PRELIMINARY STUDY OF TiN AND TiCN COATINGS FOR STAINLESS STEEL SURGICAL INSTRUMENTS

Marina Roxana ŞOLEA (IORDĂCHESCU)[1], Augustin SEMENESCU[2], Adriana ILEANA (BLĂJAN)[3], Ana-Iulia BIŢA[4*], Robert CIOCOIU[5], Iulian ANTONIAC[6]

The main justification for using stainless steels in the production of surgical instruments is their exceptional corrosion resistance and wide range of mechanical qualities, making them very suitable for a wide variety of applications. Typically, stainless steel surgical instruments are used and reused until they degrade. Corrosion is the primary factor leading to the failure of metallic surgical instruments. Corrosion may manifest either gradually or aggressively when the protective layer that forms on the surface of the metallic material is compromised. Corrosion-induced surface flaws may facilitate the contamination of instruments by holding residual substances, which can subsequently result in post-surgical infections. The objective of this study was to examine two prospective coatings, titanium nitride (TiN) and titanium carbonitride (TiCN), that may be applied on surgical tools to reduce the possibility of surface degradation.

Keywords: surgical instruments, stainless steel, titanium nitride, titanium carbonitride, coatings

1. Introduction

Hospitals and medical clinics have stringent and explicit rules in place for the use of surgical instruments to ensure the safety of both patients and medical professionals. That is why, in all medical units, dirt and microbial levels are carefully monitored [1]. Typically, the majority of surgical instruments are non-disposable and must be cleaned and sterilized many times for reuse. The

[1] PhD std., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: solearoxana@yahoo.com
[2] Prof., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: augustin.semenescu@upb.ro
[3] PhD std., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: adriana.ileana@stud.sim.upb.ro
[4*] Lect., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: ana_iulia.blajan@upb.ro
[5] Lect., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: robert.ciocoiu@upb.ro
[6] Prof., Faculty of Materials Science and Engineering, National University of Science and Technology POLITEHNICA Bucharest, Romania, e-mail: iulian.antoniac@upb.ro

instruments must be manufactured from materials that are suited to enduring frequent exposure to severe circumstances, such as high levels of humidity, extreme temperatures, and intense pressure [2]. Corrosion, integrity and functionality are important factors to consider owing to the potential for defects and higher roughness generated by corrosive processes. These imperfections may trap residues and promote the development of bacteria [3, 4]. Cleaning is the elimination of extraneous substances, such as dirt and organic particles, often accomplished by the use of water and cleaning solutions. It is necessary to thoroughly eliminate both the inorganic and organic substances that remain on the surfaces of the instrument. Alternatively, the presence of scraps might impede the efficacy of succeeding processes, such as disinfection and sterilization [5].

Austenitic stainless steel is a highly adaptable material that finds extensive use in several industries, including maritime, structural, and biomedical sectors. The popularity of this product may be ascribed to its outstanding resistance to corrosion, sufficient mechanical strength, and great ductility. Still, when the material interacts with other surfaces, environments, or chemicals, it might undergo distinct chemical reactions on its surface, leading to the deterioration of the protective layer and thereby reducing the lifespan of the products. Consequently, the process of surface modification of austenitic stainless steel has become a widespread method for enhancing its physical, mechanical, and tribological characteristics [6-9].

The development of materials in the configuration of thin films is unquestionably a topic of significant interest from both academic and technical perspectives. The focus of studying and developing coatings and thin layers should be on enhancing the appearance and functionality of materials, while also striving for ongoing improvement and cost reduction in manufacturing [10, 11]. By using the technique of thin film deposition, an initial barrier may be created to provide effective protection, hence resolving several practical issues [12-14]. Consequently, the extensive investigation of coating methods and the effectiveness of the resulting layers in enhancing corrosion resistance is a topic of growing interest [15].

