

## RESEARCH INTO MORPHOLOGY AND PROPERTIES OF TiO<sub>2</sub> – NiAl ATMOSPHERIC PLASMA SPRAYED COATING

Andrzej Maruszczuk<sup>1</sup>, Agata Dudek<sup>2</sup>, Mirosław Szala<sup>3</sup>

<sup>1</sup> Institute of Materials Engineering, Częstochowa University of Technology, Armii Krajowej 19, 42-200 Częstochowa, Poland, e-mail: amaruszczyk@gmail.com

<sup>2</sup> Institute of Materials Engineering, Częstochowa University of Technology, Armii Krajowej 19, 42-200 Częstochowa, Poland, e-mail: dudek@wip.pcz.pl

<sup>3</sup> Department of Materials Engineering, Mechanical Engineering Faculty, Lublin University of Technology, 36 Nadbystrzycka St., 20-618 Lublin, Poland, email: m.szala@pollub.pl

Received: 2017.05.15

Accepted: 2017.08.01

Published: 2017.09.03

### ABSTRACT

Titania (TiO<sub>2</sub>) based coatings are ceramic products with unique properties that make them widely applicable (e.g. in automotive industry, optoelectronics, chemical processing or medicine). Atmospheric plasma spray process enables to deposit TiO<sub>2</sub> with addition of NiAl feedstock material which has an influence on coating cohesion and adhesion to substrate. However, the literature and technical notes give little information about parameters of spraying of TiO<sub>2</sub>-10 wt.% NiAl feedstock powders enables producing coating without nonuniformities including cracks and delamination form substrate. The aim of the work was to verify the parameters of plasma spraying by evaluation of the morphology and properties of manufactured the TiO<sub>2</sub>-10 wt.% NiAl coatings. Titania based coatings were deposited by means of atmospheric plasma sprayed on steel substrate using TiO<sub>2</sub>-10 wt.% NiAl feedstock powders. Morphology and microstructure were examined using light optical microscope (LOM) and scanning electron microscope (SEM). Coating chemical composition were analysed by means of SEM-EDS method. Coating surface topography and Knoop microhardness were determined. Porosity and thickness were evaluated by using quantities image analysis programme. Plasma spraying parameters used in our research allow to obtain uniform coating without cracks and delamination at coating-substrate interface. It acknowledges that uniformity of coating technological properties as well manufactured coatings can be put to wear tests, such as high temperature oxidation, corrosion, erosion or cavitation erosion resistance evaluation.

**Keywords:** microstructure, titania, TiO<sub>2</sub>-NiAl, atmospheric plasma spray, TiO<sub>2</sub> coating, lamellae, microhardness, porosity.

### INTRODUCTION

Titania (TiO<sub>2</sub>) based coatings are manufactured with different methods such as thermal spray processes (e.g. plasma arc, electric arc, flame or kinetic). Atmospheric plasma arc (APS) is one of the particularly used in industry applications of thermal spray process, and Fig. 1 illustrates idea of APS. In plasma sprayed coatings, the hot gas jet

created by a plasma arc expands, entrains powder particles, heats the particles, and accelerates them toward the substrate, where they impact, deform, and resolidify to form a coating. Plasma sprayed coating exhibits higher deposit densities and bond strengths compared to most flame and electric arc spray coatings. The low porosity of plasma sprayed coatings can equal that of high-velocity oxyfuel and detonation-gun-type coatings [5, 12,

