SELECTED ASPECTS OF CERAMIC COATINGS PREPARED BY THERMAL SPRAYING WITH WATER PLASMA ARC STABILIZATION

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Received: 27.06.2012
Accepted: 16.11.2012

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Abstract

The paper was focused on research of selected aspects of ceramic coatings prepared by thermal spraying with water plasma arc stabilization. Before spraying, the steel substrate low carbon steel of grade S235JRG2 was pre-treated by blasting with using the brown corundum as a blasting media. A ceramic matrix of coating - zircon silicate was used in two types: $ZrSiO_4$ applied by flame thermal spraying on nickel interlayer and composite of $ZrSiO_4$ with different addition of nickel (6, 12 and 16 wt. %). The basic characteristics of ceramic coatings were determined by thickness and microhardness measurement. The fracture surfaces were documented by SEM. Adhesive and abrasive properties were evaluated by pull-off adhesion test and abrasive wear test. The results showed that the composite coatings on $ZrSiO_4$ basis with the addition of Ni meet the increased requirements for abrasion resistance while maintaining sufficient adhesion. The addition of Ni to a ceramic matrix of coating improved the final structure of coatings and it had a positive effect on the resulting adhesion. On the other hand, with the increasing of Ni addition the microhardness values of coatings decreased.

Keywords: composite ceramic coatings, plasma spraying, adhesion, wear

1 Introduction

The most important properties for using thermally sprayed coatings in engineering practise are: wear resistance, excellent tribological properties, resistance to oxidation, corrosion, attacks by environment and their resistance to extreme temperatures. The great advantage of these coatings is that they can be applied to all conventional ferrous or nonferrous metals [1, 3 - 5].

The coating formation can be classified as the heating and melting of additional material. Molten or semi molten particles are accelerated, propelled and sprayed on prepared basic surface. The particle impact on the substrate surface causes their partial or complete deformation (flatting), quickly cooling, solidification and finally transformation into lamellar heterogeneous structure [2, 4, 6, 7, 8].

A Plasma spraying is an innovative form of thermal spraying processes, which is characterized by high concentration of heat and working temperature. For spraying of powdered materials there are available many types of different equipments. They consist of complex parts, where the powerful spray unit is a plasma torch. According to a type of stabilization media there are plasma torches with gas and water stabilization. It is characterized by higher temperature

DOI 10.12776/ams.v19i1.85 p-ISSN 1335-1532
e-ISSN 1338-1156

plasma, high performance of coating application and etc. This technology is particularly suitable for spraying of high fusible ceramic and composite coatings based on ceramic basis [1, 3, 5, 9, 10].

Commercially produced water stabilized plasma torches consist of arc chamber, rotary-cooled copper anode and graphite cathode. The mechanism of arc plasma formation is based on evaporation of inner cylindrical wall of water vortex which surrounds the arc column. Evaporation is induced by absorption of part the Joule heat arc. The steam does not flow; its heating creates the pressure in the inside of arc chamber and the plasma is accelerated to the nozzle hole. The properties of arc are controlled during processes that influence evaporation from the wall and by radial transport of energy from the centre of arc to walls (inner surface of the water vortex). The resulting properties of the generated plasma beam are strongly dependent on a stream [1, 6, 9].

Typical material for plasma spraying is oxide ceramics which consists of one or mainly one refractory oxide. Some of basic substances are already in nature in the form of oxides; others are prepared chemically or by thermal decomposition. Final properties of coatings are substantially different such as properties of raw materials. It is due to many factors that enter into the process from the flight of sprayed particles by plasma beam and in the process of coating formation. To enhance the properties of thermally sprayed coatings there are used besides the basic component the “dopants” (plastic, metallic, ceramic) [1, 6, 9]. A zircon silicate ($ZrSiO_4$) exhibits properties such as high thermal shock resistance, good corrosion resistance, low wettability, etc. Its major application is the production of rocket engines, aircraft turbines, as a structural material in nuclear reactors and other similar applications. Zircon is one of the technologically important oxide ceramic materials used for its refractoriness, its low thermal expansion and low thermal conductivity [12 - 20].

The main aim of our paper is to study the structure and selected aspects of ceramic coatings on $ZrSiO_4$ basis which was applied on nickel interlayer and as composite coating with different addition of nickel (6, 12, 16 wt. %).