Titanium (Ti) compounds, such as TiC, TiN, TiCN, TiSiN, and TiAlN, are extensively used in many industries owing to their low mass and exceptional strength-to-weight ratio. Moreover, these chemicals are very appropriate for modifying the surfaces of biomaterials used in the medical field, encompassing both implants and surgical equipment. Ti-based coatings provide a substantial enhancement in qualities, including superior corrosion resistance, high temperature resistance, as well as improved mechanical and electrical properties, to the material on which they are applied [16]. Given the considerable study conducted so far on multilayer coatings and the inherent high corrosion resistance of Ti, it is expected that its TiN and TiCN compounds will provide enhanced surface attributes, including surface functionalization, surface roughness, and corrosion strength. Ti-rich films provide a unique blend of characteristics such as exceptional strength, resistance to corrosion, lightweight nature, compatibility with living organisms, ability to withstand high temperatures, resistance to wear, and strong adhesion. These attributes make Ti-rich films very beneficial for enhancing the mechanical properties of materials across many applications [17-19].

This study conducts initial comparative research on the use of thin TiN and TiCN layers for modifying and enhancing the surface of austenitic stainless steel, which is often utilized in the production of surgical tools. TiCN is a composite material formed by combining TiN with TiC. It is anticipated to possess the benefits and features of both components, resulting in a highly desired material with exceptional performance attributes [17].

2. Materials and methods

The use of stainless steels for manufacture of surgical instruments is mainly justified by their corrosion resistance and a wide range of mechanical properties that make them suitable for most applications. Standards such as ASTM F899 and ISO 7153 offer a survey on the selection and use of stainless steels for surgical cutting and non-cutting instruments, as well as fitting parts and other assemblies.

Stainless steels from the austenitic class, 302, 303, 304 and 316 appear to be the most used in manufacture of instruments for cutting (knives, chisels, gouges, curettes) and non-cutting and instrument parts (cannula, forceps, retractors, specula, tunnelers, probes and so on). Their corrosion resistance is highest of all stainless steel classes, but the mechanical properties are lowest. Thus, an improvement of the surface characteristics would improve their wear resistance.

Table 1

The deposition parameters

Parameters	TiN	TiCN
Cathode	Ti 99.99% purity	Ti 99.99% purity
Work pressure	$3x10^{-4}$mbar	$3x10^{-4}$mbar
Argon flow	10cc/min	10cc/min
Nitrogen flow	110cc/min	80cc/min
Methane flow	-	30cc/min
Current intensity	90A	90A
Substrate polarization potential	-150V	-150V
Deposition duration	30min	30min

To achieve two coatings, titanium nitride (TiN) and titanium carbonitride (TiCN), a 304 stainless steel was coated using the cathodic arc evaporation process, taking into account the factors described earlier. The objective of the research was to investigate the topographical and mechanical characteristics of various coatings in order to identify the most suitable one for commercial use. The coatings were obtained in a conventional cathodic arc evaporation setup using a 304 stainless steel strip as substrate (Tabel 1 – process parameters).

The substrate was previously degreased and cleaned ultrasonically in trichloroethylene, dried using carbonic ice and cleaned by argon bombardment for 5 minutes using an accelerating voltage of 950V. The topography and morphology of the coatings were investigated by scanning electron microscopy (SEM) using a HITACHI TM3030Plus. The surface roughness and coating thickness were determined using a Dektak 150 Veeco-Brucker profilometer. Vickers microhardness tests were also performed using the hardness tester feature of the TriboLab UMT, Brucker, using a load of 100g-f.

3. Results and discussion

The SEM micrographs presented in Fig. 1 show the topography of the TiN.

