PREPARATION AND CHARACTERIZATION OF TITANIUM-CARBIDE/AMORPHOUS CARBON NANOCOMPOSITE COATING

Ph.D. thesis

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Budapest 2018

1. INTRODUCTION AND OBJECTIVES

The development of nanomaterials involves a number of disciplines of science, including materials science and within the composite materials. In order to satisfy the ever increasing demand for appropriate materials behavior, the combination of different materials can provide the properties on the macroscopic level that cannot be achieved with the individual components. Different nanoparticles may often have some sort of outstanding properties that are different from the bulk material. These are dosed as a composite amplifying phase can improve optical-, mechanical-, biological properties, adhesion characteristics, wear-, and corrosion resistance of the core material.

Most of the metal medical implants are made of titanium (Ti) or their different alloys due to their favorable biocompatibility. Ti has excellent chemical, physical and mechanical properties. After implantation, however, Ti ions (and / or alloying elements) can be detected in the body - due to corrosion or metal scraping - which may cause inflammation; lead to allergic symptoms, and in the worst case, removal of the implant may be necessary. In order to avoid the release of ions, increase the metal corrosion resistance and biocompatibility, several methods can be used. One of them is the passivation of the surface with different nanocomposites. In my dissertation, I have written about the use of a such like passivating, corrosion resistance and biocompatible titanium carbide (TiC) / amorphous carbon (a:C) coating to increase the lifespan of surgical implants, where one of the components (a:C matrix) is contiguous and surrounds the dispersion phase (TiC nanocrystals).

Over the last decades in the MFA Thin Film Physics Laboratory several thin films ranging from multifarious nanocomposites - C–Ti, C–Ni, Cu–Ag, Al to polycrystalline-TiN, Al / single crystal-TiN –were successfully produced for different applications. The properties and application possibilities of TiC, TiN, TiCN have also been tested. During my doctoral research I will produce TiC/a:C nanocomposite thin films to increase the structural and mechanical stability of different implant substrates as well as to reduce the likelihood of tissue inflammation by a simple and relatively inexpensive method. Combining carbon based films with different nanoscale metal particles can improve the physical properties of the bulk material. Mechanical properties of the material can be controlled by the size of the embedded nanocrystal in the amorphous matrix. The structure consisting of an amorphous C matrix and a TiC nanocrystalline crystal is suitable for increasing the hardness. The production of thin films will be accomplished using the DC magnetron sputtering, which is the simplest of the methods to be considered. A sufficiently high yield can be achieved with this method, while the properties of the films can be well controlled by the power of the sources and thus it can be used potentially in industrial conditions.

In my PhD research I’m going to focus on the following objectives:

1. The effect of Ti content on the growth mechanism of the films and the formation of TiC crystals.

2. Study of the microstructure of the films and their composition dependence on sputtering parameters.

3. Interfacial energies affecting the composition of the films.

4. Investigating the effect of TiC/a:C on the mechanical properties of thin film structures.

5. Optimum adhesion of the films by different surface treatment methods besides sandblasting on the metal substrates prior to sputtering.

6. Corrosion resistance of the films will be tested by potentiodynamic and EIS measurements perform in various electrolytes.

7. Biocompatibility of the coatings will be analyzed in culturing of MG-63 human bone cells for 1, 3, 7 and 14 days, respectively.

2. EXPERIMENTAL

TiC/a:C coatings of different structures were developed by simultaneous deposition of Ti and C on SiO_2/Si, commercially pure (CP) titanium (ISO5832-2), on smooth (unblasted) and sandblasted TiAl6V4 alloy (ISO5832-3) and sandblasted CoCrMo alloy (ISO5832-12) physiological implant material. A DC magnetron sputtering system and 2.5 x 10^{-3} mbar background Ar gas pressure was used for deposition at room temperature. The implants were always purchased from Protetim Medical Instruments Ltd. Depending on the time of simultaneous deposition of 2" Ti (99.995 %) and C (99.999 %) originating from Kurt & Lesker and by varying the sputtering power of the targets, nanocomposites of different compositions were produced. The thin films grown at fixed carbon target power (150 W) were examined versus increasing titanium target power (5 - 150 W). In order to determine the deposition rate and the density of Ti and C, a C/Ti/C/Ti/C/Ti multilayer was prepared.