2 Materials and Experimental Procedure

The substrate material was low carbon steel grade S235JRG2. Chemical composition and required mechanical properties of substrate material are shown in **Table.1** and **Table.2**.

Table 1 Chemical composition of substrate material grade S235JRG2

Chemical composition [wt.%]					
C_{max}	Mn_{max}	N_{min}	P_{max}	S_{max}	Fe
0.17	1.400	0.009	0.045	0.045	balanced

Table 2 Required mechanical properties of substrate material grade S235JRG2

Mechanical properties [MPa]	
UTS	YS_{min}
363 - 441	≥ 235

Before thermal spraying, the substrate material was pre-treated by blasting on the pneumatic blasting equipment TJVP 320. As a blasting media the brown corundum with grain size 1.2 mm was used. Blasting media was applied with a pneumatic spray nozzle (ϕ 9 mm) at air of pressure of 0.4 MPa. Immediately after blasting, the selected thermal spraying technology was used. The Ni interlayer was applied by traditional flame spraying and then the layer of zircon silicate $ZrSiO_4$ with plasma torch WSP PAL - 160 with water plasma arc stabilization was deposited. The composite coatings $ZrSiO_4$ + 6 wt. %, 12 wt. %, 16 wt. % of Ni were created by the already mentioned, plasma torch, which was characterized by its high performance (up to 160 kVA) and high enthalpy plasma [2]. Distance deposit of samples from the hole of the torched nozzle was 300 mm.

The thickness of ceramic coatings was measured with thickness gauge type QuaNix Keyless, Germany. The microhardness measurement HV0.1 was realized according to standard STN EN ISO 6507 - 1. The indentation was carried out for indentation load of 980.7 mN (10 g) and indentation time of 15s. The selected structures of ceramic coatings were documented on the scanning electron microscope JEOL JSM 7000-F.

Specific characteristics of ceramic coatings were determined by adhesion pull - off test (STN EN 582) and abrasive wear test during sample wading in an abrasive mixture. The adhesion strength was expressed as a tensile stress (MPa) which is required to coating destroying. For the realization of this test, the blasted cylinders (ϕ 25 x 95 mm) with applied coatings were prepared and glued with the ChS EPOXY 1200 to the tested counterpart. The test was realized on the equipment ZDM 10/91 at 10 % of deformation rate. The abrasive wear test was realized on the equipment type Di-1. New experimental samples (ϕ 20 x 10 mm) were clamped in a plate rotating head which was moving on a circular orbit in an abrasive with the same peripheral speed. As an abrasive the brown corundum with grain size 1.2 mm was used. The sample speed in abrasive was 1.74 $m.s^{-1}$ (n =123 rpm^{-1}), an impact angle 45° and 75°, a depth of sample immersion in abrasive was 60 mm. The results of this method were determined as coating weight losses per unit wading distance during the sample wading in an abrasive.

3 Results and Discussion

The results of thickness and microhardness measurement summarize **Table 3** and **Table 4**. The thicknesses of ceramic coatings vary from 138.4 μm at $ZrSiO_4$ with Ni interlayer to 178 at $ZrSiO_4$ + 6 wt. % of Ni. Measured values of thicknesses are in tolerance of thickness requirements for this type of coatings.

The average values of microhardness for selected coatings vary in the range from 459.3 HV0.1 to 572.6 HV0.1. The microhardness decreases with an increasing addition of Ni dopant in the base matrix. The microhardness of interlayer does not over the average value of 145.3 HV0.1. The highest microhardness 773.3 HV0.1 is measured at $ZrSiO_4$ applied on Ni interlayer; microhardness value represents only a coating consisting of particles of $ZrSiO_4$.

The structure of ceramic coatings documents SEM analysis with EDX spectrums of selected fracture areas. Plasma sprayed coatings are characterized by their specific sandwich structure. In **Fig. 1 and Fig. 2** we can see the complex and detail view of selected fracture surfaces of composite coatings $ZrSiO_4$ with Ni addition. All composite coatings have heterogeneous lamellar structure with the flattened particles (named in literature as splats) of various shapes and sizes. This is a typical for thermal spraying [2, 4, 11, 18]. The nickel particles are placed in the figures as bright areas which are alternated with ceramic component.

