

PHASE COMPOSITION, MICROSTRUCTURE, SURFACE
HARDNESS, AND CORROSION RESISTANCE OF SURFACE
PLASMA GAS NITRIDED TITANIUM ALLOY
Ti-10V-2Fe-3Al WITH INDIRECT PLASMATRON

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Abstract

This study investigates and analyzes the influence of plasma gas nitriding with indirect plasmatron on the phase transformations, microstructure, surface microhardness, and corrosion resistance of titanium alloy Ti-10V-2Fe-3Al. In order to achieve this, the limits of the power used in this process are a minimum of 12 kW and a maximum of 35 kW. The thermochemical treatment time intervals are set at 5, 10, and 15 min. It is found that the phase composition of the surface layer after plasma gas nitriding consists of α -Ti, (N, O), TiN, and TiO₂. Titanium oxides are detected only on the outermost surface of the nitrided layers. The measured hardness of the plasma gas nitrided layers obtained of Ti-10V-2Fe-3Al is up to 650 HK0.05. Potentiodynamic polarization analysis indicates that the subjects nitrided using 18 kW of power for 15 min have the lowest corrosion rate, while the highest corrosion rate is observed in those nitrided at 25 kW for 15 min.

Key words: surface treatment, plasma spray, nitriding, indirect plasmatron, titanium alloy

Introduction. The surface of the material is the interface where interactions and chemical reactions occur, as it acts as a protective shield, providing resistance

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to corrosion or wear. Modification of surface parameters, such as morphology, hardness, and so forth, is important for enhancing the durability, longevity, and performance of the working details. For the past 70 years, titanium has gathered the attention of engineers and various research groups, and as a result of their endless efforts now, there is a variety of high-performance titanium alloys available. Titanium alloys offer a superior set of properties, but their low surface hardness and insufficient wear and abrasion resistance still limit their mechanical engineering utilization [1–4].

One of the commonly used commercial titanium alloys is Ti-10V-2Fe-3Al. Typically, this alloy is used for the construction of various structural components for the aerospace and automotive industries. For example, in each Boeing 777 alone there are over 200 different parts made of this alloy. Regarding its properties, this alloy offers excellent hardenability, high strength, and fatigue resistance. By the nature of its structure, Ti-10V-2Fe-3Al is classified as near beta titanium alloy. It consists of about 15%wt. α and β stabilizing elements, including 10% vanadium, 3% aluminum, and 2% iron. Due to the high amount of stabilizing elements, severe segregation of α and β phases can occur leading to “beta flecks” in the microstructures. During heat treatment soft beta-segregation zones surrounded by harder material are formed. This leads to the nucleation of cracks and their early propagation, which grows over time under loading conditions. Thus, the mechanical properties of titanium alloy Ti-10V-2Fe-3Al are compromised [5–8].

Over the years, different surface modification procedures, methods, and approaches are employed to improve the mechanical properties and corrosion behaviour of titanium and titanium alloys. In the field of thermochemical treatment of titanium alloys, nitriding is the most frequently used process by far. The nitriding process of titanium and its alloys has been the subject of research for many years and it has been effectively used for protection against wear. It has been found that nitrogen strengthens the surface layers significantly. However, the variety of technological processes and approaches usually take a substantial processing time. The surface plasma gas nitriding using indirect arc plasmatron operating in a chamber with a controlled nitrogen atmosphere is one of the most recently developed methods for titanium nitriding [9–12].

In the present work, the microstructure, phase transformations, and microhardness of titanium alloy Ti-10V-2Fe-3Al after plasma gas nitriding using different power for various periods of time are studied. The data on nitriding of Ti-10V-2Fe-3Al titanium alloy presented here is part of a broader study on the nanotubular growth of oxide layers on titanium, aimed at investigating the effects of various surface treatments on the material’s properties.

Experimental. Samples of titanium alloy Ti-10V-2Fe-3Al were cut on a low-speed cutting machine to dimensions of $20 \times 20 \times 4$ mm. The chemical composition and properties of the titanium alloy samples are available in [8]. Prior to nitriding the samples were mechanically ground and polished. The last polishing step was

performed using a diamond suspension of 250 nm particles. After polishing the samples were cleaned with acetone, rinsed with deionized (DI) water, and dried. Then a series of plasma gas nitriding using PPN 800 apparatus, completed with indirect plasmatron in a chamber was performed. The chamber was initially filled with high-purity (99.998%) nitrogen (N_2) gas, and a constant flow rate of 100 ml/min was maintained. The nitriding process was performed under 12 kW, 18 kW, 25 kW, and 35 kW of power for 5, 10, and 15 min. The tip of the plasmatron nozzle was placed at 120 mm from the titanium samples for the duration of all experiments. The samples were held stationary while the nozzle was set in edge-to-edge motion on their surface at a constant velocity of 4 m/min. During the plasma gas nitriding, the surface layer of the thermochemically treated samples did not melt.