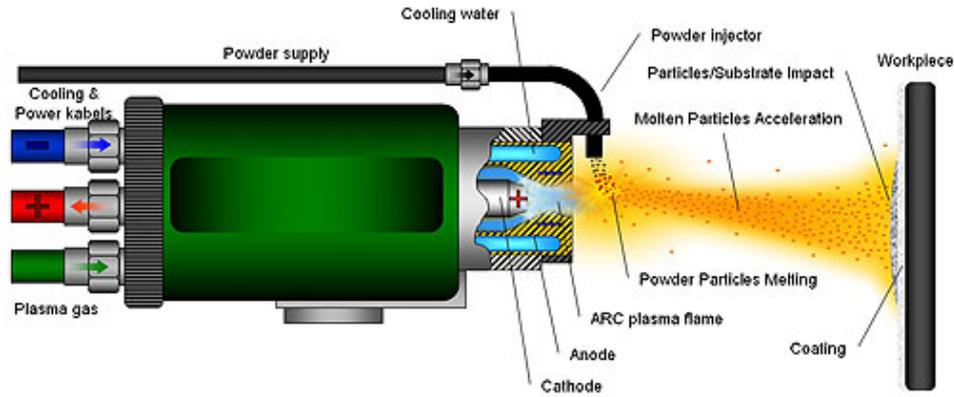


Fig. 1. Plasma spray process [28]

13, 18]. Plasma spraying method enables to constitute resistant to wear coating [1, 4, 11–13, 17, 19, 21, 22] with properties comparable to overlay padded coatings [5, 12, 23, 24]. APS process is a very perspective method enables producing metal, ceramic and composite coatings therefore APS coatings are considered as good candidates for application on different substrates (e.g. iron, titanium, magnesium, cobalt, nickel and aluminium based alloys) [5, 7, 10, 12, 13, 18, 23, 25, 26].

Plasma sprayed coatings incorporate properties such as the wear resistance, as a thermal barrier coatings (TBC) resistant to high temperature and oxidation hence are widely applicable for elements of aero gas turbine, in energetics industry, combustion chamber and diesel engines e.g.  $\text{TiO}_2$ - $\text{Al}_2\text{O}_3$  [11]. Medical application of hydroxyapatite APS coating is systematically studied. Hydroxyapatites modified with zirconium are deposited on the surface of implants [6]. In optoelectronics and production of photovoltaics panels, as well as in chemical processing to neutralize  $\text{NO}_x$  and  $\text{SO}_x$  compounds,  $\text{TiO}_2$  coatings are implemented [5, 6, 12, 13, 27]. Moreover,  $\text{TiO}_2$  coatings with addition of NiAl can be sprayed on engine elements because of their resistance do high temperature oxidation and creep [3, 5, 12, 13]. However, microstructure and properties of  $\text{TiO}_2$  with addition of  $\text{Al}_2\text{O}_3$  powders are discussed in particular, as stated in the literature [11, 16, 20]. In the specialised literature and technical notes, a little information about coatings deposited with  $\text{TiO}_2$ -10 wt.% NiAl feedstock powder is given.

As a result of literature survey it can be stated that coating adhesion to substrate, sprayed coating morphology and hardness are crucial features which influence the operating properties of coated

machine parts and elements. The improvement of materials used in plasma sprayed coatings processes exact detailed study of the morphology of coating [2, 7, 14, 20]. Moreover, the influence of plasma spraying process parameters on properties of coatings is systematically studied [4, 8, 15]. For industry applications coating adhesion to substrate is crucial. Manufacturing coatings without defects including such as coating cracks and delamination in substrate-coating zone is a substantial issue. The literature provides a little information about parameters of spraying of  $\text{TiO}_2$ -10 wt.% NiAl feedstock which enables producing coating with demanded morphology and properties.

The aim of the work was to verify the parameters of plasma spraying by evaluation of the morphology and properties of manufactured the  $\text{TiO}_2$ -10 wt.% NiAl coatings.

## MATERIAL AND METHODS

In the present study mixture of  $\text{TiO}_2$  with the 10 wt. % of NiAl powder was used as feedstock and deposited on low alloyed steel plates grade 40Cr4 (nominal hardness 208-252 HBW and chemical composition: 0,35-0,45% C, 0,-0,9% Mn, 0,1-0,35% Si, Ni 0-0,15%, Cr 0,9-1,2%, V 0,05%, Sn 0,02%, max. 0,35% S, Fe – rest [29]). Thickness of substrate equals 5 mm. Before spraying steel surface was sandblasted and chemically cleaned. Coating was produced using atmospheric plasma spraying (APS) process by means of Plamotron PN-200 facility. The APS parameters used to fabricate the  $\text{TiO}_2$ -10 wt.% NiAl coatings are given in Table 1.

