

Microstructure characterization of chromium carbides coatings deposited by thermal spraying processes

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ABSTRACT

Purpose: The Cr_3C_2 -NiCr coatings were deposited by plasma spraying (PS) and high velocity oxy-fuel (HVOF) processes. The objective of the work concerns characterization of microstructure of sprayed coatings. In the investigated samples, apart from Cr_3C_2 carbide particles, the carbides Cr_7C_3 were also present according to the reported through X-ray diffraction analyses. It is likely that Cr_7C_3 carbides were formed thorough decarburization of Cr_3C_2 . The microstructure of the thermal sprayed Cr_3C_2 -NiCr coatings was characterized by optical (MO), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The fine-grained and nano-crystalline microstructure was found in the investigated coatings. The microhardness of coatings was measured. It was found that the coatings deposited in HVOF process have higher microhardness than the plasma spraying one. The formation of chromium carbide phases in the coatings was discussed based on the microstructure observation results.

Design/methodology/approach: The investigations of coating microstructure by optical microscopy (MO) Olympus GX51, scanning electron microscopy STEREOSCAN 420 and transmission electron microscopy JEM2010 ARP (TEM) were performed. The examination of phase consistence was determined by Brucker D8 Discover - Advance diffractometer with copper tubing. The microhardness of coatings was measured by Vickers method.

Findings: The microstructures of Cr_3C_2 -NiCr coatings were observed and analyzed. On the base of the microstructure investigations and content of the chromium carbides the mechanism of thermal sprayed coating formation was discussed.

Practical implications: The performed investigations contribute to the improvement of microstructure and properties of thermal spraying coatings used in the industrial applications.

Originality/value: It was assumed that thermal spraying processes are able to form nano-crystalline microstructure of the chromium carbide coatings.

Keywords: Plasma sprayed and high velocity oxy-fuel processes; Microstructure; Cr_3C_2 carbides

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1. Introduction

Lately, an increasing interest in thermal spraying coatings with the nanostructured materials has been observed. Thermal spraying methods are a well-established processes and preferred technique for deposition of corrosion, wear protection, and thermal barrier coatings [1]. High velocity oxy-fuel (HVOF) thermal spraying has been applied successfully in producing coating with higher density, superior bond strengths, and less decarburization due to its unique advantage of high momentum and low thermal output [2-5]. The HVOF coatings have very high bond strengths, fine as-sprayed surface finishes and low oxide levels [6]. Coatings from chromium and tungsten carbides are very often used in the industry conditions for protection against the wear and erosion [7]. Opposite to HVOF, plasma sprayed coats showed larger porosity, the existence of more not molten droplets and oxides [8]. Coatings consist of lamellas elongated in the direction parallel to the coating surface. Plasma spraying and HVOF method have been successfully used to produce different kinds of coatings on the alumina substrates [7].

The use of materials with reduced grain size has improved some properties like hardness and toughness, sliding and abrasion resistance [9-12]. However, for thermal spray coatings, in which the spraying process and the properties of feedstock materials have a great importance, wear resistance is normally lower than that of conventional coatings. This lack of performance of thermally sprayed nanostructured coatings has been attributed to their higher tendency to decarburization [13]. The using the same material, corrosion resistance can be enhanced by reducing the porosity, avoiding cracks, and increasing inter splat adhesion. For those reasons, the nanostructured coatings can be expected to have better behavior on aggressive media. The thermal spraying coatings are the effective wear resistant protection preserving the surface of the different appliances, machines and plants in the industry conditions [14,15].

The objective of this work was to study the properties of nanostructured $\text{Cr}_3\text{C}_2\text{-NiCr}$ coatings, deposited by High Velocity Oxy-Fuel (HVOF) and thermal spraying processes, as well as microstructure characterization and its phase composition.

2. Experimental basis

The High-Velocity Oxy-Fuel spraying (HVOF) and Plasma Sprayed techniques were used for coats spraying. The HVOF deposition parameters are presented in the Table 1. The Plasma Spraying parameters are presented in Table 2. The thickness of HVOF coatings was found of about $300 \pm 80 \mu\text{m}$. In the case of the Plasma Spraying samples the thickness of coating was found of about $300 \pm 20 \mu\text{m}$.

The Table 3 contained chemical composition of the investigated in the work coatings. The composition of coatings consisting from chromium carbides spraying by HVOF and plasma spraying techniques. The coatings were sprayed at the AISi substrate.