For characterization of the acquired surfaces, we have used an optical microscope LM-308 equipped with a digital camera and image processing software, an X-ray diffractometer (Philips PANanalytical, using $Cu-K\alpha$ radiation), and a DVK 1-AT semi-automatic Vickers microhardness tester. A Corrtest CS350 potentiostat/galvanostat was used to evaluate the corrosion properties of the nitrided subjects. In the process, a three-electrode setup including a Pt counter electrode, an Ag/AgCl reference electrode, and a test sample used as a working electrode was used. Before testing the nitrided samples were cleaned with acetone, rinsed with DI water, and air-dried. Subsequently, the nitrided samples were exposed to a solution of sodium chloride (NaCl) having a concentration of 3.5% wt. until stable open circuit potential (OCP) was reached. After stable OCP was achieved, potentiodynamic polarization was performed. The surface area exposed to the salt solution was limited to 1 cm². All of the experiments were performed with freshly prepared solutions at room temperature.

Results and discussion. The plasma gas nitriding process induces changes in the surface colour of the thermochemically treated titanium alloy Ti-10V-2Fe-3Al, which can serve as a visual indicator for the occurrence of structural alteration. When subjected to 12 kW of power, the surface appears pale yellow, regardless of the treatment time. The nitrided samples exhibit a bright golden surface when 18 kW of power is used. Grey shades were observed on the nitrided surfaces after 5 min of treatment using both 25 kW and 35 kW of power. After 10 min, as well as 15 min of treatment, using the same power, the nitrided surfaces acquire a brownish-red hue.

Phase analysis. The phase composition of the plasma gas nitrided Ti-10V-2Fe-3Al samples has been studied in a series of experiments employing different technological regimes. Phase analysis of the plasma gas nitrided samples using power in the range of 12 kW to 35 kW shows that the surface of titanium alloy Ti-10V-2Fe-3Al consists of α -Ti(N, O), TiN, and TiO₂. X-ray diffraction patterns exhibiting the phase composition of the substrate material, before and after plasma gas nitriding for different periods of time are displayed in Fig. 1.

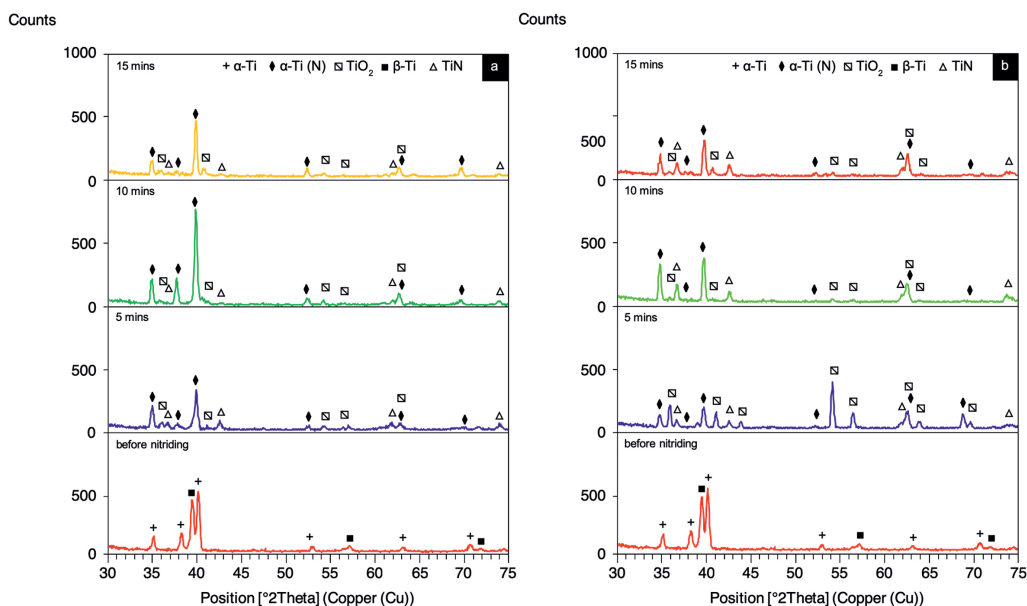


Fig. 1. Diffraction patterns and phase analysis of Ti-10V-2Fe-3Al before and after plasma gas nitriding for 5, 10, and 15 min using a) 25 kW, b) 35 kW of power