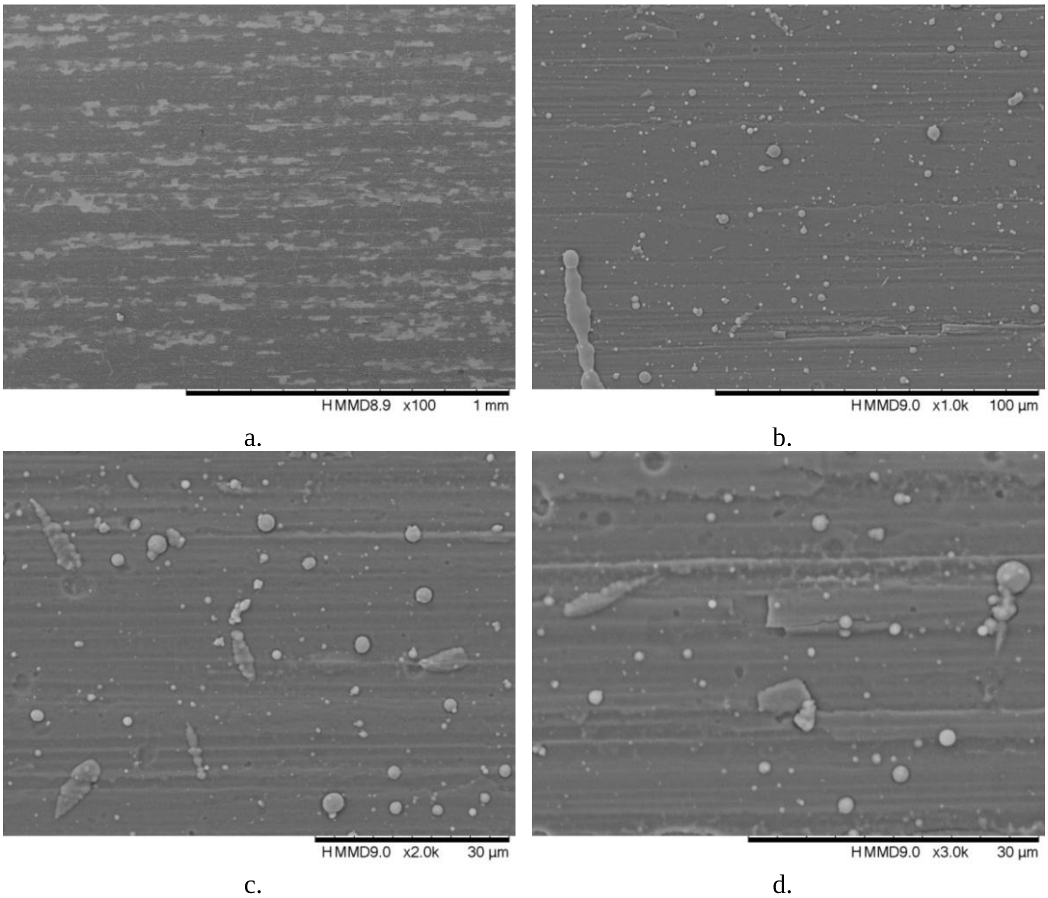


Fig. 1 The topography of the TiN coating

In Fig. 1.a the coating appears to have a texture caused by the substrate finish. The coating appears to be homogenous, continuous, without voids and exfoliations. In Fig. 1b and at higher magnifications, Fig. 1c and d circular features appear that are normal for the method used. The splatter features have an average Feret diameter of 0.93±0.56µm and a frequency distribution depicted in Fig. 2.

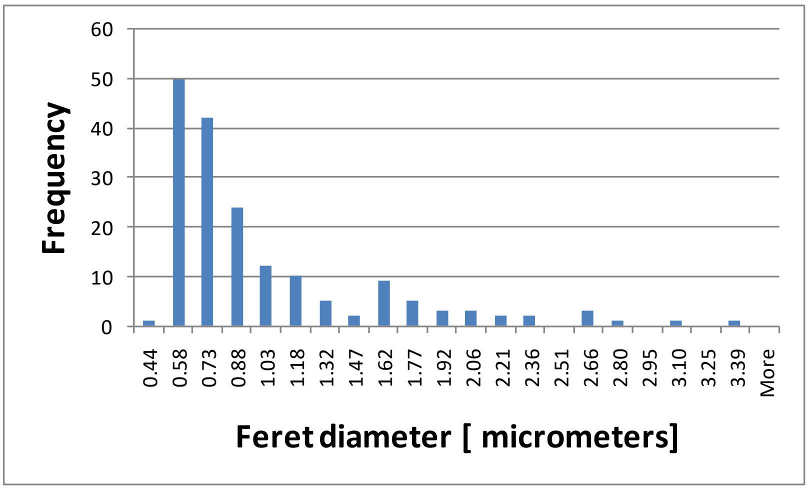


Fig. 2 Frequency distribution of the Feret diameter

The distribution reflects a large number of features with low Feret diameter, 94.32% of the counted particles have a Feret diameter up to 2.06µm.

