Journal of Achievements in Materials and Manufacturing Engineering
VOLUME 46
ISSUE 1
May
2011

Effect of the annealing on the microstructure of HVOF deposited coatings

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Received 15.01.2011; published in revised form 01.05.2011

Manufacturing and processing

ABSTRACT

Purpose: The objective of this paper is to present how process of the coatings annealing deposited by high velocity oxy-fuel (HVOF) method influence on the microstructure changes. The differences in the microstructure and microhardness after different variants of the annealing in the comparison to the HVOF deposited coats were presented.
Design/methodology/approach: Two different coatings: WC-Co and Cr_3C_2-NiCr deposited on the AK9 substrate by HVOF method were investigated. The coats were annealing at the nitrogen in the conditions as follows: a) T = 550°C, t = 5.5 h, b) T = 500°C, t = 24 h. After, the samples were subjected by using optical (MO) and scanning electron microscopy (SEM). Also the microhardness was determined by Vickers method, the applied load was 200 gram.
Findings: The microstructure of the WC-Co and Cr_3C_2-NiCr coatings was build from the equiaxial grains distributed relatively uniform. Also characteristic was large number of discontinuous, voids and pores, especially in the WC-Co coat. After annealing, both WC-Co and Cr_3C_2-NiCr coating, the microstructure was more homogenous. It was observed reduction of the pore and voids amount. The microhardness after annealing was almost at the same level as after HVOF deposition.
Practical implications: The performed investigations could be useful in the industrial practice and give the information about working WC-Co and Cr_3C_2-NiCr coats at the elevated temperatures.
Originality/value: The HVOF deposited and successive annealed WC-Co and Cr_3C_2-NiCr coats have more uniform microstructure which could contribute to the improvements of some properties, for example wear resistance.
Keywords: High velocity oxy-fuel techniques (HVOF); Annealing; WC-Co coats; Cr_3C_2-NiCr coats; Microstructure

Reference to this paper should be given in the following way:
M. Richert, B. Leszczyńska-Madej, Effect of the annealing on the microstructure of HVOF deposited coatings, Journal of Achievements in Materials and Manufacturing Engineering 46/1 (2011) 95-102.

1. Introduction

There are plenty of different technologies for coatings deposition. One of such method which allows producing the wear resistance coatings is physical vapour deposition technologies (PVD). The main limitation of this method is the chamber size, which limit the size of the elements for coating deposition. PVD process is used to deposit thin films from the range of a few angstroms to several dozen nanometers [1-5].

The other technique which allows producing wear resistance coatings is High Velocity Oxyfuel (HVOF) method. Thermally sprayed tungsten carbide and chromium carbide coatings are widely used for a variety of wear resistance applications, for example in gas turbine, steam turbine, aero-engine to improve the resistance to sliding, abrasive and erosive wear. The wear resistance of such deposited coatings is three to five times higher than electroplated chromium. It was found, that the wear behaviour of coatings depends on the microstructure and the volume fraction of carbides being preserved during the deposition process [6-9].

The problem, which can appear during thermal spraying, is decarburization of tungsten carbide, which reduces the WC to a dicarbide (W_2C) and metallic tungsten. Also possible phases which can form have been identified as: $CoWO_4$, $Co_xW_yC_z$. WC carbide can be degraded when the WC + M powder particles travel with the HVOF flame and new phases are formed because of the loss of carbon by oxidation and reaction of the W with metallic phase presented, e.g., Co. The wear resistance of WC-Co cermets is determined by uniformly distributed fine WC carbides in the cobalt matrix. Therefore, the reduction of the tungsten carbide particles after spraying will reduce the wear resistance of the coating [10-12]. Also during thermal spraying of the Cr_3C_2-NiCr coating some substantial variations are possible to appear due to exposure to high temperature accelerating gas. Carbide phase can dissolute into the alloy matrix, reducing the carbide concentration. As a result carbon can be lost as CO or CO_2 phase, altering the composition of the carbide phase, while the matrix composition can vary from regions dominated by Cr through to the Ni rich [8, 9].

The HVOF deposited coatings contain low porosity and low oxides content. To improve the density and homogeneity of sprayed coatings, the post-spray treatments such as laser remelting, shot peening, HIP or furnace heat treatment are used [13]. The results of the work [14] show, that heat treatment of the coatings significantly improved the erosion resistance under the high velocity impact conditions. This is result of the improved inter-splat cohesion. The as-sprayed coatings are in metastable state, therefore when they are exposed to elevated temperature, the microstructural and compositional transformations can occur. The most probable changes are the precipitation of fine carbides or possibly oxides accompanied by recrystalisation of the matrix and pore and voids reduction. Also probable is the properties changes, in particular microhardness [8, 15, 16].

