Structure, Mechanical and Tribological Properties of HVOF Sprayed (WC-Co+Al) Composite Coating on Ductile Cast Iron

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Abstract: The paper presents the results of examinations of WC-Co coating sprayed on ductile cast iron by high velocity oxygen fuel spray process (HVOF) with powder containing Al particles in an amount of 10%. The impact of Al particles added to the tungsten carbide coating on the structure, mechanical and tribological properties in the system of (WC-Co)/ductile cast iron was examined. The microstructure of the thermal sprayed WC-Co+Al coating was characterized by light, scanning electron (SEM) and transmission electron (TEM) microscopes as well as the analysis of chemical and phase composition in micro areas (EDS, XRD). It was found that by supersonic thermal spraying with WC-Co powders with the addition of Al particles, the coatings of low porosity, high hardness, a very good adhesion to the substrate, compact structure with molten Al particles and finely fragmented WC particles embedded in a cobaltic matrix, reaching the nanocrystalline sizes were obtained.
Moreover, the results were discussed in reference to examination of bending strength considering cracking and delamination in the system of (WC-Co+Al)/ductile cast iron as well as hardness and wear resistance of the coating. It was found that the addition of Al particles was significantly increase resistance to cracking and wear behaviour in the studied system.

1. INTRODUCTION

One of the promising coating materials for use on highly loaded parts of ductile cast iron in the automotive and aerospace industries is tungsten carbide due to its high resistance to wear and high temperature corrosion, hardness and thermal conductivity. By utilizing surface engineering technology, it is possible to improve these properties; a particularly promising treatment is to modify the chemical composition of the ceramic powders by admixing pure metal particles in ultrasonic high-speed powder spray process (HVOF - High Velocity Oxy Fuel). The process of ultrasonic spraying with a relatively low temperature of the spray jet (approx. 2600°C), and the short staying time of the powder particles in the spray jet has significantly reduced the detrimental effects associated with changes in the phase composition of coatings, present in the conventional plasma spraying, such as: carbide disintegration, drastic reduction of the range of the oxidation of metallic and carbide materials, which in turn increased the performance characteristics of the coatings [1-3].

The coatings produced using the high-speed HVOF technology have excellent wear resistance and reduced porosity and increased adhesion as compared to the conventional plasma spraying. Coating quality, the strength, hardness, density, adhesion and related characteristics depend on the speed of the powder particles, which in this method exceeds the speed of sound. High-speed collisions are able to induce very high pressure and severe plastic deformation together with the occurrence of rotation mechanism. Hence, a unique feature of this technology is that, in contrast to other methods of thermal spraying, it provides the coatings in pressure stress. Pressure stress in the coating greatly increases the adhesion of the spray to the substrate (adhesion-diffusion resistance of the coating with the substrate greater than 80 MPa) and is also advantageous from the standpoint of the fatigue properties of coated materials [4-7].

The aim of the study was to assess the impact of the modification of the chemical composition of the carbide...
coating WC-Co sprayed on ductile iron using HVOF on the structure, mechanical properties, and wear properties of the system type composite coating (WC-Co+Al)/ductile cast iron in combination with analysis of cracking and delamination of the coating in the area of interface.

2. EXPERIMENTAL DETAILS

2.1. Materials

Composite coating was prepared using the supersonic flame spraying of carbide powder with the composition WC-12Co (88% WC-12% Co) with a grain size of 45±15µm, to which 10% of the Al particles were introduced with the size of 20 µm. Spray coating uses ultrasonic spraying system HV-50 HVOF System in the company Plasma System SA, in which the spraying process used a mixture of kerosene and oxygen as a fuel. The substrate made of ductile iron EN-GJS-500-7 having the chemical composition: 3.61% C, 2.29% Si, 0.45% Mn, 0.045% P, 0.009% S, 0.03% Cr, 0.01% Ni, 0.057% Mg, 0.75% Cu, the rest Fe, was characterized by the following mechanical properties: $R_m = 500$ MPa $R_{p0.2} = 340$ MPa, $A_s = 7\%$, 220 HB. The substrate samples had dimensions of 100x15x5 mm. The surface of substrates before spraying had been subjected to blasting with loose corundum of grain size of 20 mesh. The parameter of the substrate surface roughness $R_a$ was 5.8 µm. Spray parameters are given in Table 1. The average thickness of the coating was 200 µm.