The Cr_3C_2 coating with the intermediate layers of NiCr are sprayed by using High Velocity Oxy-Fuel method. The spraying distance of 370 mm and gun speed 35 m/min were used.

Table 1.

HVOF spraying deposition parameters

	O ₂ l/min	Kerozyna l/h	N ₂ l/min	Distance mm	Powder g/min
HVOF	944	25.5	9.5	370	92

Table 2.

Plasma Spraying deposition parameters

	Ar l/h	voltage V	current A	Distance mm
Plasma Spraying	3000	52	500	90

Table 3.

The chemical composition of deposited coatings

No	Chemical composition of coatings	Deposition method
1	$\text{Cr}_3\text{C}_2\text{-NiCr}$	Plasma Spraying
2	$\text{Cr}_3\text{C}_2\text{-NiCr}$	Plasma Spraying with propane - butane shield
3	$\text{Cr}_3\text{C}_2\text{-NiCr}$ (nano) + 5% Ni17Cr4Fe4Si 3.5BIC	Plasma Spraying with propane - butane shield
4	$\text{Cr}_3\text{C}_2\text{-NiCr}$	HVOF

The special vibratory disc feeder CPF-2 Thermico firm, allowing feeding of powders with very low granulation $10\text{-}2 \mu\text{m}$ with the precision $\pm 2\%$, was used.

The plasma sprayed 80% Cr_3C_2 - 20% NiCr (wt.%) coats were prepared by MIM40 device. The argon 3000 l/h and hydrogen 873 l/min were used for melting powders particles before their impact onto the substrate. The spraying distance of 90 mm and gun speed 25 m/min were used. The thermal spraying was realized without shield and with the propane - butane shield. The deposition of coatings was performed in enterprise Plasma System S.A., Siemianowice Śląskie, Poland.

The following powders, prepared in H Hogan company, were using for HVOF and Plasma Spraying deposition. The $\text{Cr}_3\text{C}_2\text{-NiCr}$ 75-25% powder with grain size - $45\text{-}15 \mu\text{m}$ / Cr_3C_2 1 μm , agglomerating and sintering was used to deposition. The microstructure of coatings was studied by Olympus GX50 optical microscopy (MO). Thin foils prepared from samples by the cross section technique were observed by JEOL 2010 ARB transmission electron microscopy (TEM) with the Energy Disperse Spectrometer (EDS) for identification of chemical composition in microareas of layers. The microhardness of coats was measured by using PMT3 microhardness tester at load 200 G. The samples to light and scanning microscopy observations were polished mechanically applied Struers equipment and technique. They were grinded, than polished in diamond pastes and in the suspension OPS. Thin foils, for TEM investigations, were prepared from cross sections by cutting grinding and ion sputtering, using Struers and Gatan instruments.

The investigations of phase composition of plasma sprayed and HVOF coatings were performed by using Bruker D8 Discover-Advance diffractometer with copper lamp (40 kV, 30 μA , $\lambda=1.540598 \text{ \AA}$). The method measurement superficial layer and software Diffract Plus Evaluation was used for inspect of layers composition.

3. Investigation results

The microstructures of Cr_3C_2 -NiCr coatings are presented in Fig. 1. - Fig. 4. In Fig. 1, related to the HVOF coating, the characteristic, numerous, almost equiaxial Cr_3C_2 carbides are observed inside the NiCr matrix. Fig. 2 presented plasma sprayed Cr_3C_2 - NiCr coating with the propane - butane shield and Fig. 3. coating without the propane - butane shield. The microstructure observed in Fig. 2 is similar to the HVOF coating presented in Fig. 1. Coating in Fig. 3, deposited without the propane - butane shield, exhibited numerous pores, which are visible as the black places. It suggests the lower density and worst smoothness of the coating surface. The lower density of coating deposited without propane - butane shield expressed in the lower level of the microhardness (Table 4). The values of microhardness of sprayed coatings presented in Table 4 indicated that the highest level of microhardness presented composite coating Cr_3C_2 -NiCr + 5% Ni17Cr4Fe4Si3.5B1C thermal sprayed with the propane - butane shield. Its microstructure is presented in Fig. 4.