The aim of the presented paper was to examine the effects of post-sprayed annealing on the microstructure and microhardness changes of HVOF - sprayed WC-Co and Cr_3C_2-NiCr coatings.

2. Experimental basis

Two different coatings Cr_3C_2-NiCr and WC-Co were deposited on the AK9 substrate by the High - Velocity Oxy - Fuel spraying (HVOF) technique in Plasma System S.A. The Cr_3C_2-NiCr coating was sprayed using HP/JP 5000 Gun Kit with oxygen 850 l/min and kerozyna 24 l/h. The selected powders were: 75% Cr_3C_2 + 25% NiCr with the grain size 15-45 μm for the NiCr and 1 μm sintered agglomerates of the Cr_3C_2. The WC-Co coating was sprayed using HP/JP 5000 Gun Kit with oxygen 944 l/min and kerozyna 25.5 l/h. The powder was composed from: 88% WC + 12% Co with the grain size 5-30 μm for the Co and 1 μm sintered agglomerates of the WC powders. The spraying distance for both of the powders was 370 mm.

The coatings were successive annealing at the nitrogen in the conditions as follows: a) T = 550ºC, t = 5.5 h, b) T = 500ºC, t = 24 h.

Microstructures of the samples were subjected by using Olympus GX51 optical microscope (MO) and also using Tesla BS300 and Hitachi SU 70 scanning electron microscopy (SEM). The chemical composition was determined by using EDX (Energy dispersive X-ray spectroscopy). The microhardness was measured by Vickers method, the applied load was 200 gram. Additionally the mean grain size of the carbides observed in the microstructure both of the layers was measured.

The samples for microstructure observations and microhardness measurements were prepared using Struers apparatus. They were mechanically grinded and then polished using diamonds pasts and OPS suspension.

3. Results and discussion

The microstructures of the Cr_3C_2-NiCr layer obtained by using optical microscopy are presented in Fig. 1.

The microstructure of the Cr_3C_2-NiCr coatings was built from the equiaxial carbide particles distributed relatively uniform in the matrix. Characteristic was large number of discontinuous, voids and pores.

After annealing at the nitrogen at T = 550ºC, during t = 5.5 h, the microstructure become more homogenous. The noticeable reduction of pores and voids amount was found (Fig. 1b).

With the annealing time prolongation the further diminishing of voids amount was observed (Fig. 1c).

The pores, discontinuous and voids in the Cr_3C_2-NiCr coatings localize near carbides, were detail observed by SEM investigations (Fig. 2). They are visible as black areas.

After the annealing in conditions: T = 550ºC, t = 5.5 h it was found that some of the discontinuities near carbides were treated, what is visible in the Fig. 2b.

S. Matthews et al. [8] find that during annealing process preferential nucleation occurred in the carbide free zones, where the greatest degree of dissolution had occurred during spraying. The variation in the magnitude of dissolution generated a variety of carbide distributions and morphologies with heat treatment.

Fig. 3. presented the microstructure and chemical composition of the particles finding in the intermediate layer, between the substrate and Cr_3C_2-NiCr carbide coating after the annealing at T = 550ºC, t = 24 h. The following elements as: Cr, Ni, Si and Al were found.