2.2. Characterization of the Coating/Substrate System

The study of the structure and chemical composition of the system type: coating/substrate used a light microscope (LM), scanning electron microscope (SEM) and transmission electron microscope (TEM) with EDS spectrometers. The coating/substrate preparations for transmission microscope in the form of a thin film were obtained by using ion thinning in a special device Gatan PIPS691V3.1 for low-angle thinning [8]. Phase composition tests were carried out on a diffractometer XPert Pro P analytical in the angular range of 20-90° with CuK radiation. The porosity measurements of the carbide coating were carried out on microscopic photographs (LM) using Aphelion 3.0 for analysis of stereological parameters of microstructure. Micro-hardness measurements of the coating were performed on microsections performed on cross-sections of normal samples to their surface, using Vickers method with Hanemann microhardness tester mounted on the microscope Neophot 2 with 1N load. As an experiment, measurements of surface roughness of coatings produced by plasma spraying were performed. The coating/substrate bond strength was determined in a three-point bending test on the fatigue testing machine INSTRON 8800M, using a specially designed holder for coating/substrate type samples with dimensions of 100x15x5 mm. Distance between supports was 70 mm and strain rate was 1 mm/min. For a single test, 3 samples were used. Observations of the fracture surfaces after the 3-point bend test were performed by scanning electron microscopy. The coating quality and adhesion to the substrate was analysed using the scratch test with Rockwell penetrator. The test was conducted on the multifunction measuring platform equipped with a nano and micro-hardness tester and Anton Paar scratch test heads. The length of a scratch was 5 mm. The tests were carried out using a Rockwell C diamond radiused 50 µm. Changes in the load values for the coatings were linear, and the range on the entire length of the scratch was 1 to 30 N. The sliding speed of the indenter was 5 mm/min. The parameters measured during the test was the penetration depth of the indenter $P_d$, the depth remaining after scratching $R_u$ the force acting on the indenter $F_N$ and acoustic emission $A_e$.

3. RESULTS AND DISCUSSION

3.1. Microstructure of the WC-Co+Al/Ductile Cast Iron System

The selected results of the observation of metallographic composite coatings (WC-Co+Al) sprayed with HVOF technique onto a substrate made of ductile iron are presented in Figure 1. A typical lamellar structure was obtained, characteristic of thermal spraying, i.e. flattened grains arranged in layers formed by the powder particles, which in the HVOF process are subject to severe plastic deformation and geometrical changes. These severe geometrical changes to particles of coating material applied in succession and a good compactness and adhesion of coatings show a plastic deformation of the composite coatings (WC-Co+Al) in the HVOF process conditions. In particular, Al particles, forming a soft phase in comparison with the brittle tungsten carbide grains are more susceptible to plastic deformation. The structure of the coatings shows small, different size particles of tungsten carbide embedded in a cobalt matrix, and the band-like placed Al particles, which upon hitting the substrate turn from spherical to elongated shape, reduce their height and extend parallel to the substrate surface. In Nomarski interference contrast, there are visible details of the structure of coatings with light molten particles of Al, arranged in bands parallel to the coating/substrate interface (Figure 1c).

The distinctive feature of the coatings is, among others, low porosity and the developed surface in the area of the coating/substrate interface. The coating is of compact structure and without micro cracks and with good adhesion to the substrate (the interface between the substrate and the

| Feed rate, mm/s | Oxygen, l/min | kerosene, l/h | Powder feed rate g/min | Powder feed gas, l/min | Spraying distance, mm |
|----------------|--------------|--------------|------------------------|------------------------|----------------------|
| 583            | 944          | 25.5         | 92                     | nitrogen, 9.5          | 370                  |

Table 1: HVOF Spraying Conditions
coating is continuous), indicating favourable conditions for the application process, ensuring adequate adhesion of the coating to the substrate. The structure of the cast iron near of the coating/substrate interface at the substrate side, no changes were observed after the spraying process (the initial and after-spraying matrix of cast iron is ferrite and pearlite - Figure 1d).