Initially, the studied samples are composed of α -Ti + β -Ti. The overall reaction that takes place during the nitriding process can be depicted as α -Ti + β -Ti $\rightarrow$ α -Ti(N) + TiN + TiO_2 . Analysis of the chemical composition shows that the same phases are present on the nitrided surfaces, regardless of the used nitriding regime. Despite the fact that Ti-10V-2Fe-3Al contains a large amount of vanadium, no compounds including vanadium were detected on the plasma gas nitrided surfaces.

Microstructure. Optical micrographs showing cross sections of plasma gas nitrided Ti-10V-2Fe-3Al samples with indirect plasmatron, using 12 kW, 18 kW, 25 kW, and 35 kW of power, for 5 and 15 min are available in Fig. 2.

Analysis of the microstructure indicates the presence of three zones: a composite layer covering the outermost surface, a diffusion zone, and the base material. The surface composite layer is continuous, and uniform, and its thickness varies depending on the employed nitriding regime. In the samples nitrided at 35 kW for 15 min it can reach up to 10 μm . Below the composite layer, a diffusion zone is formed.

The microstructure of all plasma gas nitrided samples using 12 kW of power appears homogenous. As the power increases, the microstructure acquires a more pronounced inhomogeneous appearance. This is probably related to both the heat transfer mechanisms as well as the resulting phase transformations. The increase of power normally leads to higher temperatures on the thermochemically treated surfaces of the titanium alloy subjects, while the process duration allows the growth of thicker nitrided surface layers. Using that amount of power presumably leads to temperatures higher than the β -transus for Ti-10V-2Fe-3Al.

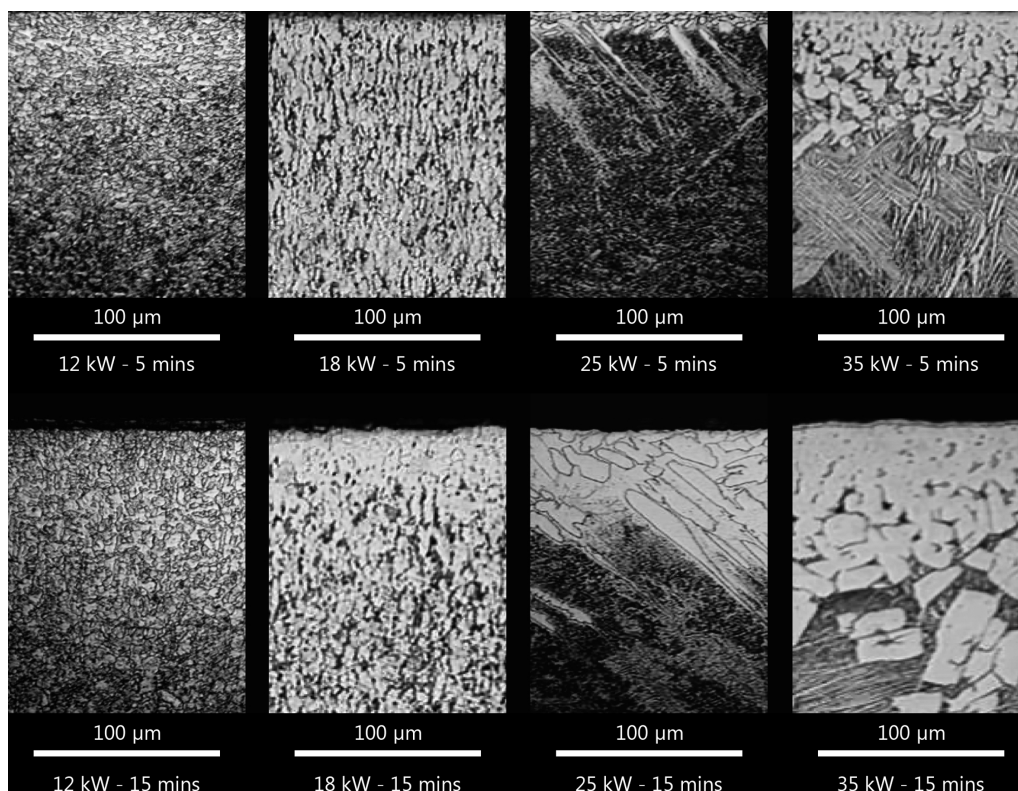


Fig. 2. Optical micrographs of plasma gas nitrided Ti-10V-2Fe-3Al samples with indirect plasmatron, using 12 kW, 18 kW, 25 kW, and 35 kW of power, for 5 and 15 min