The specimens were cut out from coated steel plates. Microstructure of coatings on the top sur-

**Table 1.** APS spraying parameters for TiO<sub>2</sub>-NiAl coatings

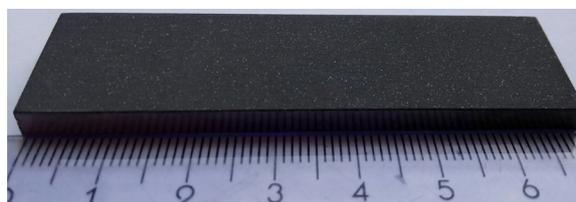
Current intensity	Arc voltage	Distance of torch tip to substrate	Plasma gases mixture	
			Type of gas	Flow rate
350 A	50 V	100 mm	argon	3 m <sup>3</sup> /h
			hydrogen	0,5 m <sup>3</sup> /h

face and cross section specimen were studied. Metallographic specimens were prepared by grinding and polishing. With the use of Light optical microscope (LOM) type Axiovert 25 (prod. Carl Zeiss) and scanning electron microscope (SEM) type JSM-6610LV (prod. JEOL) equipped with LaB<sub>6</sub> electron gun and energy dispersive X-ray analyser (EDS), the coating structure was investigated. The presence of coating cracks and coating-substrate delamination was examined. Coating porosity was determined by image processing programme (prod. ImagePro) on the basis of LOM microstructure. To recognize microstructure uniformity of the coating, a chemical microanalysis was conducted, using SEM-EDS method. The morphology of surface of coating with different magnifications was estimated by means of SEM method. The topography was investigated using a special scanning electron microscope mode with surface roughness measurement programme. The plasma sprayed coatings, as well as substrate hardness, were measured using Knopp hardness tester. Microhardness tester FM-800 (Future Tech) was employed to achieve the microhardness indentation measurements. Parameters including load 0,025 kG, and dwelling time 10 s were used. Indentations in samples cross-section at random locations were made. To enable comparison, the results of Knopp (HK) hardness measurements according to ASTM E140 standard to Vickers (HV) and Brinell (HBW) parameters were converted.

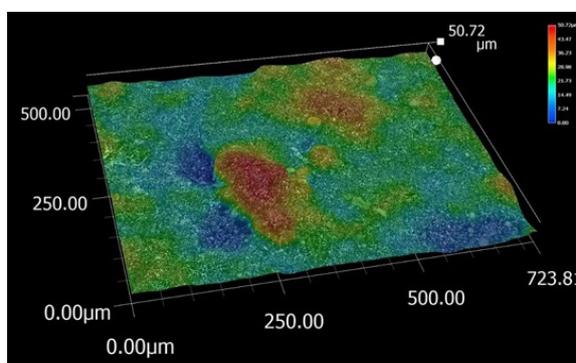
**RESULTS AND DISCUSSION**

Manufactured TiO<sub>2</sub>-10 wt.% NiAl plasma sprayed coating is shown in Fig. 2. The results presented in Fig. 2 and Fig. 3 confirm that topography of coating surface was uniform. The reported range between pits and hills equals no more than 50 μm (Fig. 3). Uniform and repeatable surfaces stereometry parameters can have beneficial effect for prevention of friction wear.