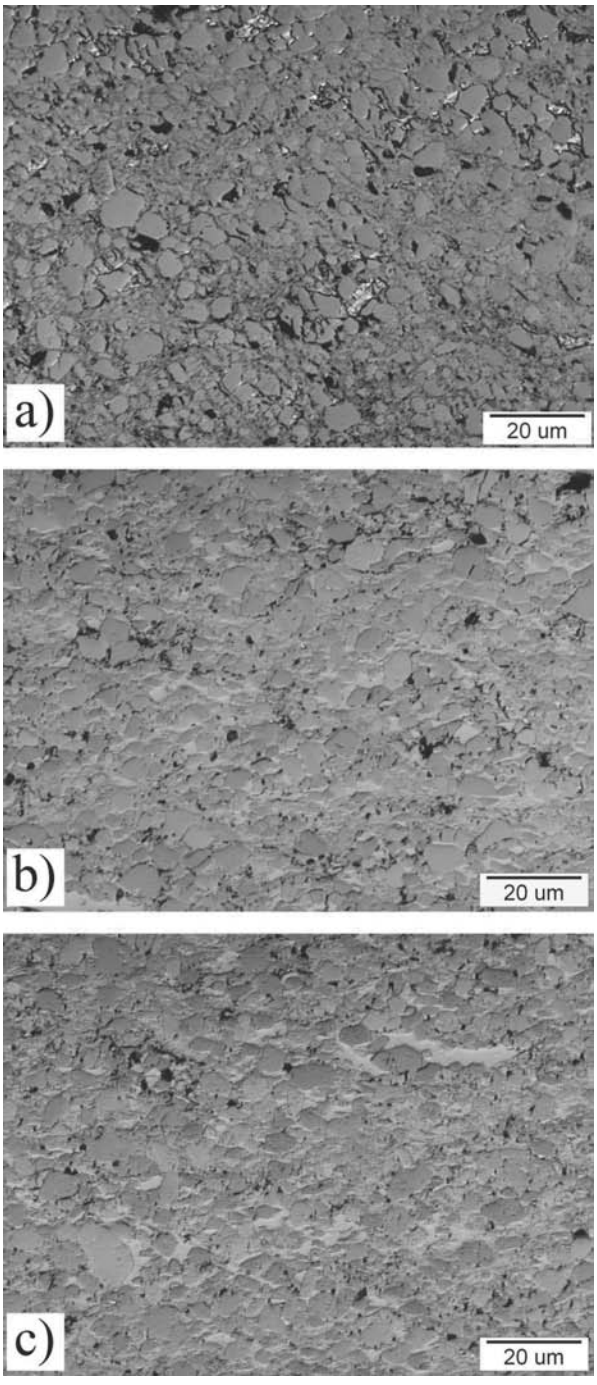

Fig. 1. Microstructures of the HVOF sprayed Cr_3C_2-NiCr coatings; a) HVOF sprayed, b) HVOF sprayed and annealed at the conditions: T = 550ºC, t = 5.5 h, c) HVOF sprayed and annealed at the conditions: T = 500ºC, t = 24 h

Fig. 4. shows an example of distribution of chemical elements in the Cr_3C_2 coatings , intermediate layer and substrate. The maps of distribution of chemical elements indicated that between the coating and substrate the SiC carbides appeared after the annealing at T = 500ºC, during t = 24 h. It suggests that some part of carbide from Cr_3C_2 coating could be arrested in SiC. The SiC at Fig. 3 is identified as white particles.

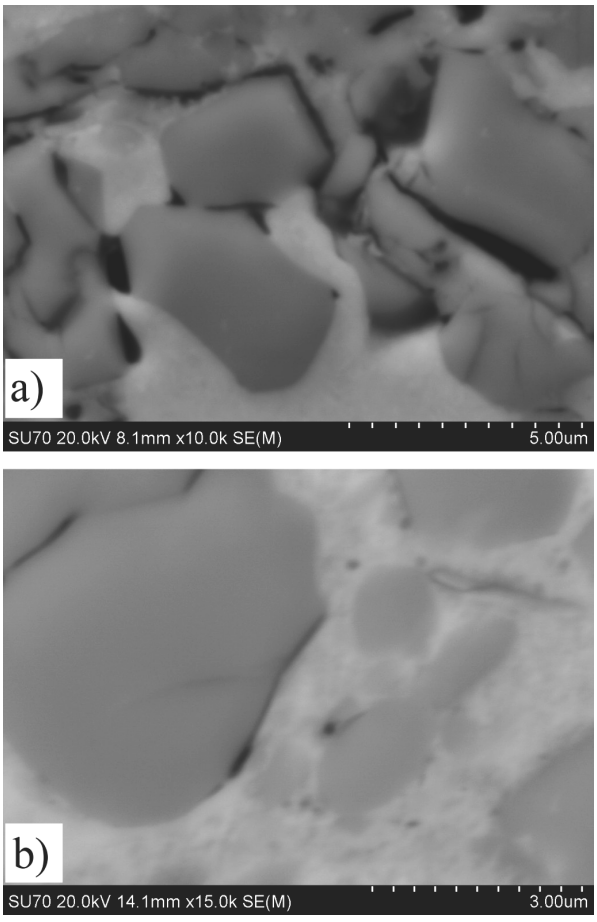

Fig. 2. Cracks localized in the neighbouring of the carbides in the HVOF sprayed Cr_3C_2-NiCr coatings; a) HVOF sprayed, b) HVOF sprayed and annealed at the conditions: T = 550ºC, t = 5.5 h

It was found that the amount of SiC carbides increased after the prolongation of the annealing process.