A general observation in this study is that the thickness of a nitrided layer tends to increase with higher power and longer treatment time. The thickness of the layers obtained within the scope of this research falls within the range of approximately 50 μm to 350 μm . However, determining the exact thickness of a nitrided layer from microstructural images can be challenging due to the absence of a distinct boundary between the diffusion zone and the substrate.

Microhardness. Figure 3 exhibits the influence of power and treatment time on the microhardness of the plasma gas nitrided samples with indirect plasmatron. In addition to the observations of the microstructure, the thickness of the plasma gas nitrided layers can be detected using a microhardness profile of a cross-section such as those displayed in Fig. 3a. The conducted analysis of the microhardness of the plasma gas nitrided Ti-10V-2Fe-3Al samples confirms that the thickness of the nitrided layers is in the mentioned range.

The results obtained from the microhardness analysis indicate a clear trend of increasing surface hardness of the plasma gas nitrided Ti-10V-2Fe-3Al alloy with higher power levels. Similarly, a consistent increase in surface hardness is observed with longer treatment times, ranging from 5 to 15 min. These findings suggest

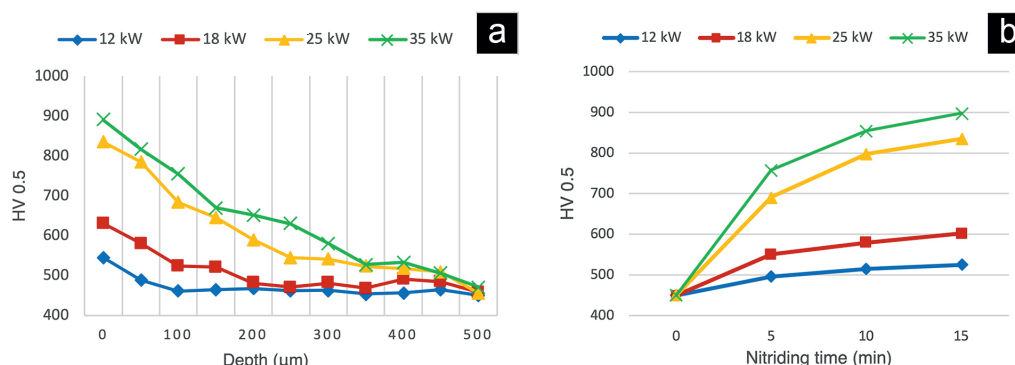


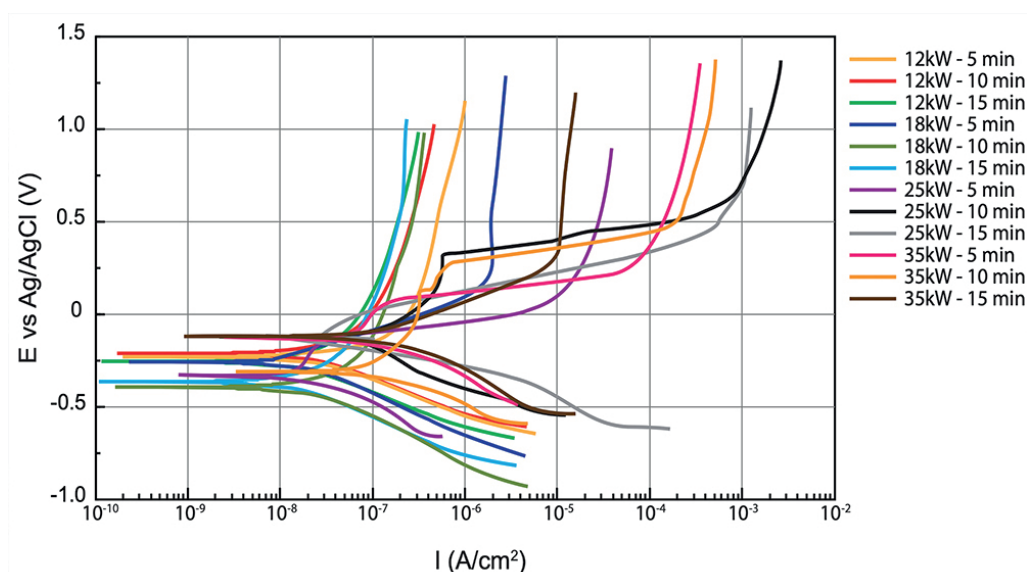
Fig. 3. Microhardness of Ti-10V-2Fe-3Al after plasma gas nitriding with indirect plasmatron using 12 kW, 18 kW, 25 kW, and 35 kW of power a) measured cross sections after 15 min of treatment, b) measured on the surface vs. treatment time

