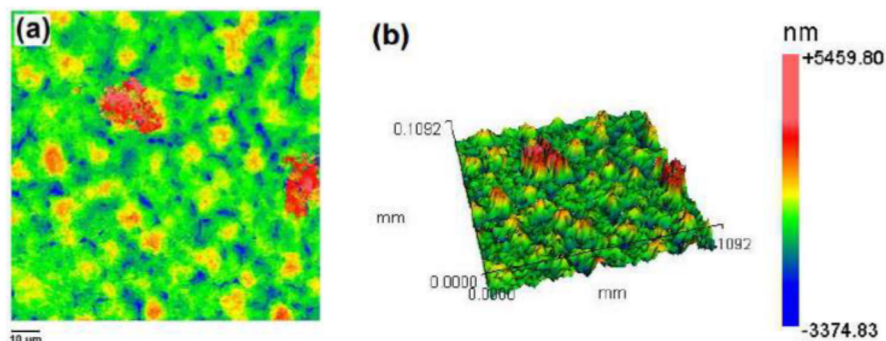
### RESULTS AND DISCUSSIONS

Surface modification of titanium generally depends on the laser output parameters (energy density, intensity, pulse duration, number of accumulated pulses, etc.), physicochemical characteristics of the material, as well as on irradiation conditions (working atmosphere and pressure). Laser induced morphological features depend, among other, from the temperature attained at the irradiated surface area and the heat affected zone. Under the applied experimental conditions, the heat affected zone was of the order of micrometers. A nanosecond TEA CO<sub>2</sub> laser interaction with titanium was accompanied by a series of processes, such as heating, melting, vaporization of the molten materials, dissociation, ionization of the vaporized material,

plasma creation, shock waves in the vapour and in the solid, etc. Surface features, generated during the interaction, can be described as follows:

**N<sub>2</sub> ambience:**

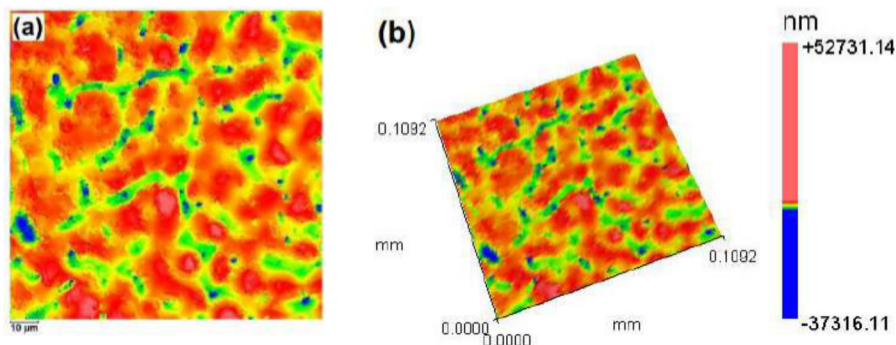
Irradiation of Ti-target in N<sub>2</sub> ambience was conducted at the pressure of one atmosphere. The obtained surface variations (Fig. 1.), can be summarized as follows: (i) superficial target damages with sporadic cracking (damage depth at 300 pulses was several micrometers); (ii) generation of conical forms; (iii) creation of the golden color layer and, (iv) creation of plasma which had yellow-white color. The appearance of the golden colored layer may imply a possible creation of TiN [5]. In the region close to the target, plasma emission mainly consisted of neutral and singly ionized spectral lines of titanium and nitrogen atomic lines.



**Figure 1.** Interferometric profilometry (IP) analysis. (a) 2D- and (b) 3D-view of Ti-surface after irradiation with 300 pulses in N<sub>2</sub> ambience.

**CO<sub>2</sub> ambience:**

Irradiation of Ti-target in CO<sub>2</sub> ambience was conducted at the pressure of one atmosphere. Obtained morphology changes were different from those obtained in N<sub>2</sub> ambience (Fig. 2.). Changes can be summarized as follows: (i) superficial damage with intensive cracking (central zone); (ii) appearance of hill-like structures; (iii) creation of black and white colored regions; (iv) creation of intensive plasma which had blue-white color. Appearance of the characteristic colored locations may imply formation of Ti-oxides and Ti-carbide layer at the surface. In CO<sub>2</sub> gas, analysis of plasma emission showed the presence of Ti-atomic and ionic spectral lines, oxygen lines as well as CO bands.



**Figure 2.** IP analysis. (a) 2D- and (b) 3D-view of Ti-surface after irradiation with 300 pulses in CO<sub>2</sub> ambience.

### CONCLUSION

Irradiation of titanium implant target by pulsed TEA CO<sub>2</sub> laser, in controllable gas ambience of N<sub>2</sub> and CO<sub>2</sub>, resulted in intensive morphological changes. Generally, the surface roughness was increased with simultaneously possible formation of layers such as, TiN, Ti-oxides, Ti-carbide. Irradiation process was accompanied by plasma creation in front of the target which can provide additional effects at the surface, i.e. sterilization effect.

### Acknowledgements

This work was partially supported by the: (i) Ministry of Education, Science and Technological Development of Republic of Serbia. Project No. 172019 and No. 171011 and, (ii) International Atomic Energy Agency (IAEA), Contract No. 20636.

### REFERENCES

- [1] Patschger, A. Hopf, M. Gupner, J. Bliedtner, *Laser Tech. Jour.*, 2016, **13**, 24-27.
- [2] M. Long, H. J. Rack, *Biomaterials*, 1998, **19**, 1621–1639.
- [3] M. Bereznai, I. Pelsoczi, Z. Toth, K. Turzo, M. Radnai, Z. Bor, A. Fazekas, *Biomaterials*, 2003, **24**, 4197–4203.
- [4] F. Guillemot, F. Prima, V. N. Tokarev, C. Belin, M.C. Porte-Durrieu, T. Gloriant, C. Baquey, S. Lazare, *Appl. Phys. A*, 2004, **79**, 811–813.
- [5] J. Ciganovic, J. Stasic, B. Gakovic, M. Momcilovic, D. Milovanovic, M. Bokorov, M. Trtica, *Appl. Surf. Sci.*, 2012, **258**, 2741–2748.
- [6] M. Kuzmanovic, M. Momcilovic, J. Ciganovic, D. Rankovic, J. Savovic, D. Milovanovic, M. Stoiljkovic, M. S. Pavlovic, M. Trtica, *Physica Scripta*, 2014, **T162**, 014011 (4pp).

544(082)  
66.017/.018(082)  
502/504(082)  
663/664:658.56(082)  
615.31:547(082)

INTERNATIONAL Conference on Fundamental and Applied Aspects of Physical Chemistry (13 ; 2016 ; Beograd)

Physical Chemistry 2016 : proceedings. Vol. 2 / 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry, Belgrade, 26-30 September 2016 ; [editors Željko Čupić and Slobodan Anić]. - Belgrade : Society of Physical Chemists of Serbia, 2016 (Belgrade : Jovan). - IV, 507-930 str. : ilustr. ; 24 cm

Tiraž 200. - Bibliografija uz svaki rad.

ISBN 978-86-82475-33-0

1. Society of Physical Chemists of Serbia (Beograd)

а) Физичка хемија - Зборници б) Наука о материјалима - Зборници  
в) Животна средина - Заштита - Зборници д) Животне намирнице - Контрола квалитета - Зборници  
е) Фармацеутска хемија - Зборници  
COBISS.SR-ID 225802508

08.09.2016