The chemical composition of studied ceramic coatings documents the selected fracture areas. Data from EDX analysis are summarized in **Tab. (s) 6, 7, 8, 9.** Their EDX spectrums show **Fig. (s) 3 - 6.**

Table 3 The results of thickness measurement

Type of Coating	$ZrSiO_4$ with interlayer	$ZrSiO_4$ + 6 wt.% of Ni	$ZrSiO_4$ + 12 wt. % of Ni	$ZrSiO_4$ + 16 wt. of Ni
Thickness [□m]	138.4	178	166.3	126.2

Table 4 Vickers microhardness HV 0.1 of experimental ceramic coatings

Type of coating	**HV0.1**
$ZrSiO_4$ with Ni interlayer	789.3
$ZrSiO_4$ + 6 wt.% of Ni	572.6
$ZrSiO_4$ + 12wt.% of Ni	499.6
$ZrSiO_4$ + 16 wt.% of Ni	459.3

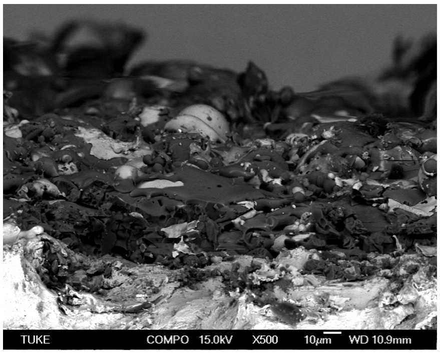

Fig. 1 Complex view on structure of composite coating $ZrSiO_4$ with Ni addition, SEM

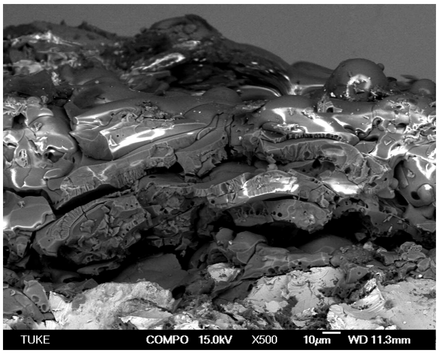

Fig. 2 Detail view on structure of composite coating $ZrSiO_4$ with Ni addition, SEM

The results of adhesion pull - off test show **Table 5**. To destroying the coating from the substrate material occurred in 3 of 4 studied ceramic coatings in the force range 16-16.5 MPa. The greatest adhesion 23.5 MPa was achieved at $ZrSiO_4$ with 12 wt. % of Ni. The appearance of coating fractures was studied in the presence of adhesive residues.

Table 5 The results of adhesion pull - off test

Type of ceramic coating	**Adhesion strength [MPa]**	**Fracture evaluation**
$ZrSiO_4$ with Ni interlayer	16	Cohesion fractures in adhesive
$ZrSiO_4$ with 6 wt. % of Ni	16.5	
$ZrSiO_4$ with 12 wt. % of Ni	23.5	
$ZrSiO_4$ with 16 wt. % of Ni	16.5	

Table 6 The chemical composition of ceramic coating with Ni interlayer

Element	**Wt. %**	**At. %**
O K	28.05	62.02
Si K	11.56	14.56
Zr L	60.39	23.42
Totals	100.00	

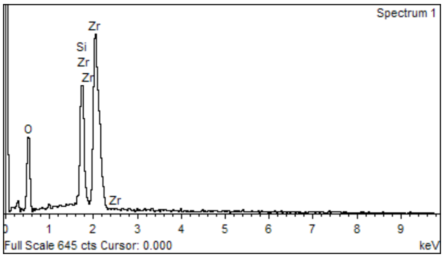

Fig. 3 EDX spectrum of ceramic coating $ZrSiO_4$ with Ni interlayer

Table 7 The chemical composition of composite coating with 6 wt. % of Ni

Element	Wt. %	At. %
O K	43.10	74.18
Si K	11.96	11.73
Ni K	3.18	1.49
Zr L	41.75	12.60
Totals	100.00	