Fig. 4 and Fig. 5 present microstructure of coatings obtained with various magnifications, using LOM and SEM respectively. The results of the chemical analysis in specific microstruc-



**Fig. 2.** TiO<sub>2</sub>-NiAl plasma sprayed coating manufactured on steel substrate (scale in mm)



**Fig. 3.** Coating surface topography, SEM

ture phases is presented in Fig. 6. The analysis of microscopic study revealed the structures typical for sprayed coatings, i.e. lamellar particle shapes, porosity and presence of non-melted or partially-melted particles of the feedstock powders (visible as brighter areas in Fig. 4). In the samples cross-section, the coating porosity (dark areas in Fig. 4) can be recognised. Based on quantitative image analysis, the coating porosity was determined at 5%, and average coating thickness was determined as 50 μm. Lamellar microstructure is clearly visible in Fig. 4C, Fig. 5 and Fig. 6. Non-melted or partially-melted particles corresponding to NiAl particles are the clearest areas in Fig. 5 and Fig. 6. Microstructural observations are in accordance with the chemical composition measurements. The chemical microanalysis reveals the presence of titanium and oxygen elements in the darkest lamellar coating areas (Fig. 6A), as well as mainly aluminium and nickel elements in clearest structure phases (Fig. 6B) correspond-

ing to Titania lamellar matrix, and non-melted of partially-melted NiAl particles. Mixture of  $\text{TiO}_2$  with 10 wt.% NiAl is advantageous to increase the coating cohesion and the adherence of coating to substrate. Salman and Cizmeciglu [21] present research done with and without NiAl bonding coating for different ceramic coatings. They conclude that the improvement of the NiAl bonding coating application was obtained due to the exothermic reaction that occurred during the coating process.

Manufactured coating does not demonstrate cracks or delamination; therefore the parameters of coatings plasma spraying were adequate. Uniform morphology of coating was acknowledged. Interface coating – substrate demonstrates the presence of porosity and various depth of surface pores penetration by coating material. Kromer et al. claim [14] that pores near the interface would be localized as zones for crack initiations and propagations. In their work, the authors proposed to enhance adhesion bond strength for thermal spray process for small and large in-contact area proper volume particles and topography parameters. The results of microscopic and hardness examination indicate that  $\text{TiO}_2$ -10 wt.% NiAl plasma sprayed feedstock forms uniform coating.

Coatings cross-section hardness measurements are presented in Fig. 7. Bertrand et al. [2] described that the hardness values published for the rutile  $\text{TiO}_2$  are between 580 and 700 HK and the values commonly measured for the anatase  $\text{TiO}_2$  are between 550 and 580 HK. The results obtained for coating microhardness measurements  $602 \pm 5$  HK are on the similar level as presented in [2], however the lower level than hardness depicted for  $\text{TiO}_2$  [8, 9] and  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  [16, 19] plasma sprayed coatings. It indicates the influence of plasma spraying process on hardness results. Measured hardness of plasma sprayed coating was more than two times higher than steel substrate Fig. 7. Spread of Knopp hardness measurements of  $\text{TiO}_2$ -NiAl coating equals 10 HK. Such restrained hardness values acknowledge about technological uniformity of coating properties.

## CONCLUSIONS

In the work the parameters of plasma spraying were positively verified by evaluating the morphology and properties of manufactured the  $\text{TiO}_2$ -10 wt.% NiAl coatings. The results demonstrated that plasma sprayed parameters allow to obtain uniform coating without cracks and delamination at