that both power and time have an impact on the microhardness of the nitrided surface layers. Perhaps, the elevated microhardness of the layers produced using higher power and longer treatment time may be attributed to greater nitrogen diffusion into the titanium alloy and the subsequent formation of larger amounts of nitride phases.

Corrosion resistance. The corrosion resistance of the plasma gas nitrided Ti-10V-2Fe-3Al samples was evaluated by potentiodynamic polarization tests in 3.5% NaCl solution at room temperature. The results, illustrated by the obtained polarization curves and the extracted corrosion parameters are available in Fig. 4.

The results obtained during the electrochemical tests show that all of the plasma gas nitrided samples with indirect plasmatron demonstrate excellent corrosion resistance, which is typical for nitrided titanium alloys in general. However, the corrosion rates show variation across different regimes and treatment times. Further analysis reveals that the samples nitrided using lower power levels (12 kW and 18 kW) exhibit slightly better corrosion resistance compared to those nitrided at higher power levels (25 kW and 35 kW). Moreover, for the samples nitrided at 12 kW and 18 kW, the corrosion resistance tends to improve with the increased duration of the thermochemical treatment. In contrast, for the samples nitrided at 25 kW and 35 kW of power the corrosion resistance tends to decrease, particularly in the interval between 10 to 15 min of treatment. It was found that the best corrosion resistance was exhibited by the samples nitrided at 18 kW for 15 min, while those nitrided at 25 kW and 35 kW of power for 15 min show the highest corrosion rate.

Conclusions. Plasma gas nitriding was successfully performed on the Ti-10V-2Fe-3Al titanium alloy using an indirect plasmatron, varying the power (12 kW, 18 kW, 25 kW, and 35 kW) and treatment time (5, 10, and 15 min) to investigate the resulting effects on microstructure, microhardness, and corrosion resistance. The results obtained in this study are summarized as follows:



Regime	CR (mm/a)	E_{corr} (Volts)	i_{corr} (A/cm ²)
12 kW - 5 min	0.0029587	-0.21982	2.5223E-07
12 kW - 10 min	0.0028313	-0.21035	2.4134E-07
12 kW - 15 min	0.0010223	-0.25619	6.0332E-08
18 kW - 5 min	0.0010479	-0.26259	6.1841E-08
18 kW - 10 min	0.0005050	-0.38597	2.9802E-08
18 kW - 15 min	0.0004810	-0.36759	2.8383E-08
25 kW - 5 min	0.0039095	-0.32312	2.3071E-07
25 kW - 10 min	0.0039671	-0.12374	3.3796E-07
25 kW - 15 min	0.0055611	-0.12031	3.2818E-08
35 kW - 5 min	0.0038516	-0.12014	3.2812E-07
35 kW - 10 min	0.0038328	-0.31678	2.2619E-07
35 kW - 15 min	0.0054612	-0.11814	3.2227E-08

Fig. 4. Potentiodynamic polarization results of plasma gas nitrided Ti-10V-2Fe-3Al samples with indirect plasmatron tested in 3.5% NaCl

1. The phase composition of the outermost surface layer after plasma gas nitriding consists of α -Ti (N, O), TiN, and TiO₂. Titanium oxides are formed only on the outermost part of the sample surface.