The elemental mapping performed by energy dispersive spectrometry (EDS) depicted in Fig. 3 reflect a uniform distribution of N and Ti on the surface, confirming the uniform coating.

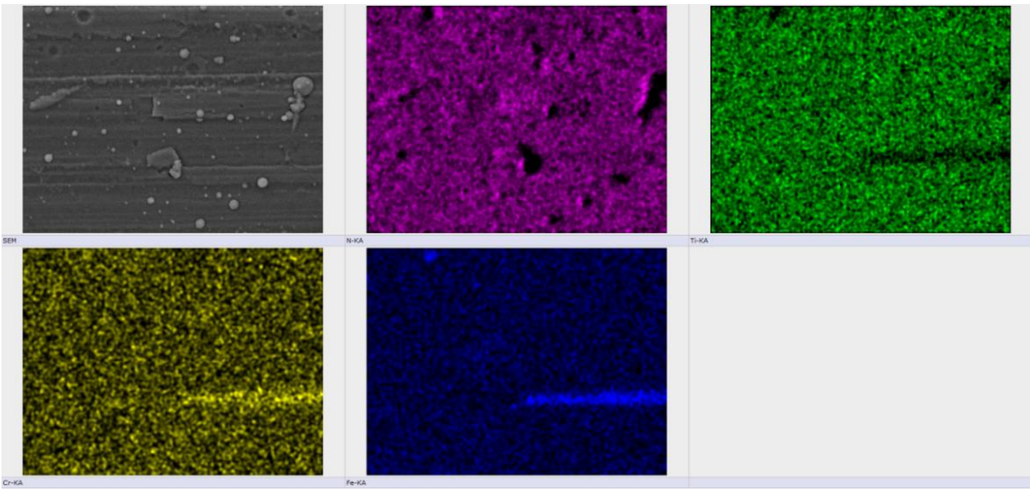


Fig. 3 Elemental mapping on the TiN coating

Circulars splatters of pure titanium are observed along elements from the substrate (Fe, Cr), more concentrated in a region where the substrate roughness alters the coating thickness.

The topography of the TiCN coating is presented in fig.4.