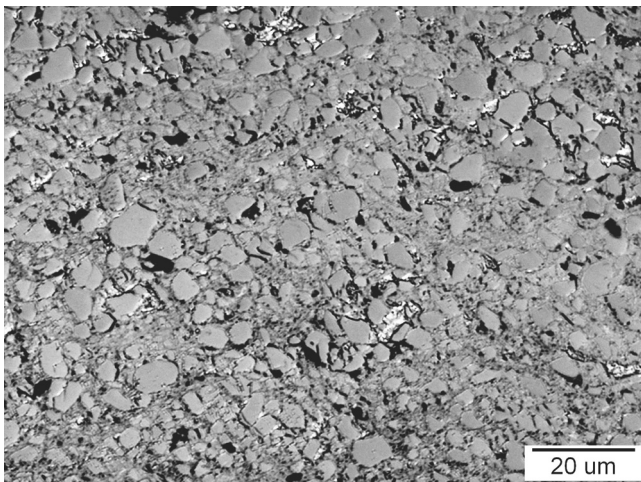


Fig. 1. Cr_3C_2 -NiCr coating deposited by HVOF technique (MO)

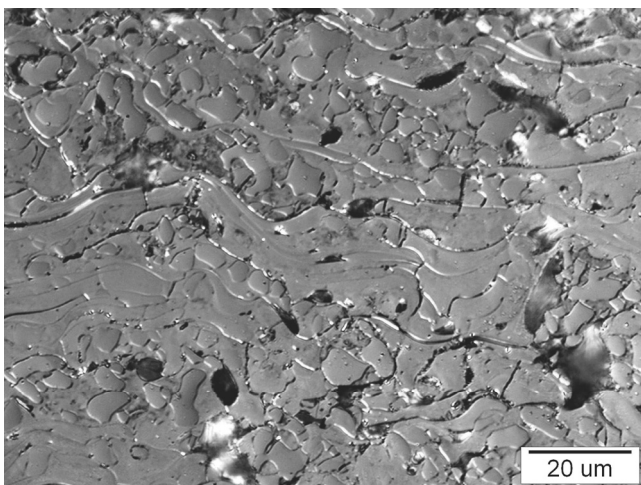


Fig. 2. Cr_3C_2 - NiCr deposited by plasma spraying with the propane - butane shield (MO)

Table 4.

The microhardness of deposited coatings

No	Coating	Deposition method	Microhardness
1	Cr_3C_2 -NiCr	Plasma Spraying	665
2	Cr_3C_2 -NiCr	Plasma Spraying with propane - butane shield	790
3	Cr_3C_2 -NiCr	HVOF	863
4	Cr_3C_2 -NiCr +5% E (Ni17Cr4Fe4Si3.5B1C)	Plasma Spraying with propane - butane shield	950

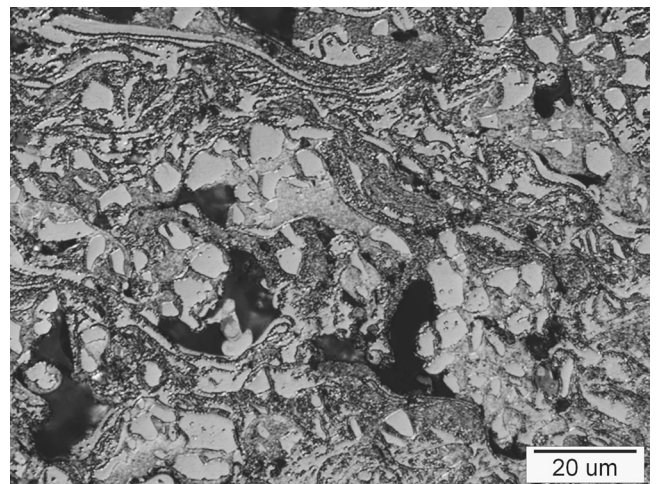


Fig. 3. Cr_3C_2 - NiCr deposited by plasma spraying without the propane - butane shield (MO)