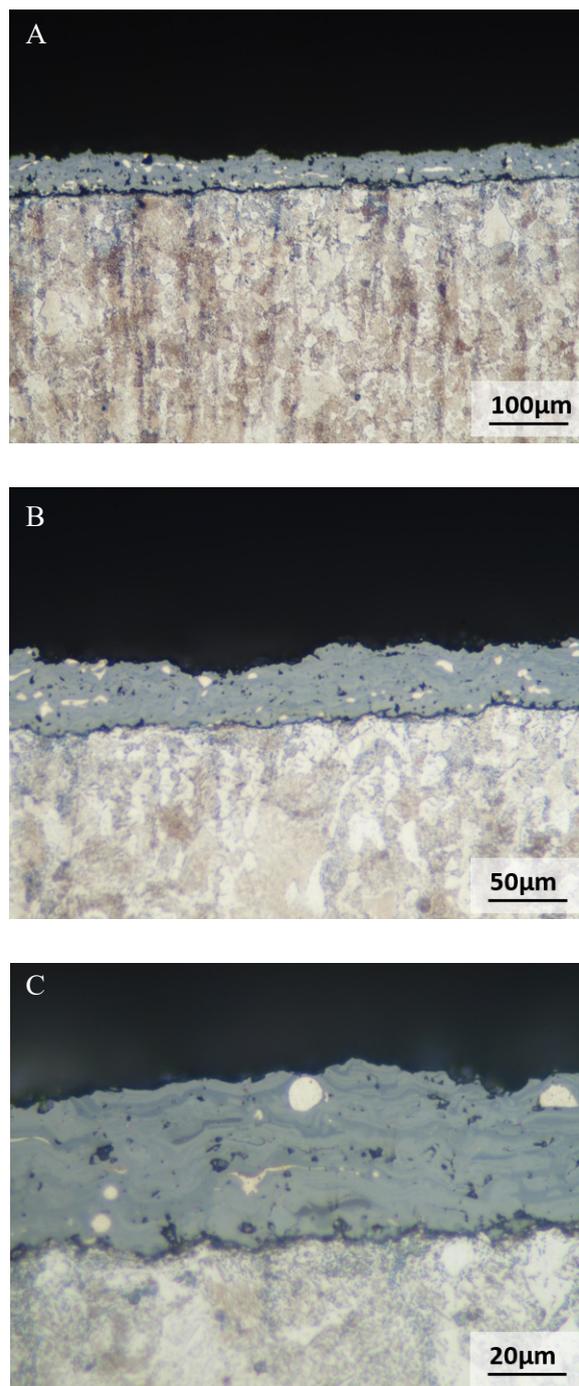


Fig. 4. Cross-section of plasma sprayed  $\text{TiO}_2$ -NiAl and substrate, LOM

coating-substrate interface. Therefore, it acknowledged about uniformity of coating technological properties thus manufactured coatings can be put to wear tests, such as high temperature oxidation, corrosion and erosion resistance evaluation.

Titania ( $\text{TiO}_2$ ) based coatings are ceramic products with unique properties that make them widely applicable (e.g. in automotive or heavy industry, for engine elements or as biomaterial