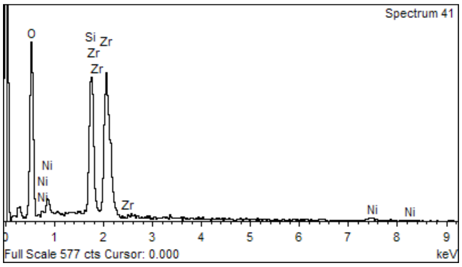

Fig. 4 EDX spectrum of composite coating $ZrSiO_4$ with 6 wt.% of Ni

Table 8 The chemical composition of composite coating with 12 wt. % of Ni

Element	Wt. %	At. %
O K	19.35	41.63
Al K	13.84	17.65
Si K	2.83	3.47
Fe K	51.04	31.45
Ni K	4.43	2.60
Zr L	8.51	3.21
Totals	100.00	

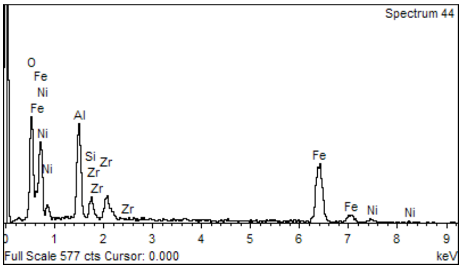

Fig. 5 EDX spectrum of composite coating with 12 wt. % of Ni

Table 9 The chemical composition of ceramic coating with 16 wt. % of Ni

Element	Wt. %	At. %
Al K	0.75	1.52
Si K	4.31	8.41
Cr K	9.71	10.24
Fe K	4.40	4.32
Ni K	80.84	75.51
Totals	100.00	

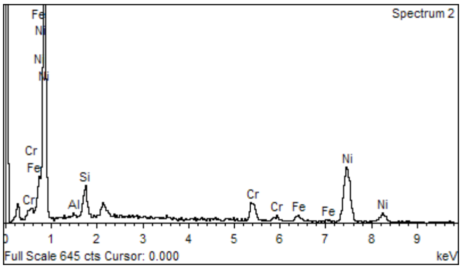

Fig. 6 EDX spectrum of ceramic coating $ZrSiO_4$ with 16 wt.% of Ni

The evaluation criterion for abrasive wear test was relative resistance to abrasive wear (ψ). A reference sample was the $ZrSiO_4$ with Ni interlayer with relative resistance to abrasive wear of 1. The results of relative resistance to abrasive wear at impact angle 45° and 75° are summarized in **Table 10**.

Table 10 The results of relative resistance to abrasive wear at impact angle 45° and 75°

Type of ceramic coating	Impact angle	
	45°	75°
	Relative resistance to abrasive wear ψ	
$ZrSiO_4$ with Ni interlayer	1	1
$ZrSiO_4$ with 6 wt.% of Ni	0.62	5.29
$ZrSiO_4$ with 12 wt.% of Ni	1.12	3.47
$ZrSiO_4$ with 16 wt.% of Ni	3.10	6.04

The increasing of Ni dopant content in the ceramic matrix was demonstrated in all coatings at the impact angle 45° except of coating $ZrSiO_4$ with 6 wt. % of Ni, whose value of relative resistance dropped to 0.62. At the impact angle 75° it was also registered an increase of the abrasive wear resistance with an increasing the dopant content.

Final weight losses of studied coatings per unit of wading distance at various impact angles (45º, 75º) are plotted in **Fig. 7** and **8**. The results show, that the process of abrasive wear is closely related with a roughness and porosity of thermally applied coatings. After the initial increasing of the abrasive wear, the values began stagnate with a stabilizing the linear functional dependence. Differences of dependence were probably caused by non homogeneous coating structure or potential structure defects (unmelted particles, oxide inclusions and etc.) At the impact angle 45°, the abrasive wear was the highest at $ZrSiO_4$ with 6 wt. % of Ni. The other coatings reached significantly lower values, but the process of wear was very similar. In the initial stages of testing, the coatings with 12 wt. % of Ni reached the lowest value, in the later stages of test the lowest value recorded coating with 16 wt. % of Ni. This fact can be attributed to presence of coating porosity and coating hardness. At the impact angle of 75°, the highest value of wear was reached at ceramic coating without addition of metal components. The achieved weight losses were significantly higher than the coatings with Ni component. The wear values of doped coatings in a freely abrasive had a similar process; the higher removal of coating was at coating with 12 wt. % of Ni. In comparison of the wear values of both impact angles, it is necessary to say that higher weight losses were obtained at the impact angle 75°. The higher removals of coatings were achieved at the impact angle 75º. The addition of metal component in a ceramic matrix was very positive, because the weight losses were smaller. The initial increasing of abrasive wear was than alternated with the gradual stabilization with an approximately linear functional dependence. Differences from this dependence can be probably caused by surface topography of coating or by some heterogeneity of coatings. Other factor which can influence the resistance of coatings is an open porosity, which can be a potentially place for fixation of abrasive particles under the coating splats. This abrasive particle can ripped out these splats from the coating structure. The Ni addition to matrix can increase the density and cohesive strength of coating, so we can say that the Ni increase the coating resistance in abrasive wear conditions.