The properties of the obtained TiC/a:C nanocomposite thin films were analyzed by several methods. The morphology and crystal structures of the films were studied using the electron microscopes Philips CM-20 (TEM) with a resolution of 0.27 nm operated at 200 keV and JEOL-3010 (HRTEM) with a resolution of 0.17 nm operated at 300 keV. In all cases cross-section of the films were analyzed. The structure of the sample could be revealed by scanning the thin cross-section (*interface*) perpendicular to the surface of the sample. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) were used to study and compare the chemical compositions and morphologies of the deposited TiC/a:C protective thin films. SEM measurements of the films before and after electrochemical stability tests were performed in a SEM-LEO 1540 XB microscope operated at 2, or 5 keV.

The elemental composition of the films was determined by energy dispersive X-ray spectroscopy (EDS). The chemical composition of the nanoparticle samples was identified by X-ray diffractometry (XRD). The GADDS 2D detector system was applied to detect scattered radiation, while the ICDD PDF database was used to evaluate the diffractograms. To measure the thickness of C and Ti layers, a Nanoscope Multimode 8 type atomic force microscope (AFM) was applied in a contact mode. Near-infrared Raman spectroscopy (NIRS) was used to characterize the amorphous part of TiC/a:C thin films through its bonding configuration. The measurements were carried out in the range of 100 - 1700 cm^{-1} by a Renishaw1000 B micro-Raman spectrometer using the 488 nm line of an Ar-ion laser and a 785 nm diode laser as excitation sources.

Mechanical characteristics of the TiC/a:C coatings at room temperature were measured by a Nanoindenter Agilent G200 (USA) device with a Berkovich diamond indenter. The hardness and the indentation modulus values were calculated using the measuring standards based on the work of Oliver and Pharr. The tribological behavior of the films at room temperature was assessed by a ball-on-disk tester (CSM tribometer) moving on circular trajectory. The sliding velocity was 0.05 m/s in air.

Electrochemical potentiodynamic and electrochemical impedance spectroscopy (EIS) tests were performed to establish the corrosion behavior of coated and uncoated surgical implant materials and the stability of the protective layer. First TiC/a:C thin film coated, sandblasted TiAl6V4 alloy and sandblasted CoCrMo alloy implant-materials were tested in solutions with 3 different pH values (pH = 6; 1 and 13), and subsequently corrosion tests were performed in simulated body fluids (SBF). The dissolution characteristics of the TiC/a:C thin film coated as well as the uncoated Ti and TiAl6V4 substrates were quantitatively analyzed by measuring the metal ions by a simultaneous Spectro Genesis inductively coupled plasma optical emission spectrometer (ICP-OES). The sputtered films were also subjected to hydrophilicity and biocompatibility tests.

3. NEW SCIENTIFIC RESULTS

1.a. I described in the first time the microstructure of TiC/a:C thin films formed titanium and carbon at room temperature with a direct magnetron sputtering depending on the titanium content, based on electron microscopy, X-ray diffraction and elemental analytical determination. I proved that the microstructure of TiC/a:C thin films deposited at room temperature as a function of the phase composition was similar to the higher deposition temperatures of 150 - 350 ° C.

1.b. I have found that by the systematic alteration of the titanium content, the films were characterized by an amorphous phase at 17.5 at% titanium content, in films containing above 18 at% titanium, fcc crystalline TiC was formed. The particle size of the TiC crystals showed an increasing tendency in the growth of titanium content, initially in the form of separate particles and then transformed into a columnar structure. The amount of amorphous carbon surrounding the nanocrystals gradually decreased and then completely disappeared above 47 at% of titanium content.

1.c. Considering the interfacial energies, nucleation barriers and nano-thermodynamics of different phases I have given an explanation for the formation of structures characteristic of different compositions. The structural changes followed the the two-component system zone model however, based on the macroscopic Ti - C phase diagram I did not find the expected phase transformations over 47 at% titanium content, no hcp-Ti phase formed even the Ti-content was up-to 60 at% and the carbon remained amorphous throughout [S4] [S6].

