# ASSESSMENT OF PROPERTIES THERMAL SPRAYED COATINGS REALISED USING CERMET BLEND POWDER

Received – Prispjelo: 2013-11-18 Accepted – Prihvaćeno: 2014-04-20 Preliminary Note – prethodno priopćenje

The article deals with the assessment of selected properties of plasma sprayed coatings based on  $ZrSiO_4$  doped with different volume fractions of metal dopant (Ni). Mixed powders are cermet blends. Aim of the work consists of verificating the possibility to replace the application of Ni interlayer by adding Ni directly to the ceramic powder and apply them together in a single technological operation. The coatings were studied from point of view of their structure, porosity, adhesion of the coatings in relation to the volume of dopant added and wear resistance. The best properties reached composite coating doped with 12 % Ni.

Key words: plasma spraying, composite ceramic coatings, adhesion, porosity, wear.

## INTRODUCTION

Thermal spraying technology of ceramic coatings is very frequent possibility for improving the functional properties of mechanical parts and components and increasing their operational life. Apart from the common used and conventional method of high velocity oxy fuel spraying (HVOF), the plasma spraying technology with water arc stabilization offers several advantages. Plasma spraying technology with water arc stabilization is characterized by higher temperature plasma,high performance of coating application and so on. This method is particularly suitable for spraying of high fusible ceramic and composite coatings based on ceramic basis [1-9].

A zircon silicate (ZrSiO<sub>4</sub>) exhibits properties such as high thermal shock resistance, good corrosion resistance, low wettability, etc. Zircon is one of the technologically important oxide ceramic materials used for its refractoriness, its low thermal expansion and low thermal conductivity [9-15]. To increase adhesion and compensation of thermal expansion changes of the substrate the interlayer based on nickel is often applied. But using interlayer increases economic demands of the coating formation and often requires other technological equipment.

The main aim of this contribution was to evaluate the structure, formation and selected properties of prepared ceramic coatings - conventional way (zircon silicate applied to nickel interlayer) and new way (composite of zircon silicate with different vol. % addition component (5, 12, 16 vol. %) of nickel to suggest and create the suitable combination of coating components (one composite coating) without using any interlayer for applications in extreme conditions.

## **EXPERIMENTAL MATERIALS AND METHODS**

As a substrate material the low carbon steel of grade S235JRG2 (EN 10025A1) was used. Tensile strength is 363-441 MPa and yield strength min 235 MPa. Chemical composition of steel substrate is shown in Table 1.

Table 1 Chemical composition of steel substrate / mas. %

C <sub>max</sub>	$Mn_{max}$	Al <sub>min</sub>	S <sub>max</sub>	P <sub>max</sub>	$N_{\min}$	Fe
0,17	1,40	0,02	0,045	0,045	0,009	bal.

Before thermal spraying the steel substrate was pretreated by blasting technology. Based on previously acquired knowledge in our workplace the grit blasting media (hereafter BM) type brown corundum grain size (dz) = 0,7 mm was used, diameter of spray nozzle ( $\phi$  9 mm), air pressure 0,4 MPa. Immediately after blasting, the selected thermal spraying technology followed. In the first case, the nickel (Ni) interlayer was applied by flame spraying and then the layer of zircon silicate (Zr-SiO<sub>4</sub>) with plasma torch with water plasma arc stabilization was deposited. In the second case the composite coatings (ZrSiO<sub>4</sub> + 5 vol. %, 12 vol. %, 16 vol. %) Ni) were also created by plasma torch [7, 16, 17]. Distance of samples from torch was 300 mm.

The basic formation and structure of selected ceramic coatings was documented on the fracture surfaces by scanning electron microscope. The basic microscopic observation was implemented by micro hardness measurement.

Specific characteristics of the selected ceramic coatings were determined by coating adhesion measurement (pull-off test - EN 582) For the realization of this test the cylinders (dimensions:  $\emptyset$  25 x 95 mm) were used. There was measured also porosity of composite coatings using two different methods - based on image anal-

J. Brezinová, A. Guzanová, E. Spišák – Faculty of Mechanical Engineering, Technical University of Košice, Slovak Republic

ysis of metallographic sections with software NIS Elements and by mercury porosimetry.

Next test for determination of the composite coatings quality was erosive wear test in simulated conditions. Erosive wear was simulated with help of laboratory mechanical abrasive blasting equipment. Parameters of abrasive blasting: abrasive: brown corundum, grain size: 0,5 mm; impact speed of grains: 70,98 m·s<sup>-1</sup>. The quality of coatings was evaluated at two different impact angles of abrasive: 45  $^{\circ}$  and 75  $^{\circ}$ . The wear rate was determined considering mass loss of coatings. Next, relative wear resistance based on mass loss of the coating and reference material tested considering their specific density were calculated. Reference material was ZrSiO<sub>4</sub> coating applied on Ni interlayer. Its relative erosive wear resistance was considered to be 1 ( $\psi = 1$ ). Other coatings – blends of ZrSiO<sub>4</sub> with Ni dopant were compared to this reference coating.