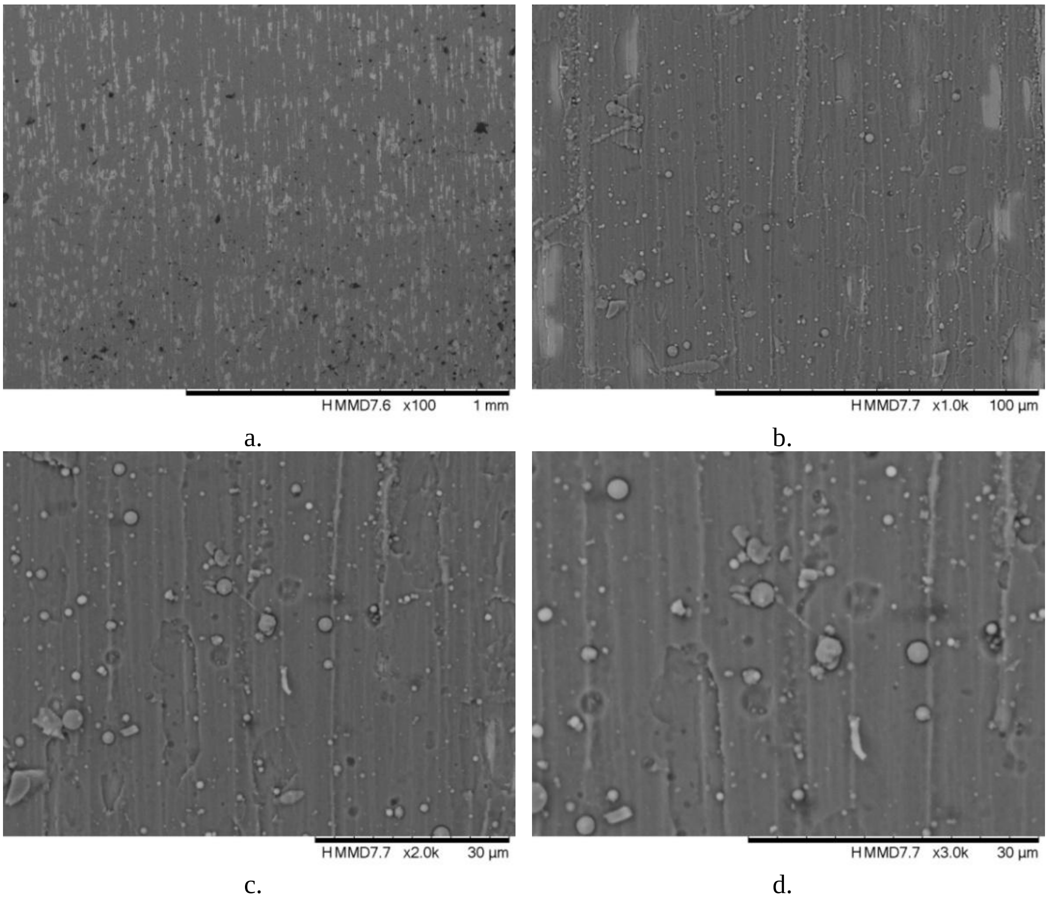


Fig. 4 The topography of the TiCN coating

Similar to TiN coating a texture can be observed in Fig. 4.a induced by the substrate roughness and same circular features caused by cathode splatter are seen in Fig. 4.b, c and d. The mean Feret diameter of these features is 0.85±0.35μm, slightly smaller than those on the TiN coating.

The frequency distribution according to Feret diameter is presented in Fig. 5.

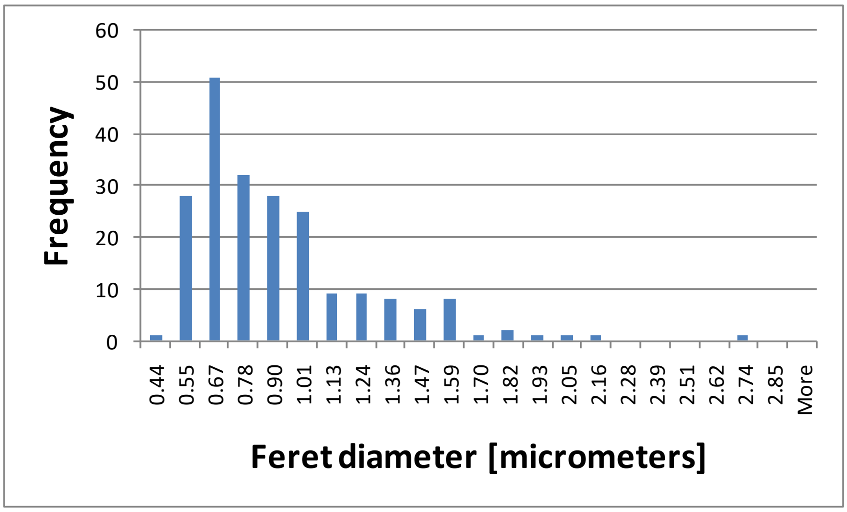


Fig. 5 Frequency distribution of the Feret diameter

The frequency distribution on the TiCN coating strongly resembles the one on the TiN coating, with a larger number of smaller particles, yet in this case 99.06% of the counted particles have a Feret diameter up to 2.05 µm.