2. I proved with measurements that the elemental composition, microstructure, local mechanical and tribological properties of sputtered TiC/a:C films were only depending on the power of the targets, but it did not depend on either the applied substrate or the layer thickness. [S1] [S4] [S5].

3. I have proved that the optimal microstructure and phase composition thin film for hardness and friction properties was that nanocomposite film which containing 38 at% Ti yielding TiC grains of 4 ÷ 10 nm separated by 2 ÷ 3 nm thin amorphous matrix with globular fcc TiC nanocrystals. I also proved with experimental results that the hardness and the tribological characteristics of the bare Ti or TiAl6V4 implant materials with the deposition of this optimal TiC/a:C nanocomposite coating were improving by many times [S3] [S6].

4.a. I have demonstrated that the optimal TiC/a:C coated sandblasted TiAl6V4 alloy had the highest polarization resistance and contains the smallest amount of corrosion products during the corrosion testing of various TiC/a:C thin films sputtered on different substrates.

4.b. I also proved that the optimal TiC/a:C protective coating deposited on sandblasted TiAl6V4 surface prevented the dissolution of both Ti and Al ions in simulated body fluid at pH of 7.4 [S2] [S5].

4. OWN PUBLICATIONS RELATED TO THE PRESENT THESIS

[S1] **<u>Oláh N</u>**, Veres M, Sulyok A, Menyhárd M, Gubicza J, Balázsi K: **Examination of nanocrystalline TiC/amorphous C deposited thin films**
JOURNAL OF THE EUROPEAN CERAMIC SOCIETY 34:(14) pp. 3421-3425. (2014)
(IF 2.36) doi:10.1016/j.jeurceramsoc.2013.12.006; Journal Article/Article/Scientific

[S2] **<u>Nikolett Oláh</u>**, Zsolt Fogarassy, Mónika Furkó, Csaba Balázsi, Katalin Balázsi: **Sputtered nanocrystalline ceramic TiC / amorphous C thin films as potential materials for medical applications**
CERAMICS INTERNATIONAL 41:(4) pp. 5863-5871. (2015) **(IF 2.086)**
doi:10.1016/j.ceramint.2015.01.017; Journal Article/Article/Scientific

[S3] **<u>Oláh Nikolett</u>**, Fogarassy Zsolt, Sulyok Attila, Szívós János, Csanádi Tamás, Balázsi Katalin: **Ceramic TiC/a:C protective nanocomposite coatings: Structure and composition versus mechanical properties and tribology**
CERAMICS INTERNATIONAL 42:(10) pp. 12215-12220. (2016) **(IF 2.758)**
doi:10.1016/j.ceramint.2016.04.164; Journal Article/Article/Scientific

[S4] **<u>Nikolett Oláh</u>**, Zsolt Fogarassy, Attila Sulyok, Miklós Veres, George Kaptay, Katalin Balázsi: **TiC crystallite formation and the role of interfacial energies on the composition during the deposition process of TiC/a:C thin films**
SURFACE AND COATINGS TECHNOLOGY 302: pp. 410-419. (2016) **(IF 2.139)**
doi:10.1016/j.surfcoat.2016.06.047; Journal Article/Article/Scientific

[S5] **<u>Nikolett Oláh</u>**, Mónika Furkó, Zoltán May, Attila Sulyok, Katalin Balázsi: **Mechanical characterization and corrosion behavior of protective TiC/amorphous C nanocomposite coating as surface thin film**
RESOLUTION AND DISCOVERY 2:(1) pp. 43. 10 p. (2017) **(WITHOUT IF)**
https://doi.org/10.1556/2051.2017.00043; Journal Article/Article/Scientific

[S6] Fogarassy Zsolt, **<u>Oláh Nikolett</u>**, Cora Ildikó, Horváth Zsolt Endre, Csanádi Tamás, Sulyok Attila, Balázsi Katalin, **The structural and mechanical characterization of TiC and**

TiC/Ti thin films grown by DC magnetron sputtering, JOURNAL OF THE EUROPEAN CERAMIC SOCIETY 38:(7) pp. 2886-2892. (2018) **(IF 3.411)** https://doi.org/10.1016/j.jeurceramsoc.2018.02.033; Journal Article/Article/Scientific