Fig. 5 presented data connected to the increase of thickness of the intermediate layer with the increase of the annealing time and temperature. The lover annealing temperature take effects in formation of the thinner ‘interlayer’ which measure average 25 μm Annealing at the temperature 550ºC resulted formation of the coarse “interlayer” which measure average 35 μm. (Fig. 5). The increase of interlayer width is connected with the diffusion of elements and formation of new compounds.

Presented in the Figs. 5 a, b c cross sections of the HVOF Cr_3C_2-NiCr samples show that formed between coating and substrate “interlayer” can weaken the joint. Characteristic is an occurrence of the voids, discontinuity and also some great phase precipitates. It is probably that during working at the elevated temperatures (from the range of 500-550ºC and higher), the coating can be devastated and removed from the substrate.

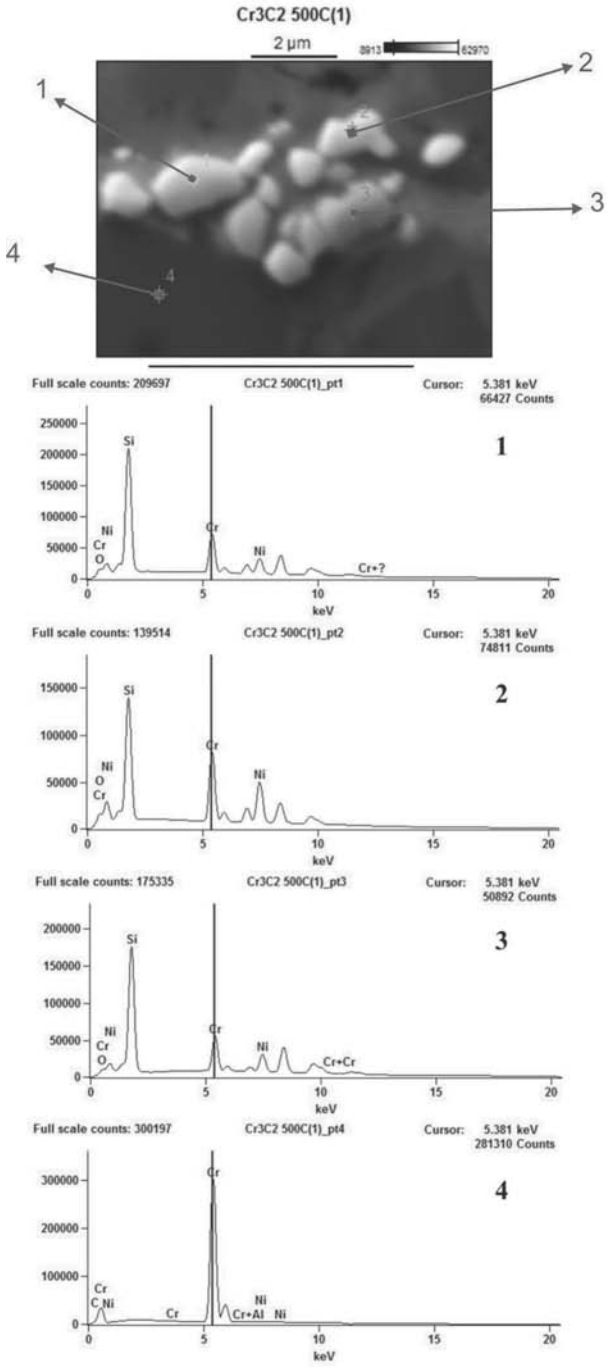

Fig. 3. Microstructure and chemical composition of the particles presented in the HVOF sprayed Cr_3C_2-NiCr coating and annealed at the conditions: T = 500ºC, t = 24 h

The identification of other elements existing inside the interlayer has been performed by EDS technique. Fig. 6. presented the maps of chemical element distribution. The prepared maps of the elements distributions show the Ni and Al occurs in this "interlayer" region.

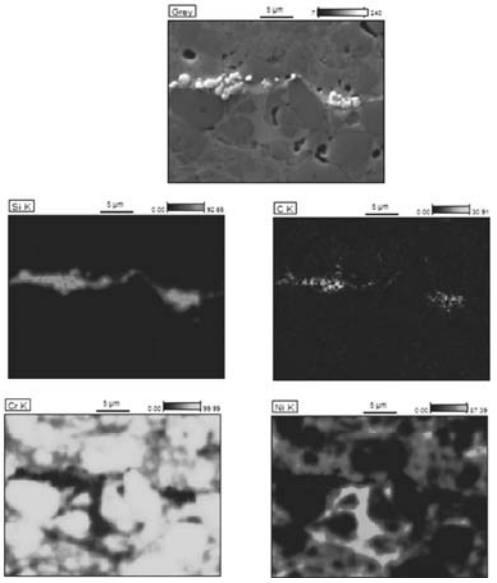

Fig. 4. Microstructure of the HVOF sprayed Cr_3C_2-NiCr coating and then annealing at the conditions: T = 500ºC, t = 24 h with maps of the elements distributions