The elemental mapping presented in Fig. 6 show a roughly uniform distribution of Ti, C and N on the surface, except a region where, given the undercut nature of the groove in the substrate, the coating is not present.

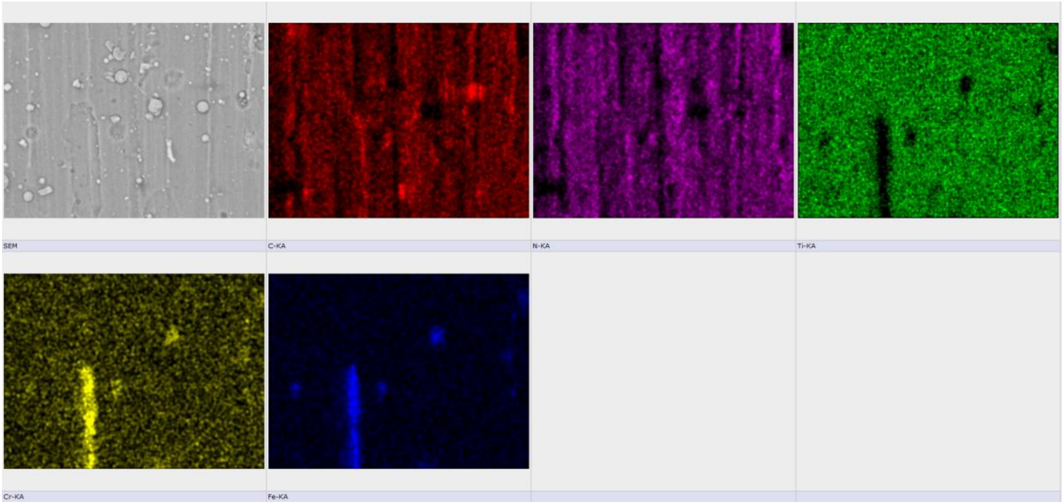
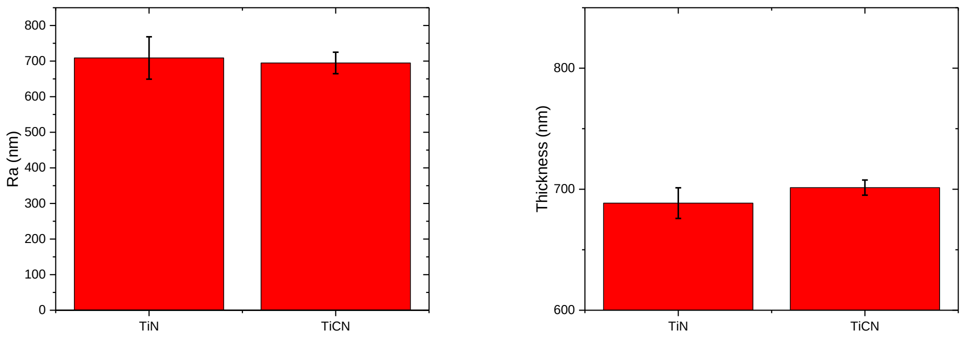


Fig. 6 Elemental mapping on the TiCN coating

Elements from the substrate, Fe and Cr are identified and appear in higher concentrations in the region without coating.

Surface roughness was determined in three regions, a comparison of the average roughness (Ra) determined for the two samples is presented in Fig. 7.a.



a. b.

Fig. 7 Comparison on a. average roughness and b. coating thickness

The average roughness samples are 708.78±59.42nm for TiN and 694.77±30.17nm for TiCN which can be considered equal from a statistical point o view, the t-test performed on the results suggests that the means are equal.

Regarding the coating thickness it can be stated that the mean values, 688±12.67nm for TiN and 701,34±6.25nm for TiCN, can be assumed to be equal from a statistical point of view. The t test result suggests an equality of the means.

A comparison regarding the Vickers microhardness results is presented in Fig. 8.