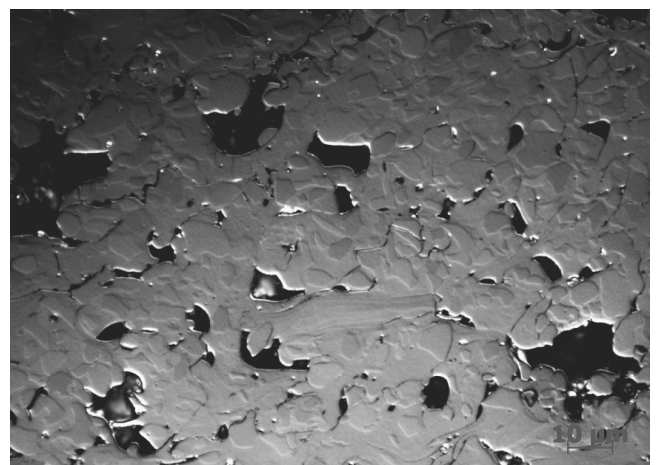


Fig. 4. Cr_3C_2 - NiCr + Ni17Cr4Fe4Si3.5B1C deposited by plasma spraying with the propane - butane shield (MO)

In the microstructure of the Cr_3C_2 -NiCr + 5% E (Ni17Cr4Fe4Si3.5B1C) randomly distributed carbides inside the matrix and numerous pores were found.

Fig. 5 to Fig. 8 presented the results of phase X-ray investigation analysis of coatings. The Cr_3C_2 , Cr_7C_3 and Cr_{23}C_6 carbides were found in the samples deposited by HVOF technique (Fig. 5). The coatings plasma sprayed with propane - butane shield show Cr_3C_2 and Cr_7C_3 carbides (Fig. 6). The Cr_7C_3 and Cr_{23}C_6 carbides were also found inside the Cr_3C_2 -NiCr coating deposited by plasma spraying method.

The existence of the Cr_7C_3 and Cr_{23}C_6 precipitations inside the thermal spraying coatings suggests development of decarburization process occurred during the coatings deposition. In the plasma spraying process, without propane - butane shield, the intensity of decarburization is very strong, because the Cr_3C_2 carbides were not found in this coating. The only Cr_3C_2 carbide was found in Cr_3C_2 -NiCr +5% E (Ni17Cr4Fe4Si3.5B1C) coating, which indicated proper conditions of deposition. The phase consistence strongly influence on the microhardness of the coating which is the lowest in decarburized samples.

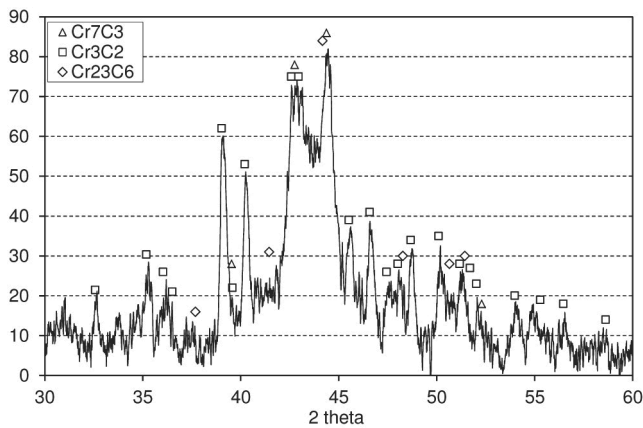


Fig. 5. Phase composition of Cr_3C_2 -NiCr coating deposited by HVOF technique

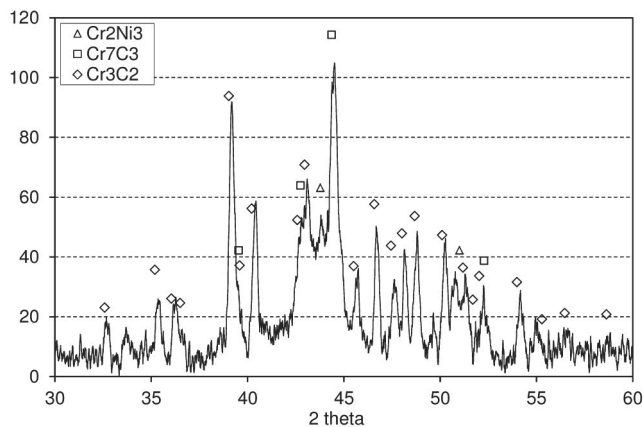


Fig. 6. Phase composition of Cr_3C_2 -NiCr coating deposited by plasma spraying with propane - butane shield