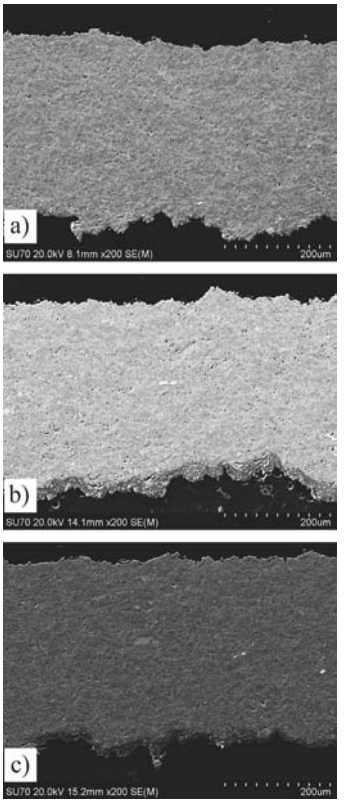

Fig. 5. Cross section of the HVOF sprayed Cr_3C_2-NiCr coating; a) HVOF sprayed, b) HVOF sprayed and annealed at the conditions: T = 550ºC, t = 5.5 h, c) HVOF sprayed and annealed at the conditions: T = 500ºC, t = 24 h

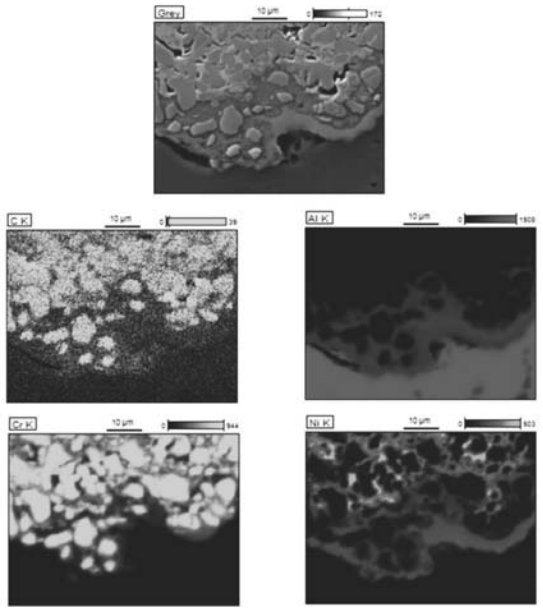

Fig. 6. Microstructure of the HVOF sprayed Cr_3C_2-NiCr coating and then annealing at the conditions: T = 500ºC, t = 24 h with maps of the elements distributions on the contact layer - substrate

Earlier investigations of the Cr_3C_2-NiCr coating deposited by HVOF method and presented in the article [1] revealed the occurrence of the Cr_3C_2, Cr_7C_3 and $Cr_{23}C_7$ carbides and NiCr phases (Fig. 7). The $Cr_{23}C_7$ and Cr_7C_3 carbides can be unstable during the annealing process. Even small amount of the carbon during disintegration of the carbides can react with silicon and form silicon carbide. As is presented in the work of Ji et al. [9] and also S.Matthews et al. [8] during the coating formation the particle of Cr_3C_2 are rebounding - off. This phenomenon is responsible for the carbon loss and the change of carbide content. As the result of such phenomenon the properties of the coatings can change.

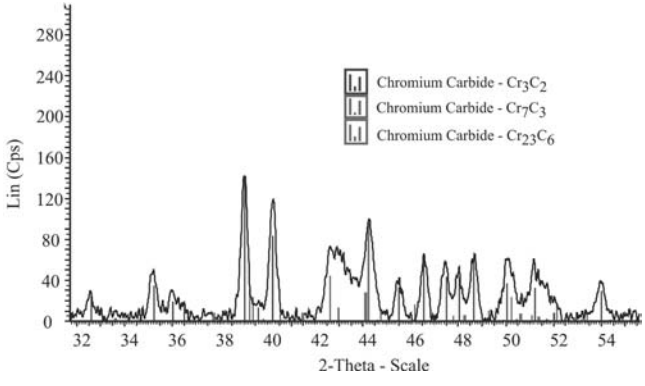

Fig. 7. Phase composition of Cr_3C_2-NiCr coating

The microhardness of the Cr_3C_2-NiCr HVOF coating was about 870 $HV_{0.2}$ (Fig. 8). After annealing at the conditions: T = 550ºC, t = 5.5 h the slight increase of the microhardnes to the value of average 926 $HV_{0.2}$ has been observed. Increase of the microhardness can be caused by the porosity lowering, what is visible in the microstructures presented in Figs. 1 a, b, c.