2. The microstructure of the plasma-nitrided Ti-10V-2Fe-3Al alloy using 12 kW and 18 kW of power for the studied periods of time appears uniform. However, with the increase of power levels, the formed nitrided layers exhibit a non-uniform microstructure regardless of the treatment time.
3. The thickness of the nitrided layers depends on the specific nitriding conditions, including time and temperature. The estimation of the nitrided layers thickness is based on observation of micrographs as well as measurements of microhardness. It ranges between 50 μm and 350 μm , depending on the employed particular process parameters.
4. During the nitriding process, using higher power levels and longer duration results in increased surface microhardness. This is attributed to the formation of the newly formed titanium nitride phases.
5. All of the studied samples demonstrate excellent corrosion resistance. Nevertheless, it was found that the thermochemically treated samples using 18 kW for 15 min demonstrated the highest resistance to corrosion in a 3.5% NaCl solution. However, the samples nitrided using 25 and 35 kW of power for 15 min exhibit slightly increased susceptibility to corrosion in the used saline media.

REFERENCES

- [1] GUPTA M. K., H. E. ETRI, M. E. KORKMAZ, N. S. ROSS, G. M. KROLCHYK et al. (2022) Tribological and surface morphological characteristics of titanium alloys: a review, *Archiv. Civ. Mech. Eng.*, **22**, 72, <https://doi.org/10.1007/s43452-022-00392-x>.
- [2] JACKSON M. J., J. KOPAC, M. BALAZIC, D. BOMBAC, M. BROJAN et al. (2016) Titanium and Titanium Alloy Applications in Medicine. In: *Surgical Tools and Medical Devices* (eds W. Ahmed, M. Jackson), Springer, Cham., https://doi.org/10.1007/978-3-319-33489-9_15.
- [3] LEYENS C., M. PETERS (2003) *Titanium and Titanium Alloys: Fundamentals and Applications*, John Wiley & Sons.
- [4] GORYNIN I. V. (1999) Titanium alloys for marine application, *Mater. Sci. Eng. A*, **263**(2), 112–116, [https://doi.org/10.1016/S0921-5093\(98\)01180-0](https://doi.org/10.1016/S0921-5093(98)01180-0).
- [5] YANG Y. F., S. D. LUO, G. B. SCHAFFER, M. QIAN (2011) Sintering of Ti-10V-2Fe-3Al and mechanical properties, *Mater. Sci. Eng. A*, **528**(22–23), 6719–6726, <https://doi.org/10.1016/j.msea.2011.05.041>.
- [6] LI L., X. ZHANG, Z. LI, Z. WANG, W. MA (2018) The mechanical behaviours of the Ti-10V-2Fe-3Al alloy under the high-temperature and dynamic loading conditions, *EPJ Web of Conferences*, **183**, 02008, <https://doi.org/10.1051/epjconf/201818302008>.
- [7] ZENG W. D., Y. G. ZHOU (1999) Effect of beta flecks on mechanical properties of Ti-10V-2Fe-3Al alloy, *Mater. Sci. Eng. A*, **260**(1–2), 203–211, [https://doi.org/10.1016/S0921-5093\(98\)00954-X](https://doi.org/10.1016/S0921-5093(98)00954-X).

- [8] <https://www.timet.com/assets/local/documents/datasheets/metastablebetaalloys/10-2-3.pdf>, accessed: 24.06.2023.
- [9] SKULEV H., D. VESELINOV (2021) Study on the influence of the technological parameters over the corrosion behavior and surface characterization of Ti-6Al-4V and Ti-6Al-7Nb alloys after plasma gas nitriding. In: Proc. UNITECH 2021, **2**, II-68–II-72.
- [10] DROUET M., L. PICHON, Y. VALLET, E. LE BOURHIS, T.L. CHRISTIANSEN (2022) Surface engineering of titanium alloy TiAl6V4 by multi-interstitial diffusion using plasma processing, Eur. J. Mater., **2**(1), 1–11, <https://doi.org/10.1080/26889277.2021.2010504>.
- [11] FRĄCZEK T., M. OLEJNIK, A. TOKARZ (2009) Evaluation of plasma nitriding efficiency of titanium alloys for medical applications, Metalurgija (Sisak), **48**(2), 83–86, ISSN 0543-5846.
- [12] SANTECCHIA E., A.M.S. HAMOUDA, F. MUSHARAVATI, E. ZALNEZHAD, M. CABIBBO et al. (2015) Wear resistance investigation of titanium nitride-based coatings, Ceramics Int., **41**(9), 10349–10379, <https://doi.org/10.1016/j.ceramint.2015.04.152>.

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