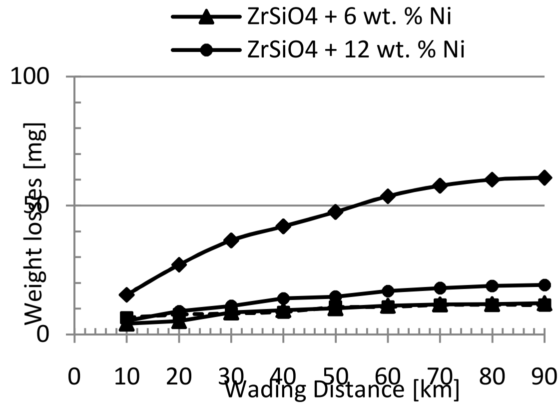

Fig. 7 The weight losses of coatings per wading distance in a freely abrasive at impact angle 45º

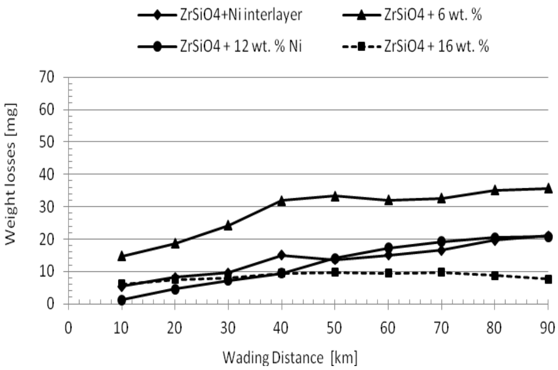

Fig. 8 The weight losses of coatings per wading distance in a freely abrasive at impact angle 75º

4 Conclusions

The contribution was focused on research of formation, structure and selected properties of composite coatings $ZrSiO_4$ applied on Ni interlayer and $ZrSiO_4$ with different addition of nickel component (6, 12, 16 wt. %). Based on the experimental results, it is possible to formulate following conclusions:

1. SEM observation of ceramic coatings showed markedly heterogeneous lamellar structure of fractures surfaces which were consisted of different shapes and sizes of disc splats. White particles of nickel were alternated with ceramic basis - $ZrSiO_4$. Only occasionally, SEM identified on surface fractures the presence of partially melted particles of additional material.
2. The highest microhardness values were measured at $ZrSiO_4$ applied on Ni interlayer (773.3 HV0.1). With the increasing amount of dopant volume the microhardness values decreased, $ZrSiO_4$ + 6 wt. % of Ni = 572.6 HV0.1, $ZrSiO_4$ + 12 wt. % of Ni = 499.6 HV0.1, $ZrSiO_4$ + 16 wt. % of Ni = 459.3 HV0.1.
3. The greatest adhesion (23.5 MPa) after pull - off test was reached at the zircon silicate with 12 wt. % of Ni as metallic addition component. Appearance and character of fracture surface was evaluated as a cohesive fracture in the adhesive.
4. Selected impact angles 45° and 75° significantly affected the results of monitored process of abrasive wear. The greatest weight losses (61.8 mg) at given type of blasting media and impact angle 75° during wading in a freely abrasive was revealed at zircon silicate applied on Ni interlayer. The weight losses of other composite coatings with Ni addition were not over 20 mg for a given wading distance. At the impact angle 45°, the greatest material removal (35.7 mg) achieved the zircon silicate with the smallest Ni additions (6 wt. %). Probably a little addition of Ni and the impact angle 45° caused a decrease of its microhardness.

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Acknowledgements

Authors are grateful for the support of experimental works by Grand Agency VEGA No1/0510/10.