5. OWN CONFERENCE PRESENTATIONS RELATED TO THE PRESENT THESIS

1. **Nikolett Oláh**, Miklós Veres, Attila Sulyok, Miklós Menyhárd, Jenő Gubicza, Katalin Balázsi, **Examination of nanocrystallite TiC/amorphous C deposited thin films**, National Materials Science Conference (OATK), Balatonkenese, 13 Oct - 15 Oct 2013 **poster**

2. **Nikolett Oláh**, Miklós Veres, Attila Sulyok, Miklós Menyhárd, Jenő Gubicza, Katalin Balázsi, **Examination of nanocrystallite TiC/amorphous C deposited thin films**, International Conference Fractography of Advanced Ceramics (FAC), Smolenice, Slovakia, 29 Sept - 2 Oct 2013, **poster**

3. **Nikolett Oláh**, Levente Illés, Attila Sulyok, Miklós Menyhárd, Csaba Balázsi, Mónika Furkó, Katalin Balázsi, **Sputtered nanocrystalline TiC/ amorphous C thin films for medical applications**, International workshop on Coatings & Surfaces for Biomedical Engineering (IWCSB) 2014, IIT Madras, Chennai, India, 16 Feb - 19 Feb 2014, **oral presentation**

4. **Nikolett Oláh**, Zsolt Fogarassy, Attila Sulyok, Orsolya Tapasztó, Csaba Balázsi, Mónika Furkó, Katalin Balázsi, **Sputtered nanocrystalline TiC/ amorphous C thin films as potential materials for medical applications**, HSM Annual Meeting, 29 May - 31 May 2014, Siófok, Lake Balaton, **oral presentation. *Special prize, my participation's fee of the Multinational Congress on Microscopy (Eger, 2015) will be paid by the Hungarian Microscopy Society.***

5. **Nikolett Oláh**, Miklós Veres, Attila Sulyok, Mónika Furkó, Zsolt Fogarassy, Csaba Balázsi, Katalin Balázsi, **Biocompatible TiC / amorphous C thin films prepared**

by DC magnetron sputtering, 15th Joint Vacuum Conference, 15 June - 20 June 2014, Vienna, Austria, **poster**

6. **<u>Nikolett Oláh</u>**, Zsolt Fogarassy, Attila Sulyok, Miklós Menyhárd, George Kaptay, Katalin Balázsi, **Microscopic study of TiC / amorphous C thin films**, 18th International Microscopy Congress (IMC) 2014 Prague, Czech Republic, 7 - 12 September 2014, **poster.** ***Scholarship, the fee of my participation was paid by the European Microscopy Society.***

7. **<u>Nikolett Oláh</u>**, George Kaptay, Zsolt Fogarassy, Attila Sulyok, Orsolya Tapasztó, Katalin Balázsi, **Comparison of experimental results with semi-empirical equation of deposited nc-TiC / C thin films**, 6th Szeged International Workshop on Advances in Nanoscience (Siwan6) Szeged, Hungary, 15 - 18 October 2014, **poster**

8. **<u>Nikolett Oláh</u>**, Miklós Veres, Attila Sulyok, Mónika Furkó, Zsolt Fogarassy, Csaba Balázsi, Katalin Balázsi, **Biocompatible TiC / amorphous C thin films prepared by DC magnetron sputtering**, 16th International Conference on Thin Films (ICTF16) Dubrovnik, Croatia, 13 - 16 October 2014, **poster**

9. **<u>Nikolett Oláh</u>**, George Kaptay, Zsolt Fogarassy, Attila Sulyok, Tamás Csanádi, Katalin Balázsi, **Characterization of deposited nc-TiC / C thin films as protective coatings**, 5th International Advances in Applied Physics and Materials Science Congress & Exhibition (APMAS 2015) 16 - 19 April 2015, Sentido Lykia Resort, Oludeniz/ Turkey, **poster**

10. **<u>Nikolett Oláh</u>**, **Biocompatible ceramic TiC / amorphous C thin films prepared by DC magnetron sputtering**, 14th International Conference European Ceramic Society (ECerS 14) 21 - 25 June 2015, Toledo, Spain, **oral presentation**. ***Participant of „ECerS student speech contest". The representative of Hungary.***