The porosity of the composite coating WC-Co+Al does not exceed 2%. For coating without the Al particles, porosity is 4%. The addition of Al is beneficial to reducing the porosity of the coating, since Al particles as compared to WC particles have a much lower melting point and better fill pores in the coating. It is worth noting that it is characterized by relatively low surface roughness, roughness parameter Ra value is 3.75 \( \mu m \). For coatings without Al particles, value of this parameter is 5.5 \( \mu m \).

For a detailed presentation of the differences in the chemical composition of the composite coating (WC-Co+Al), the surface and point analysis (Figure 2) was performed of the chemical composition using SEM-EDS microanalysis. The coatings have different-sized molten aluminium particles, zones enriched and depleted of cobalt and there is variation in the fragmentation and mixing of WC particles.

The above mentioned elements in the structure of the coatings act as elements reinforcing and plasticizing the structure of the coating. It is worth noting that light grains in the composite coating (WC-Co+Al) is a phase with a high

\[ H_{V0.1} = \text{value} \]

\[ H_{V0.02} = \text{value} \]

\[ H_{V0.01} = \text{value} \]
content of tungsten, while the darker fields form an area rich in cobalt with a small content of tungsten, and the black fields are areas of occurrence of Al phase. Microscopic observations show extensive fragmentation of the tungsten carbide grains with an average of approx. 40 µm in the initial state to approx. 0.5-1.5 µm in both the coating and in the area of coating/substrate interface. There was no permeation (diffusion) of elements from the substrate to the coating and vice versa, which in turn indicates the mechanical mixing of the coating material.

The microhardness of the tested composite coating (WC-Co+Al) on the ductile cast iron is 2144HV0,1 and then decreases to a value 230HV0,1 for the substrate. Slight variations in the microhardness of the substrate are caused by the occurring microstructure in which there are pearlite grains and graphite balls in the ferrite coating. It is worth noting at this point that there is a significant difference between the hardness of Al particle (874HV0,02), and tungsten carbide grains (2144HV0,1). The admixing of metallic particles caused local reduction in the hardness of the coating, which in turn reduces its brittleness. At the same time it is worth noting at this point that after the thermal spray of the composite coating on ductile iron, there is a 9-fold increase in the hardness of ductile cast iron in comparison to the initial state, i.e., without coating. Detailed microstructure examination of the coating performed on a thin TEM film from the sample cross-section showed nanocrystalline band-like structure. The microstructure of the coating shows longitudinal bands with a thickness of 200-400 nm parallel to each other (Figure 3) inside which there are nanocrystalline grains (5-10 nm) having a well-defined and regular shape. Electron diffraction ring patterns confirmed the nanocrystalline nature of the coating structure. In addition, based on fuzzy diffraction rings, one can also infer its amorphous nature. EDS (Energy Dispersive X-ray Spectroscopy) provided a point analysis of the chemical composition of the coating and the following elements were identified in the coating: W, Co and Al.

Phase analysis performed on the basis of the diffraction tests, besides occurrence of the WC and Al phases showed the new phases formed during the spraying process: WC and W (Figure 4). They are the result of decomposition of carbides: WC→W2C+C and W2C→2W+C due to the action of the spray jet on WC powder grains. WC is subject to decarburisation to metallic W and leads to the formation of the phase reducing the amount of WC particles during spraying (carbides are formed with a lower carbon content). In addition, volume fractions and average sizes of crystallite of the individual phases in the tested coating have been set (Table 2). The content of WC was 76.8 wt.%, and the content of the phases W2C and W was respectively 6.7 wt.% and 4.2 wt.%, and Al content was 12.3 wt.% It is worth mentioning that the average crystallite sizes of the individual phases testify to the nanocrystalline nature of the coating.