Annealing at the temperature 500ºC for 24 hours caused reduction of the microhardness level to the 816 $HV_{0.2}$.

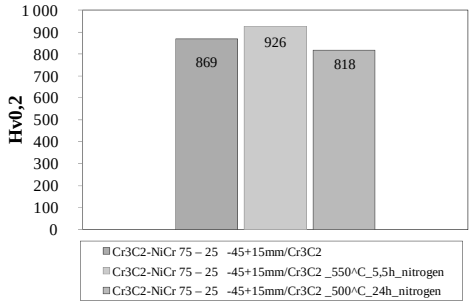

Fig. 8. Microhardness of the HVOF sprayed Cr_3C_2-NiCr coating and annealed in the different conditions

This phenomena is in agree with S. Matthews et al. Results [8] who heat treated HVOF deposited Cr_3C_2-NiCr coatings in the different periods of time: 2, 5, 10, 20, 30, 40 and 60 days. At the initial period of heat treatment they observed reduction in hardness. With continued exposure the microhardness increased, reaching stable value after 30 days of treatment. Some factor, which can contribute to the weakening of the coating after 1 day treatment is increase of the grain size, what was confirmed by the measurements.

The measured grain size for this variant was near 20% higher than obtained in HVOF sprayed Cr_3C_2-NiCr coating. They measure average 3.2 μm in HVOF Cr_3C_2-NiCr coating and 3.65 μm in HVOF Cr_3C_2-NiCr coating and then treated at the T = 500ºC, t = 24 h, respectively (Table 1).

Table 1.
Grain size of the carbides in Cr_3C_2-NiCr coatings

Material	Grain size, μm	Minimum	Maximum
Cr_3C_2-NiCr, HVOF	3.2	0.567	7.82
Cr_3C_2-NiCr, HVOF, T = 550ºC, t = 5.5 h	2.98	0.68	7.82
Cr_3C_2-NiCr, HVOF, T = 500ºC, t = 24 h	3.65	0.63	10.23

The microstructure of the WC-Co coatings similarly as Cr_3C_2-NiCr was built from the equiaxial grains (Fig. 9). Also characteristic was large number of voids, discontinuous and pores, especially after HVOF deposition.

Annealing at the temperatures 500ºC and 550ºC effected microstructure homogenization (Fig. 9). After annealing in the conditions: T = 500ºC, t = 24 h, the voids and pores disappeared almost completely, which appears as disappearance of black areas, clearly visible in Fig. 9a.