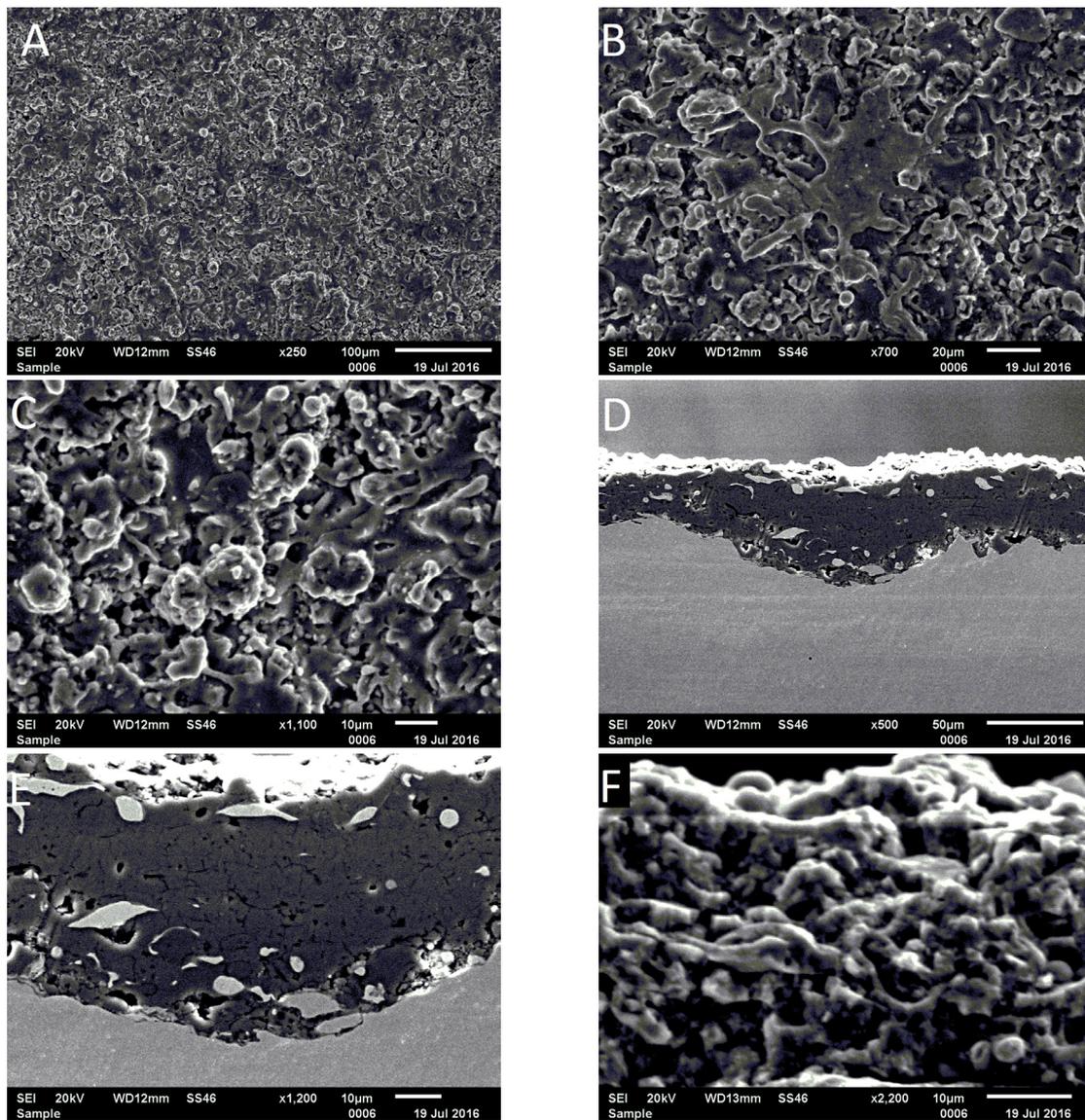


Fig. 5. Morphology of specimen, surface view (a, b, c) and cross-section (d, e, f), SEM