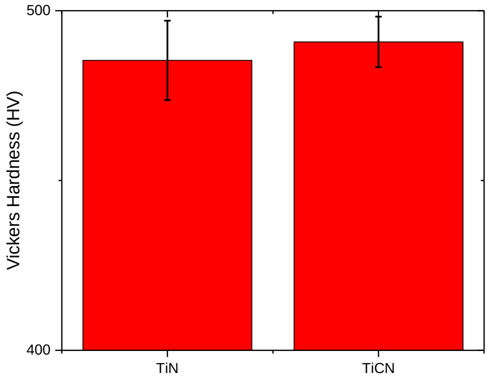


Fig. 8 Comparison of Vickers hardness values

Apparently, the hardness of the TiCN coating (490.8±7.44HV) is larger than that of the TiN coating (485.67±11.69HV), but given the spread of values, the results of the t-test performed suggest that the mean values are equal.

The hardness of TiN is, on average, 2300HV, while for TiCN a value of 3000HV is expected. In the current study a composite hardness is determined, the severe drop in values is caused by a mixed influence of substrate characteristics and layer thickness. Despite these facts a significant increase in surface hardness is present. An annealed 304 stainless steel has an average Vickers hardness of 129HV and applying the coatings the hardness almost quadruples.

4. Conclusion

Using the cathodic arc evaporation method a 304 stainless steel was coated with TiN and TiCN, the intended use being for surgical instruments. Following scanning electron microscopy studies of the coatings they were found to be homogenous and compact, with a uniform distribution on the investigated surface. Splatter was observed on both coatings, with similar distributions of the Feret diameter.

Surface roughness and layer thickness were similar for both coatings and similar Vickers microhardness values were obtained. The coatings increase the surface hardness by an almost 4 times in respect to the hardness of the substrate.

All obtained results show that the coatings are similar and it can be concluded that the process parameters for cathodic arc evaporation used for TiCN need to be optimized since it was expected to obtain a superior hardness than that of TiN.

R E F E R E N C E S

[1] *M.J. Alfa*, Monitoring and improving the effectiveness of cleaning medical and surgical devices, American Journal of Infection Control, **Vol. 41**, Issue 5 SUPPL., pp. S56-S59, 2013.
[2] *B.E.M. Zuhlsdorf, H. Floss, H. Martiny*, Cleaning efficacy of nine different cleaners in a washer-disinfector designed for flexible endoscopes, Journal of Hospital Infection, **Vol. 52**, Issue 3, pp. 206-211, 2002.
[3] *C.I. Ossai, B. Boswell, I.J. Davies*, Pipeline failures in corrosive environments - A conceptual analysis of trends and effects, Engineering Failure Analysis, **Vol. 53**, pp. 36-58, 2015.
[4] *C.M. Cotrut, A. Vladescu, I. Antoniac, A. Kiss, R. Zamfir, C.N. Zoita, M. Braic, V. Braic*, Corrosion resistance of the biocompatible nitride and carbide thin films, European Cells and Materials, **13**, 2007.
[5] *N.H. Loukil, E. Zink, S. Grandadam, M. Bientz, O. Meunier*, Effectiveness of detergent-disinfecting agents on Escherichia coli 54127 biofilm, Journal of Hospital Infection, **Vol. 57**, Issue 2, pp. 175-178, 2004.
[6] *S. Attabi, A. Himour, L. Laouar, A. Motallebzadeh*, Mechanical and wear behaviors of 316L stainless steel after ball burnishing treatment, J Mater Res Technol, **15**, pp. 3255-3267, 2021.