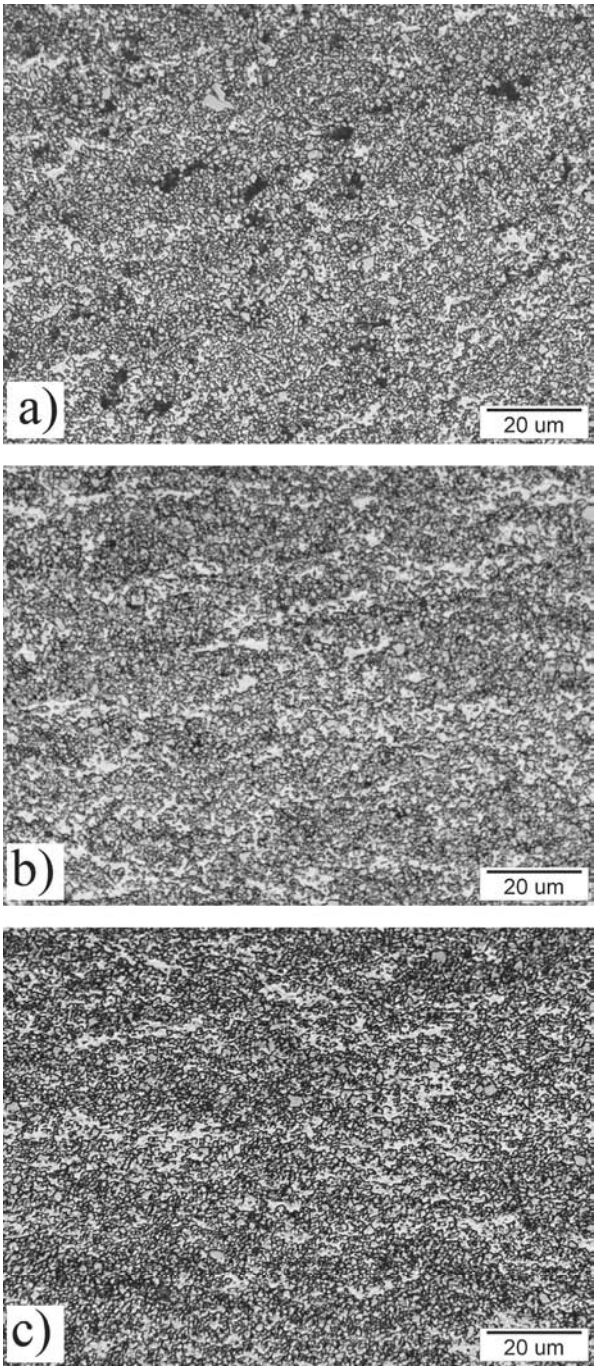

Fig. 9. Microstructures of the HVOF sprayed WC-Co coatings; a) HVOF sprayed, b) HVOF sprayed and annealed at the conditions: T = 550ºC, t = 5.5 h, c) HVOF sprayed and annealed at the conditions: T = 500ºC, t = 24 h

Fig. 10 presented EDS maps of the chemical elements distributions in the WC coating. It was found that general WC carbides are distributed uniformly in the Co matrix. However there are some areas with the concentration of the smaller carbides. The some spread of carbides sizes was found.

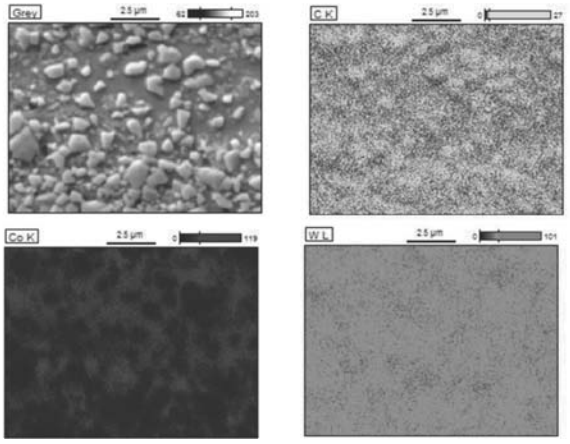

Fig. 10. Microstructure of the HVOF sprayed WC-Co coating and then annealing at the conditions: T = 500ºC, t = 24 h with maps of the chemical elements distributions

Fig. 11. presented EDS investigations of WC carbide composition for the selected particles after annealing at T = 500ºC, t = 24 h. In the all investigated particles the W an C chemical elements were found.

The properties of the WC-Co coatings is attributed to a: shape, distribution and size of carbide, solution of carbon in the cobalt matrix and matrix hardness and toughness. To achieve the optimum wear properties, a coating must retain large volume fraction of finely distributed WC monocarbide, what is dependent on the minimizing of decarburization of WC. Decarburization can occur at high temperatures associates with the thermal spray process [7, 11, 12].

The microhardness of the WC-Co HVOF coating was about 1240 $HV_{0.2}$ (Fig. 12). After annealing it was observed the increase of the microhardness value. At the conditions: T = 550ºC, t = 5.5 h the microhardness increase 14% with comparison to the initial state. Annealing at the temperature T = 500ºC in the period of time t = 24 h results subsequent microhardness increase. The average value of microhardness was equal to 1488 $HV_{0.2}$.

Increase of the microhardness value after annealing process can probably results from the porosity diminishing.

A number of hardness mechanisms responsible for the changes in hardness with heat treatment are proposed for the HVOF deposited coatings.

For carbide cermets, WC, the model of Lee and Gurlad [17] described by S. Matthews [8] has been applied (eq. 1)

$$H_C = H_{WC}V_{WC}C + H_M(1 - V_{WC}C) \quad (1)$$

where:
H_C – cermet hardness,
H_{WC} – hardness of the hard phase,
V_{WC} – volume fraction of the hard phase,
H_M – hardness of the matrix phase.