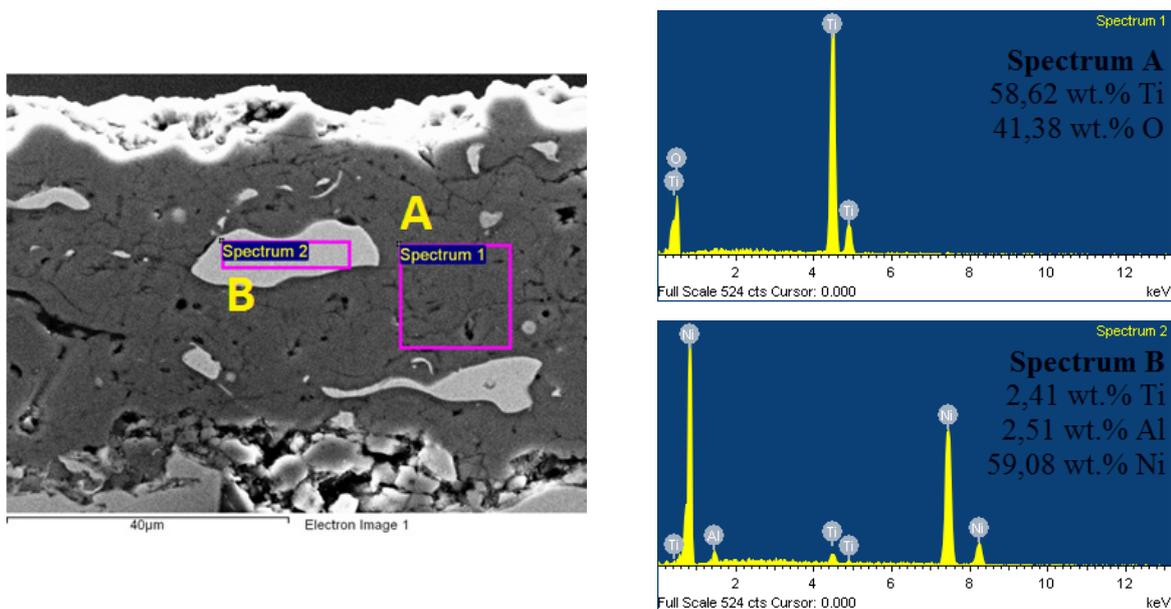
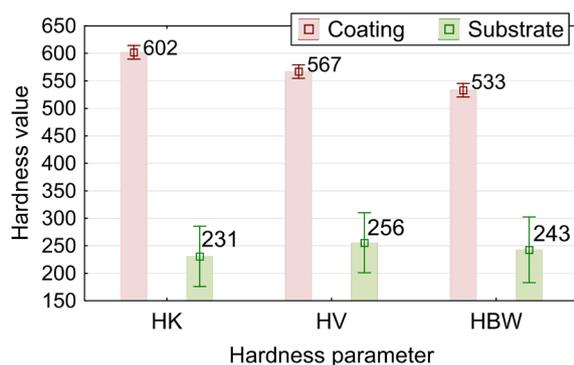


Fig. 6. Results of chemical analysis of coating cross-section, SEM-EDS



**Fig. 7.** TiO<sub>2</sub>-NiAl coating and steel substrate hardness, average value and range

coatings). NiAl addition positively influences on coating cohesion and adhesion to substrate. Morphology and uniformity of technological parameters are crucial in coating exploitation.

Measured thickness of manufactured TiO<sub>2</sub>-10 wt.% NiAl coating equals 50 μm, and the porosity was determined at 5% and Knoop hardness in range of 602±5 HK. The microscopic analysis (LOM, SEM-EDS) revealed the structures typical of plasma sprayed coatings, i.e. laminar particle shapes, porosity and presence of non-melted or partially-melted particles of the feedstock powders (corresponding to NiAl). Topography and hardness measurements indicated that plasma sprayed TiO<sub>2</sub>-10 wt.% NiAl feedstock forms uniform coating.