[7] *L. Dragomir (Nicolescu), A. Antoniac, V. Manescu (Paltanea), A. Robu, M. Dinu, I. Pana, C.M. Cotrut, E. Kamel, I. Antoniac, J. V. Rau, A. Vladescu (Dragomir)*, Preparation and characterization of hydroxyapatite coating by magnetron sputtering on Mg-Zn-Ag alloys for orthopaedic Trauma implants, Ceramics International, **49**, pp. 26274-26288, 2023.
[8] *C. Suwanpreecha, S. Songkuea, S. Linjee, S. Muengto, M. Bumrungpon, A. Manonukul*, Tensile and axial fatigue properties of AISI 316 L stainless steel fabricated by materials extrusion additive manufacturing, Mater Today Commun, **35**, Article number 105667, 2023.
[9] *I. Bordeasu, M.O. Popoviciu, I. Mitelea, B. Ghiban, N. Ghiban*, Cavitation erosion resistance of two steels with the same percentage of Chromium and Nickel but different Carbon content, International Conference On Applied Sciences (ICAS2013), **Vol. 57**, 2014.
[10] *P.M. Vilarinho, A. Mahajan, F. Sterianou, I.M. Reaney*, Layered composite thick films for dielectric applications, J. Eur. Ceram. Soc., **32** (16), pp. 4319-4326, 2012.
[11] *L. Dragomir (Nicolescu), A. Antoniac, V. Manescu, (Paltanea), A. Robu, M. Dinu, I. Pana, C.M. Cotrut, E. Kamel, I. Antoniac, J.V. Rau, A. Vladescu (Dragomir)*, Preparation and characterization of hydroxyapatite coating by magnetron sputtering on Mg-Zn-Ag alloys for orthopaedic trauma implants, Ceramics International, **Vol. 49**, pp. 26274-26288, 2023.
[12] *D. Pathote, V. Singh, D. Jaiswal, R.K. Gautam, C.K. Behera*, Improving the electrochemical corrosion behavior of stainless steel (316L) through the deposition of tantalum-based thin films, Materials Today: Proceedings, Available online 6 August 2023.
[13] *A.I. Bita, I. Antoniac, M. Miculescu, G.E. Stan, L. Leonat, A. Antoniac, B. Constantin, N. Forna*, Electrochemical and In Vitro Biological Evaluation of Bio-Active Coatings Deposited by Magnetron Sputtering onto Biocompatible Mg-0 .8Ca Alloy, Materials, **Vol. 15**, Issue 9, 2022.
[14] *B. Priyadarshini, M. Rama, Chetan, U. Vijayalakshmi*, Bioactive coating as a surface modification technique for biocompatiblemetallic implants: a review, Journal Of Asian Ceramic Societies, **Vol. 7**, NO. 4, pp. 397–406, 2019.
[15] *R.I.M. Asri, W.S.W. Harun, M. Samykano, N.A.C. Lah, S.A.C. Ghani, F. Tarlochan, M.R. Raza*, Corrosion and surface modification on biocompatible metals: A review, Materials Science and Engineering: C, Vol. 77, pp. 1261-1274, 2017.
[16] *U. Wiklund, S. Rubino, K. Kádas, N.V. Skorodumova, O. Eriksson, S. Hedberg, M. Collin, A. Olsson, K. Leifer*, Experimental and theoretical studies on stainless steel transfer onto a TiN-coated cutting tool, Acta Materialia, *Vol. 59*, Issue 1, pp. 68 – 74, 2011.
[17] *T. Polcar, R. Novák, P. Široký*, The tribological characteristics of TiCN coating at elevated temperatures, Wear, **Vol. 260**, Issue 1-2, pp. 40 – 49, 2006.
[18] *S.A. Klymenko, S.V. Lytovchenko, S.An. Klymenko, A.S. Manokhin, M.Y. Kopeykina, A.O. Chumak, Y.O. Melnychuk*, Properties of Titanium Carbonitride TiCN Coatings Obtained by Vacuum Arc Deposition, Journal of Superhard Materials, **Vol. 46**, Issue 3, pp. 204 – 211, 2024.
[19] *K. Balázsi, I.E. Lukács, S. Gurbán, M. Menyhárd, L. Bacáková, M. Vandrovcová, C. Balázsi*, Structural, mechanical and biological comparison of TiC and TiCN nanocomposites films, Journal of the European Ceramic Society, **Vol. 33**, Issue 12, pp. 2217 – 2221, 2013.