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Influence of Temperature on the Phases Changes of HVOF Sprayed Tungsten Carbide Coatings

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Tungsten carbide coatings (WC + 12 % Co) have been prepared using High Velocity Oxygen Fuel (HVOF) gun. Coatings approximately 300 µm thick were formed on the specimens surface. After deposition coatings have been heated at the temperatures between 200 °C and 1000 °C. X-ray diffraction has been used to analyze the phase transformation after spraying and heat treatment of coatings.

The WC and $W_6C_{2.5}$ phases were found. After the heat treatment above 450 °C the formation of WO_3 phase started. Above 600 °C all phases of WC and $W_6C_{2.5}$ transformed into WO_3 and $CoWO_4$ phases. Temperature influence on the crystallite size was investigated.

Keywords: HVOF, tungsten carbide, coatings, X-ray diffraction, heat treatment, phases, crystallite size, specimens.

1. INTRODUCTION

Thermally sprayed coatings are used to improve the resistance of die materials to corrosion and surface wear and to increase their heat resistance. In recent years a major trend in the thermal spray industry has been that of increasing the powder particle velocity in order to obtain high quality coatings [1].

High Velocity Oxygen Fuel (HVOF) spraying is a thermal spray process in which a material in powder form is quickly melted by a flame and with a speed of 400 to 800 m/s deposited on a surface [1]. The resulting layer is denser and more strongly bonded than layers created from other spraying processes such as flame spraying, electric arc spraying, or plasma spraying. HVOF is especially suitable for hard metal layers in which hard carbide particles are embedded in a metallic matrix (WC-Co) and when a tough, high hardness wear resistant characteristic and shock resistance are required. Due to its flexibility and cost effectiveness the high velocity oxygen – fuel thermal spraying process has been widely adapted in many industries [2].

However the physical and chemical conditions of the coatings is dependent on a large number of parameters such as the gas jet condinions (temperature, velocity, pressure), particle size, particle injection method.

During HVOF spraying WC-Co powders have to be exposed to high temperature flame jet for heating and acceleration, furthermore oxygen is usually entrained into the flame jet, the decomposition and decarburization cannot be totally eliminated. During spraying a part of WC transformed into WC_{1-x}, W_2C and metallic tungsten. Another part may dissolve into metallic cobalt to form an amorphous or nano structured Co-W-C phase or complex carbides such as Co_3W_3C, Co_2W_4C, Co_6W_6C and $Co_3W_9C_3$ [3 – 7].

The objective of this research was to investigate the influence of various heat treatment on the tungsten carbide coatings physical properties, phase transition, oxidation process character and crystallite size changes.

2. EXPERIMENTAL

2.1. Specimen surface preparation

The specimen blasting was carried out using a standard blasting nozzle of diameter 9 mm. Air pressure at the time of blastering was 5.5 kg/cm^2. Al_2O_3 grit of size 0.5...1.0 mm was used for grit blasting. The blasting nozzle was held 130 mm away from the specimen and blasting angles were kept between 60° and 90° so that an optimum surface finish is obtained.

Specimens were made from steel containing 0.45 % C, (HB200).

2.2. HVOF spraying

The high velocity oxygen-fuel process is based on a combination of thermal and kinetic energy transfer. Powder particles are fed axially into a hot gas stream using carrier gas nitrogen, then into a spray gun, are melted and propelled to the surface of the specimen to be coated. Propane gas is used as fuel gas. The gun (Fig. 1) consists of three sections: a mixing zone, combustion zone and the nozzle. During the spraying combustion chamber is cooled by water. The fuel gas and oxygen are mixed and guided to the combustion zone where external igniter initiates combustion. During combustion the gas is allowed to expand in the nozzle where it is accelerated. The powder is accelerated by a carrier gas and injected into the flame. The result of this process is sprayed coating.

In our case spherical agglomerated combination of tungsten carbide and cobalt (WC – 12 % Co) were sprayed. On the specimens surface, coatings approximately 300 µm thick were deposited. Coating thickness were measured with micrometer. Chemical composition of the powders are shown in Table 1. Particle size was in the range of 53 – 63 µm.