## REFERENCES

- Berkowski L.: Influence of the state of the surface on properties of coats after metal spraying. *Journal of Research and Applications in Agricultural Engineering*. 50 (3), 2005, 11–14.
- Bertrand G. et al.: Evaluation of metastable phase and microhardness on plasma sprayed titania coatings. *Surface and Coatings Technology*. 200 (16), 2006, 5013–5019.
- Bordes M.C. et al.: Application of plasma-sprayed TiO<sub>2</sub> coatings for industrial (tannery) wastewater treatment. *Ceramics International*. 41 (10), 2015, 14468–14474.
- Bordes M.C. et al.: Preparation of feedstocks from nano/submicron-sized TiO<sub>2</sub> particles to obtain photocatalytic coatings by atmospheric plasma spraying. *Ceramics International*. 40 (10), 2014, 16213–16225.
- Davis J.R.: *Handbook of Thermal Spray Technology*. ASM International 2004.
- Dudek A.: *Kształtowanie własności użytkowych biomateriałów metalicznych i ceramicznych*. Częstochowa 2010.
- Dudek A., Adamczyk L.: Properties of hydroxyapatite layers used for implant coatings. *Optica Applicata*. 43 (1), 2013.
- Forghani S.M. et al.: Effects of plasma spray parameters on TiO<sub>2</sub>-coated mild steel using design of experiment (DoE) approach. *Ceramics International*. 39 (3), 2013, 3121–3127.
- Gardon M. et al.: Improved, high conductivity titanium sub-oxide coated electrodes obtained by Atmospheric Plasma Spray. *Journal of Power Sources*. 238, 2013, 430–434.
- Gontarz A., Dziubińska A.: A new method for producing magnesium alloy twin-rib aircraft brackets. *Aircraft Eng & Aerospace Tech*. 87 (2), 2015, 180–188.
- Hejwowski T.: Comparative study of thermal barrier coatings for internal combustion engine. *Vacuum*. 85 (5), 2010, 610–616.
- Hejwowski T.: *Nowoczesne powłoki nakładane cieplnie odporne na zużycie ścierne i erozyjne*. Politechnika Lubelska, Lublin 2013.
- Klimpel A.: *Napawanie i natryskiwanie cieplne: technologie*. WNT, Warszawa 2009.
- Kromer R. et al.: Role of Powder Granulometry and Substrate Topography in Adhesion Strength of Thermal Spray Coatings. *J Therm Spray Tech*. 25 (5), 2016, 933–945.
- Łatka L. et al.: Thermal diffusivity and conductivity of yttria stabilized zirconia coatings obtained by suspension plasma spraying. *Surface and Coatings Technology*. 208, 2010, 87–91.
- Luo H. et al.: Alternant phase distribution and wear mechanical properties of an Al<sub>2</sub>O<sub>3</sub>-40 wt%TiO<sub>2</sub> composite coating. *Ceramics International*. 43 (9), 2017, 7295–7304.
- Madej M., Ozimina D.: Właściwości powłok kompozytowych natryskiwanych naddźwiękowo metodą HP/HVOF. *Inżynieria Maszyn*. 16 (4), 2011, 75–84.
- Morel S.: *Powłoki natryskiwane cieplnie*. Wydawnictwo Politechniki Częstochowskiej, Częstochowa 1997.
- Morks M.F., Akimoto K.: The role of nozzle diameter on the microstructure and abrasion wear resistance of plasma sprayed composite coatings. *Journal of Manufacturing Processes*. 10 (1), 2008, 1–5.
- Palacio, C.C. et al.: Effect of the mechanical properties on drilling resistance of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> coatings manufactured by atmospheric plasma spraying. *Surface and Coatings Technology*. 220, 2013, 144–148.
- Salman S., Cizmecioglu Z.: Studies of the correla-

- tion between wear behaviour and bonding strength in two types of ceramic coating. *Journal of Materials Science*. 33 (16), 1998, 4207–4212.
22. Szala M. et al.: Cavitation erosion resistance of Ni-Co based coatings. *Advances in Science and Technology Research Journal*. 21 (8), 2014, 36–42.
23. Szala M.: Coatings for increasing cavitation wear resistance of machine parts and elements - Thesis for doctore degree. Lublin University of Technology, Lublin 2016.
24. Szala M., Hejwowski T.: Improvement of cavitation erosion resistance of metal alloys by pad welding of coatings. *Przegląd Spawalnictwa - Welding Technology Review*. 87 (9), 2015, 56–60.
25. Szala M., Łukasik D.: Cavitation wear of pump impellers. *Journal of Technology and Exploitation in Mechanical Engineering*. 2 (1), 2016, 40–44.
26. Thirumalaikumarasamy D. et al.: Effect of experimental parameters on the micro hardness of plasma sprayed alumina coatings on AZ31B magnesium alloy. *Journal of Magnesium and Alloys*. 3 (3), 2015, 237–246.
27. Vismaya, S., Sunil, H.: Study on the factors affecting photocatalytic behavior of titania coatings using different plasma spray proces. *Internacional Journal of Technical Research, and Applications*. 3, 2015, 255–265.
28. Plasma Spraying - Plasma Spray Coating, <http://www.ep-coatings.co.uk/processes/plasma-spraying/>.
29. Total Materia - The world's most comprehensive materials database, <http://www.totalmateria.com/>.