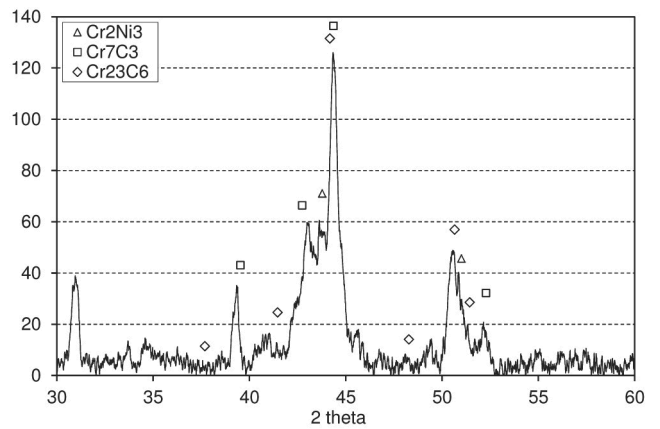


Fig. 7. Phase composition of Cr_3C_2 -NiCr coating deposited by plasma spraying (IV)

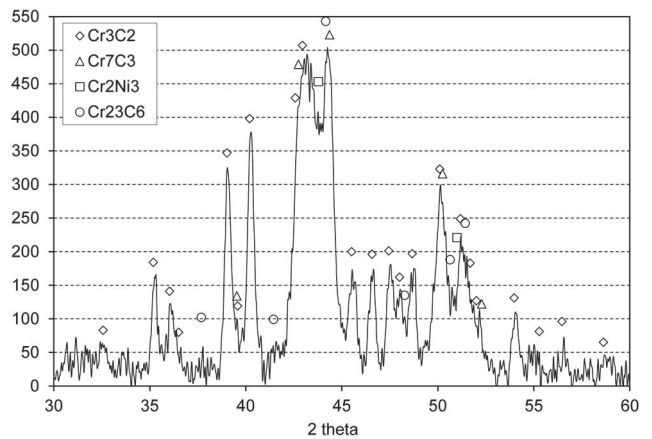


Fig. 8. Phase composition of Cr_3C_2 -NiCr +5% E (Ni17Cr4Fe4Si3.5B1C) coating deposited by plasma spraying with propane - butane shield

TEM microstructure plasma sprayed coating is presented in Fig. 9 and coating deposited by HVOF technique in Fig. 10.

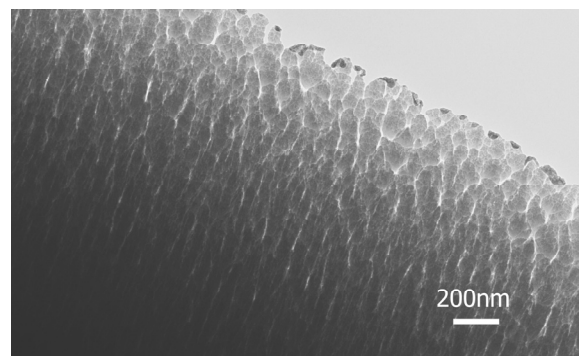


Fig. 9. Microstructure of plasma sprayed coating

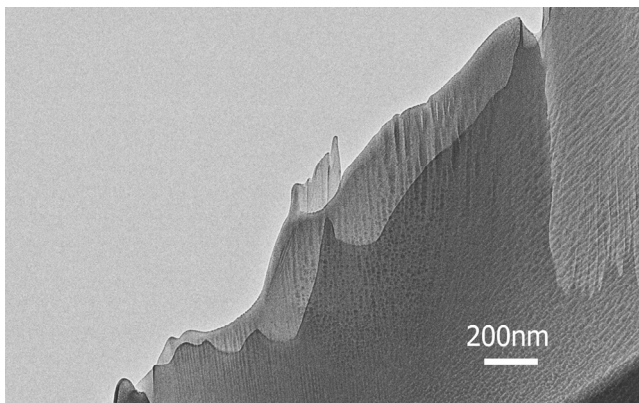


Fig. 10. The Cr_3C_2 - Ni Cr coating deposited by HVOF technique

The HVOF coating is much compacted in comparison to plasma sprayed one, in which the pores between the powder granules are visible.

4. Summary

The performed investigations show that changing process parameters and changing the method of thermal spraying it is possible to fabricate coatings with the different microstructure and level of microhardness. According to the XRD pattern of the coating, very small transformations occurred during spraying such as phase Cr_3C_2 +5% E (Ni17Cr4Fe4Si 3.5B1C), which express in the highest microhardness level. The introduction of propane - butane shield in the process of deposition contribute to the better properties of the coatings. The decarburization of coating is one of the reason microhardness diminishing.

Acknowledgements

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