Relative wear resistance of the coating:

$$\Psi = (W_{h r}/W_{h c}) \cdot (\rho_c/\rho_{rc}) (-) \tag{1}$$

where

 $W_{hrc}$  – mass loss of reference coating

 $W_{hc}$  – mass loss of assessed composite coating

 $\rho_c$  – specific density of the assessed composite coating (g·cm<sup>-3</sup>)

 $\rho_{rc}$  – specific density of reference coating (g·cm<sup>-3</sup>)

## **RESULTS AND DISCUSSION**

To enhance the adhesion properties of ceramic coatings in general it is common to use an interlayer under the outer coating. It is acceptable solution but it increases an economic demand of this technology [14].

A complex view onto investigated ceramic coatings was provided by scanning microscopy (SEM). The fracture surface is very heterogeneous and consisted of lamellar structure with the flattened particles (splats) of different shapes and sizes which is typical for thermal spraying [3, 8, 14, 15]. The values of microhardness measurement of prepared ceramic coatings are documented in Table 2.

Table 2 Vickers microhardness of evaluated ceramic and composite coatings / HV 0,05

ZrSiO <sub>4</sub> with Ni interlayer	789
ZrSiO <sub>4</sub> + 5 vol. % Ni	572
ZrSiO <sub>4</sub> + 12vol. % Ni	499
ZrSiO <sub>4</sub> + 16 vol. % Ni	463

The highest value of microhardness was shown by a ceramic coating ZrSiO<sub>4</sub> applied on the interlayer. Increasing of the metal dopant added to the ceramic matrix led to decreasing microhardness values (by about 320 units).

Surface of coatings is significantly heterogeneous, consisting of individual splats in the form of discs of different size and shape. Overheated particles produce

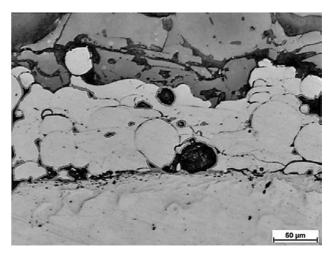


Figure 1 Evaluation of closed porosity

spattering, from which particles of globular shape separate. Voids arise due insufficient deformability of newly formed layer. Pores present in the coating are small but numerous. Locally partially melted particles occur. The internal structure of the coating is formed by layering of particles to each other. It is a characteristic sandwich structure. The better coupling between individual layers (splats in the form of discs) the fewer content of defects e.g. pores, cavities, cold joints and the more anchoring wedges will be in a layer.

The results of coating adhesion measurement are (pull-off test) in Table 3.

Table 3 Adhesion of the coatings / MPa

ZrSiO <sub>4</sub> with Ni interlayer	16
ZrSiO <sub>4</sub> + 5 vol. % Ni	16,5
ZrSiO <sub>4</sub> + 12vol. % Ni	23,5
ZrSiO <sub>4</sub> + 16vol. % Ni	16,5

Adhesion of ZrSiO<sub>4</sub> with Ni interlayer and adhesion of Ni doped composite coatings (ZrSiO<sub>4</sub> + 5 vol. % Ni and ZrSiO<sub>4</sub> + 16 vol. % Ni) were approximately the same. The greatest adhesion (23,5 MPa) was achieved by zircon silicate with 12 vol. % Ni. Increasing of Ni dopant content led to the decreasing of coating adhesion to level of pure ZrSiO<sub>4</sub> coating applied to Ni interlayer. Figure 1 shows evaluation of coatings closed (ineffective) porosity by image analysis of metallographic sections.

Closed porosity refers to pores which are closed in volume of coating and do not create connection between substrate and surrounding atmosphere. Based on image analysis there was assessed size and number of closed pores in the coatings. The closed porosity reduces the cohesion strength of coatings under load. In the coating ZrSiO<sub>4</sub> applied on the interlayer more than 50% pores of the total porosity are of size 100 µm. Coatings with the higher dopant content contained more pores of small size. The open porosity (effective) refers to the connection between substrate and surrounding atmosphere. It negatively affects the resistance of coatings in corrosive environments, allows penetration of aggressive compo-

nents of corrosive environment into the coating, or to the substrate and causes under corroding. The presence of open pores in the coatings was evaluated by mercury porosimetry. The results are shown in Table 4. Realized analysis showed the lowest open porosity in coating Zr-SiO<sub>4</sub> + 12 vol. % Ni.

Table 4 Porosity of evaluated coatings determined by mercury porosimetry / %

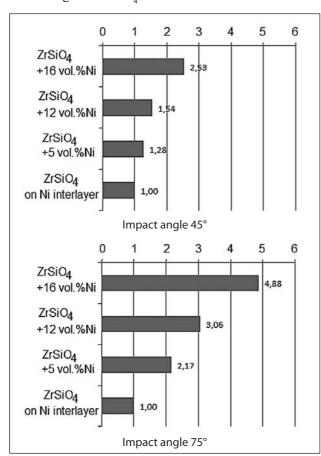
Coating	Inter-particle	Intra-particular	Total
Ni + ZrSiO <sub>4</sub>	0,3938	1,1257	1,5195
ZrSiO <sub>4</sub> +6 vol. % Ni	1,4097	0	1,4097
ZrSiO <sub>4</sub> +12 vol. % Ni	0,1704	0	0,1704
ZrSiO <sub>4</sub> +16 vol. % Ni	1,6079	0	1,6079

Results of the relative wear resistance of coatings shows Figure 2.