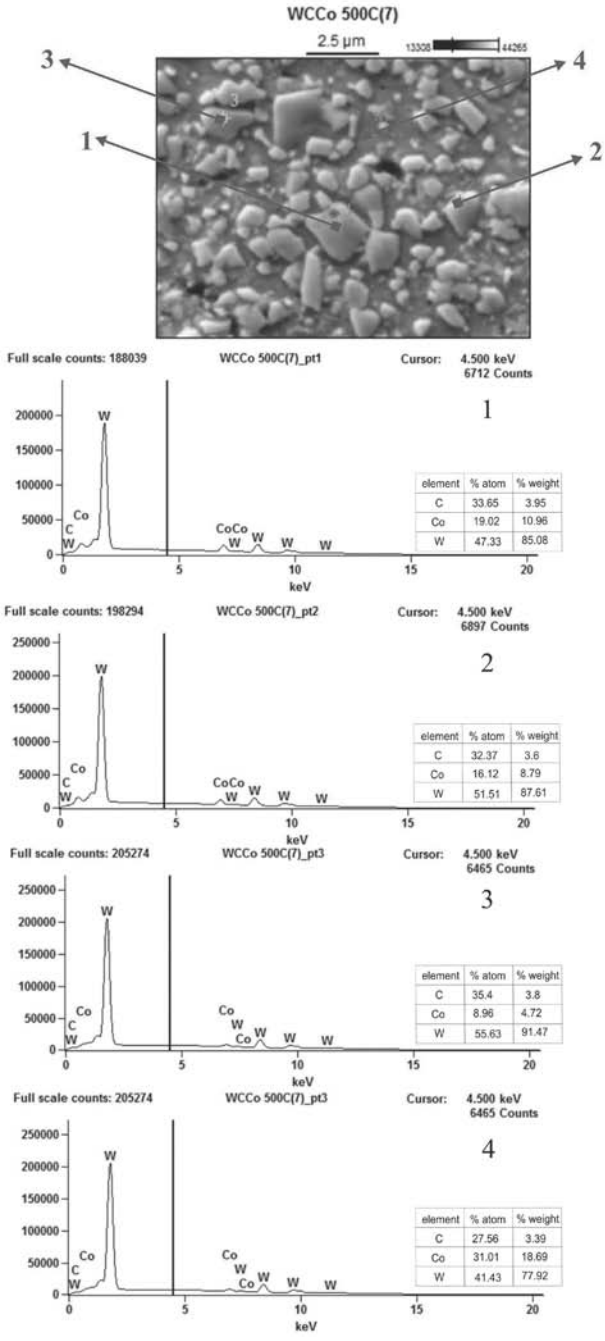

Fig. 11. Microstructure and chemical composition of the HVOF sprayed WC-Co coating and annealed at the conditions: T = 500ºC, t = 24 h

The other factors, which can contribute to the hardness level are: a) grain size of the carbides – smaller grains giving higher hardness value, b) inter-carbide spacing – the smaller give higher hardness value, c) splat - splat bonding, d) oxide formation. The role of the oxide content in HVOF deposited coatings is ambiguous. Their higher hardness increase the overall hardness, but from the other side their presence as stringers may reduce splat/splat bonding, what can reduce the overall hardness [8].

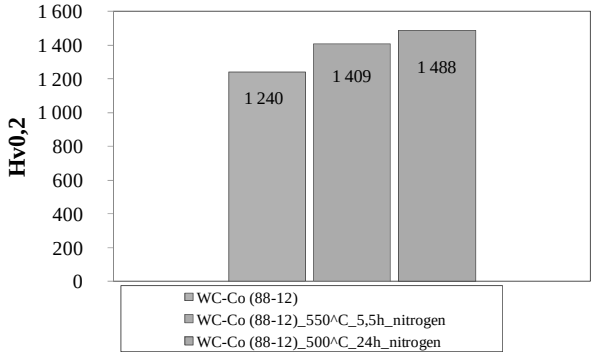

Fig. 12. Microhardness of the HVOF sprayed WC - Co coating and annealed in the different conditions

4. Conclusions

The results of the presented study Cr_3C_2-NiCr and WC-Co HVOF sprayed and then annealed coatings can be summarized as follows:

1. Microhardness of the WC-Co coatings were higher than those of the Cr_3C_2-NiCr coatings. The average value of microhardness after HVOF process was equal 870 $HV_{0.2}$ and 1240 $HV_{0.2}$ for Cr_3C_2-NiCr and WC-Co coating respectively.
2. The annealing process cause increase of the value of microhardnes HVOF WC-Co coating. After annealing at the temperature T = 500ºC and t = 24 h the average micro-hardness was equal 1488 $HV_{0.2}$. With comparison to the initial state increase was about 20%.
3. Homogenization of the microstructure in the annealed coatings was found. After annealing WC-Co coating in the temperature 500ºC, the voids and pores disappeared almost completely.
4. After annealing Cr_3C_2-NiCr coatings, at the boundary between coating and substrate voids, discontinuity and new phases appear which can weaken the joint.

Acknowledgements

The work was financially supported by polish project NR15 0001 06.

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