11. **<u>Nikolett Oláh</u>**, **Structural characterization of TiC based thin films by TEM and HRTEM**, Multinational Congress on Microscopy, MCM 2015, 23 - 28 August 2015, Eger, Hungary, **oral presentation**

12. **<u>Nikolett Oláh</u>**, Zsolt Fogarassy, Attila Sulyok, Miklós Veres, George Kaptay, Tamás Csanádi, Katalin Balázsi, **Characterization of TiC / C nanocomposite thin films for use in protective coating applications**, X. National Materials Science Conference (OATK), 11 - 13 October 2015, Balatonalmádi, Hungary, s**hort oral presentation (5 min.) + poster**

13. **<u>N. Oláh</u>**, Zs. Fogarassy, J. Szívós, A. Sulyok, M. Furkó, T. Csanádi, K. Balázsi, **Structural investigation, mechanical properties and corrosion behavior of magnetron-sputtered nanocomposite TiC/a:C thin film coatings**, HSM Annual Meeting, 19 - 21 May 2016, Siófok, Lake Balaton, **oral presentation**

14. **<u>N. Oláh</u>**, Zs. Fogarassy, J. Szívós, A. Sulyok, M. Furkó, T. Csanádi, K. Balázsi, **Structural investigation, mechanical properties and corrosion behavior of magnetron-sputtered nanocomposite TiC/a:C coatings**, 16^{th} Joint Vacuum Conference 6 - 10 June 2016, Portorož, Slovenia, **oral presentation**

15. HypOrth Meeting in Bilbao, Spain, 29 June - 2 July 2016, **2 poster**

16. **<u>N. Oláh</u>**, Zs. Fogarassy, J. Szívós, A. Sulyok, C. Balázsi, K. Balázsi, **Structural investigation, corrosion properties and adhesion behavior of magnetron sputtered nanocomposite TiC/a:C thin film coatings**, 16^{th} European Microscopy Congress, 28 August - 2 September 2016, Lyon, France, **poster.** ***Scholarship, the fee of my participation was paid by the European Microscopy Society.***

6. OTHER OWN PUBLICATIONS NOT DIRECTLY RELATED

[E1] Carta D, Loche D, Casula MF, **Oláh N**, Olasz D, Corrias A: **Nickel-based nanocrystals dispersed on SBA-16 gels: Synthesis and structural characterization**
JOURNAL OF NON-CRYSTALLINE SOLIDS 401: pp. 134-138. (2014) **(IF 1.579)**
doi:10.1016/j.jnoncrysol.2014.01.010; Journal Article/Article/Scientific

[E2] **Nikolett Oláh**, Carta Daniela, Zoltán Kónya, **Removing heavy metals from water with the help of carbon nanotubes and mesoporous silicas**, MATERIALS WORLD 12:(1) pp. 41-57. (2015) **(without IF)** http://real.mtak.hu/id/eprint/31040
Journal Article/Article/Scientific

[E3] Doina CRACIUN, Gabriel Socol, Daniel V Cristea, Maria Stoicanescu, **Nikolett Olah**, Katalin Balaszi, Nicolaie Stefan, **Mechanical properties of pulsed laser deposited nanocrystalline SiC films**, APPLIED SURFACE SCIENCE 336: pp. 391-395. (2015) **(IF 2.538)** doi:10.1016/j.apsusc.2014.12.186; Journal Article/Article/Scientific

[E4] **Nikolett Oláh**, Miklós Veres, Attila Sulyok, Zsolt Fogarassy, George Kaptay, Katalin Balázsi, **STRUCTURAL CHARACTERIZATION OF TiC-BASED THIN FILMS BY TEM AND HREM**, In: Ágnes Kittel, Béla Pécz (ed.) 12th Multinational Congress on Microscopy: MCM 2015. 599 p.
Conference: Eger, Hungary, 23/08/2015 – 28/08/2015 Budapest: Academic Press, 2015. pp. 148-150. (ISBN:978-963-05-9653-4); Book Excerpt/Abstract/Abstract/Scientific

7. SCIENTOMETRIC DATA

Peer-reviewed papers total: 9	out of this, related to the topic of thesis: 6
Cumulative impact factor: 16.871	out of this, related to the topic of thesis: 12.754
Independent citations total: 29	out of this, related to the topic of thesis: 22