3.2. Mechanical Properties of the WC-Co+Al/Ductile Iron System

Figure 5 shows a comparison of the results of the bending test for the system: WC-Co ductile iron and WC-Co+Al ductile iron in relation bending stress-deflection value. The values of the maximum bending stress for systems WC-Co ductile iron and WC-Co+Al ductile iron are respectively 515 MPa±7 and 557 MPa±12. In the studied systems, the bending curves are parabolic. Wherein the character of the stress – strain curve
for the WC-Co+Al/ductile iron indicates that the destruction mechanism is carried out in a more as for plastic materials and for the WC-Co/ductile iron like for brittle materials. For WC-Co+Al/ductile iron on the bending curve there is a long range of deflection path during which the tension gently rises and then falls. The value of deflection, followed by a decrease in tension leading to sample destruction is approx. 1.8 mm. But for WC-Co/ductile iron there is not such a long range of the deflection path. Comparing the curves, it can be stated that for WC-Co/ductile iron there is a slight reduction of force parameters of the bending process and deflection is reduced to 1.5 mm. It is worth noting that in WC-Co/ductile iron, the coating is more hard and brittle, which in turn reduces the dissipation of plastic deformation energy, and the intensely growing load causes crack propagation and a small range of deflection.
Figure 5: Bend test curves recorded for the systems type: WC-Co+Al/ductile cast iron and WC-Co/ductile cast iron.

Observations of sample fractures after the bending test carried out on a scanning electron microscope (Figure 6) indicate that in WC-Co/ductile iron destruction occurs within both the coating near the coating/substrate interface and along the coating/substrate interface, while in WC-Co+Al/ductile iron destruction occurs only along the coating/substrate interface.

Mechanical tests of surface quality (scratch-test) were performed on the systems WC-Co/ductile iron and WC-Co+Al/ductile iron. The resulting scratch on the surface of the test material was observed under a light microscope contained in the test apparatus. The program allows to obtain characteristics: normal force $F_N$, the penetration depth of the indenter $P_d$ and depth remaining after scratching $R_d$. Table 3 shows the critical load values corresponding to the appearance of the first small cracks in the tested coatings and adhesive cracks and the maximum penetration depth of the indenter. During the scratch test, there were no large cracks in the coatings tested. Detachment of the fragments of layers concerned in the near-surface layers. There was also no delamination of the coatings zones or loosening of the coating from the substrate. For the composite coating (WC-

![Diagram of graph showing bend test curves for WC-Co+Al/ductile cast iron and WC-Co/ductile cast iron.](image)

![Scanning micrographs showing fracture surface of WC-Co+Al/ductile cast iron and WC-Co/ductile cast iron systems after bend test.](image)
Co+Al), initially small cohesive cracks were observed with a load of 5.9 N. A further increase in load did not cause any major cracks or delamination, until the load of 26 N. Such load was followed by crack in the layer on the edge of the scratch track (adhesive cracks). This type of fracture is the result of large bending stress (in the direction perpendicular to the direction of the indenter) acting on the layer at a large depth of penetration of the indenter. The value of the load at which this form of wear occurred was considered critical load of the layer \( L_c \).

The tests have shown that damage to the WC-Co coating was at a load of 10 N, and the composite coating (WC-Co+Al) at a load of 26 N. In turn, the penetration depth of the indenter was lower for WC-Co coating, which is associated with greater microhardness of this layer in cross-section. Moreover, the increase in plasticity of the WC-Co coating by introducing 10% of Al particles to the WC-Co coating material reduces wear. Scratch trace for the composite coating shows micro-grooves and plastic deformation.

It is worth mentioning that at the coating/substrate interface revealed no defects that could result in lowering the resistance to wear or which could cause poor adhesion of the coating to the substrate. High resistance to wear of the composite coating (WC-Co+Al) is a result of not only the mechanical stability of WC particles strongly bonded with bonding phase - Co, but also a strong bond of molten Al particles with the WC-Co coating material, which consequently hinders their removal from the coating.

4. CONCLUSIONS

Based on the tests and analysis of the results, the following conclusions have been formulated:

- The composite coating (WC-Co+Al) applied using the HVOF method on ductile iron shows low porosity, compact structure, good adhesion and high hardness. In the structure of the coating there are molten Al particles and finely fragmented WC particles embedded in a cobalt matrix, reaching the
nanocrystalline sizes. There were no visible changes in the structure of the substrate, which bodes well for the applications of the coatings produced.

- The composite WC-Co+Al coating structure provide good resistance to cracking. Destruction occurs along the coating/substrate interface. Cracks initiated in the area of coating/substrate interface - do not pass into cracks in the substrate.

- The composite coating (WC-Co+Al) on the ductile cast iron has good resistance to tribological wear associated with the effect of plastic deformation of the coating by admixing the base ceramic powder with metallic particles.

- The applied method of modification of the chemical composition of carbide coatings by admixing metallic particles is a useful technique to improve their mechanical and wear properties.

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