Results show that the experimental cermet composite coatings achieved higher erosive wear resistance compared to reference coating. When comparing two impact angles, we can conclude that increasing dopant volume in composite coatings led to increasing their erosive wear resistance. The best wear resistance achieved coatings with 16 % of Ni dopant.

## **CONCLUSIONS**

The contribution was focused on research of basic formation, structure and selected properties of composite coatings on ZrSiO<sub>4</sub> basis with different addition of



**Figure 2** Relative wear resistance  $\Psi$  of coatings

Ni component. Based on the experimental results, it is possible to formulate following conclusions:

- the greatest adhesion (23,5 MPa) has composite coating zircon silicate with 12 vol. % of Ni as metallic addition component. Character of fracture surface was cohesive.
- the highest microhardness was shown by ceramic coating ZrSiO<sub>4</sub> applied on the interlayer. Increasing of the metal dopant added to the ceramic matrix led to decreasing microhardness values (by about 320 units).
- coating ZrSiO<sub>4</sub> + 12 vol. % Ni showed the lowest open porosity.
- at impact angle 45° the maximum erosive wear was observed in the reference coating ZrSiO<sub>4</sub> applied on Ni interlayer. Composite cermet coatings with increasing volume of dopant showed increasing of wear resistance. Relative wear resistance of coatings was higher in the impact angle of 75°. With the increasing of Ni dopant volume hardness of coatings decreased, which led to greater relative wear resistance of composite coatings at impact angle of 75°. In composite coatings with increased metallic dopant volumes the effect of impact angle of abrasive on the wear of coatings did not significantly reflect.

The best properties reached composite coating doped with 12 % Ni. It is characterized by good adhesion, relatively low porosity and relatively high hardness - about 500 HV 0,05. However, for a comprehensive assessment of the properties of the coating it is necessary to perform other experimental measurements aimed on assessment of its quality in terms of thermal cyclic stress and in tribological conditions based on simulations of real operating conditions, which coatings are really exposed to.

## Acknowledgement

The authors are grateful to APVV for support of experimental work under grant APVV-0682-11 - Application of progressive tool coatings for increasing the effectiveness and productivity of forming sheets made of modern materials.

## **REFERENCES**

- [1] R. B. Heimann, Plasma Spray Coating. Principles and Applications, 2nd ed., Wiley-VCH, Germany, 2008.
- [2] L. Pawlowski, The Science and Enginneering of thermal spray coatings, 2nd ed., John Wiley and Sons Ltd., England, 2008.
- [3] K. Šimunović, Thermal Spraying. Welding Engineering and Technology. 1st ed., Eolss Publishers, Oxford, 2010.
- [4] V. Marušić, S. Aračić, I. Samardžić, Metalurgija, 49 (2010) 1, 53-56.
- [5] D. Jakubéczyová, M. Hagarová, M. Vojtko, Acta Metallurgica Slovaca, 15 (2009) 1, 15-22.
- [6] J. Kunda, J. Bronček, B. Hadzima, Scientific basis of modern technology: experience and prospects. Jaremcze: Khmelnitsky National University, 2011, p. 299-309.

- [7] D. Jankura, D. Draganovská, J. Brezinová, Chemical letters, 105 (2011) SI16, 542-545.
- [8] J. Brezinová, A. Guzanová, Metalurgija, 51 (2012) 2, 211-215.
- [9] X. Q. Cao, R. Vassen, D. Stoever, Journal of the European Ceramic Society, 24 (2004) 1, 1-10.
- [10] P. Chráska, K. Neufuss, H. Herman, Journal of Thermal Spray Technology, 6 (1997) 4, 445-448.
- [11] A. Kaiser, M. Lobert, R. Telle, Journal of the European Ceramic Society, 28 (2008) 11, 2199-2211.
- [12] [20.5.2012] P. Ctibor, J. Sedláček, K. Neufuss, Plasma spraying and dielectric characterization of zirconium silicate. http://www.mtf.stuba.sk/docs/internetovy\_casopis/ 2007/mimorcis/ctibor.pdf
- [13] G. M. Ingo, T. Caro, Acta Materialia, 56 (2008) 18, 5177-5187.

- [14] J. Brezinová, M. Ábel, J. Viňáš, Diagnosing the quality of thermal sprayed coatings (in Slovak). Transfer inovácií, (2010) 18, 230-232.
- [15] K. Holmberg, A. Matthews, Coating Tribology. Properties, Mechanisms, Techniques and Applications in Surface Engineering, sec. ed., Elsevier Science Ltd., Amsterdam, 2009.
- [16] T. Nakamura, Y. Liu, International Jornal of Solids and Structures, 44 (2007), 1990-2009.
- [17] J. Brezinová, A. Guzanová, I. Mamuzić, Acta Metallurgica Slovaca, 18 (2012) 1, 20-27.

Note: The responsible for English language is the lecturer from TU Košice, Slovakia