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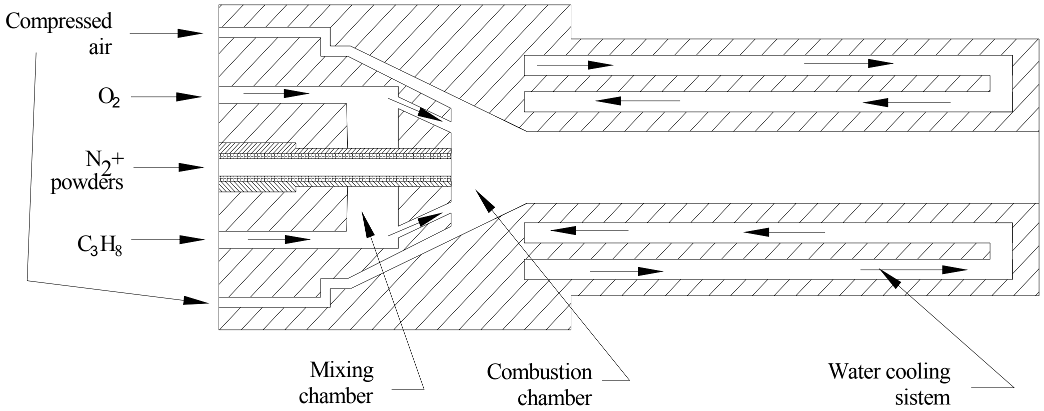

Fig. 1. Principal scheme of the HVOF gun

The gun was held 160 mm away from the specimens surface. All specimens were sprayed at the same time with the same constant technological parameters.

Table 1. Chemical composition of the WC – 12 % Co powders

W	Co	Fe	Ni	C
82.64	12	≤0.1	≤0.1	5.35

Temperature of the specimens during the spraying process was measured with an appliance "Testo 860 – T2" which was linked to computer. Typical temperature dependence of the specimen is shown in Fig. 2.

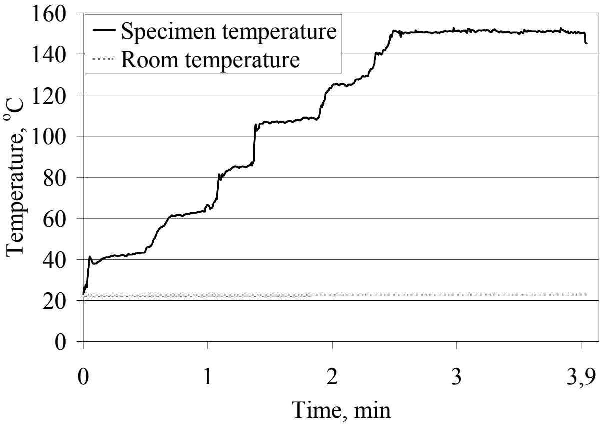

Fig. 2. The dependence of the specimen heating temperature on spraying time

2.3. Heat treatment

The heat treatment was carried out in air atmosphere. The specimens were placed in a furnace and heated at 20 °Cmin^{-1} up to the treatment temperature. Then they were annealed for 120 min and slowly cooled to room temperatures in the furnace. The heat treatment temperatures ranged from 200 ˚C to 1000 °C.

2.4. X-ray diffraction analysis

X-ray powder diffractograms were obtained on a conventional Bragg-Brentano geometry (Θ – 2Θ scans) DRON-6 diffractometer using Cu K_α radiation with generator current 20 mA and voltage 30 kV. X-ray diffraction patterns were recorded for 2Θ in the range of 10 – 90°. The WC – 12 % Co coating phases were identified comparing experimentally obtained interplanar spacing d with JCPDS data standards [9].

Win Fit computer program was used for crystallite size determination [10]. Win Fit offers a variety of methods for determination of crystallite size and strain. We have used one of them – "single line" approximation. In this method the integral width (IntW) of XRD peaks are used as a measure of peak broadening, with the α_2 component removed either during the peak – fitting process or subsequently by the method of Rachinger. The raw peak profiles are corrected for instrumental broadening b due to a strain – free sample to give values for the pure diffraction:

$$\beta = \left(B^2 - b^2\right)^{1/2}, \tag{1}$$

where B is the observed IntW after removal of the α_2 component and b is representative of the standard broadening. The broadening due to crystallite size (β_c) and to a lattice strain (β_e) are represented by:

$$\beta_c = K\lambda / L\cos\theta\,; \tag{2}$$

$$\beta_e = 4e\tan\theta\,, \tag{3}$$

where K is a shape factors for the crystallites, λ is the wavelength of the X-radiation, θ is the Bragg angle, e is the strain and L is the crystallite size.

3. ANALYSIS AND RESULTS

X-ray diffraction patterns of the WC – 12 % Co powders and as sprayed (150 °C) coatings after heat treatment from 200 °C up to 1000 °C presented in Fig. 3. A comparison between the microstructure in the powder grains and the as sprayed coating we can see at 1 and 2 curves. Sub-carbide $W_6C_{2.5}$ appears after spraying. This could be explained that during the spraying decarburization process is going on the surface of WC particle and the WC particle lost a part of carbon [8]. The fact that the cobalt peaks are detected in the powder particles and not in the as sprayed coating, suggest that most of the cobalt is retained in the nano – crystalline binder phase [8, 11].

X-ray diffraction pattern showed that after the heat treatment up to a temperature 400 °C, no transformation in the coating occurs. Following the heat treatment at 450 °C,

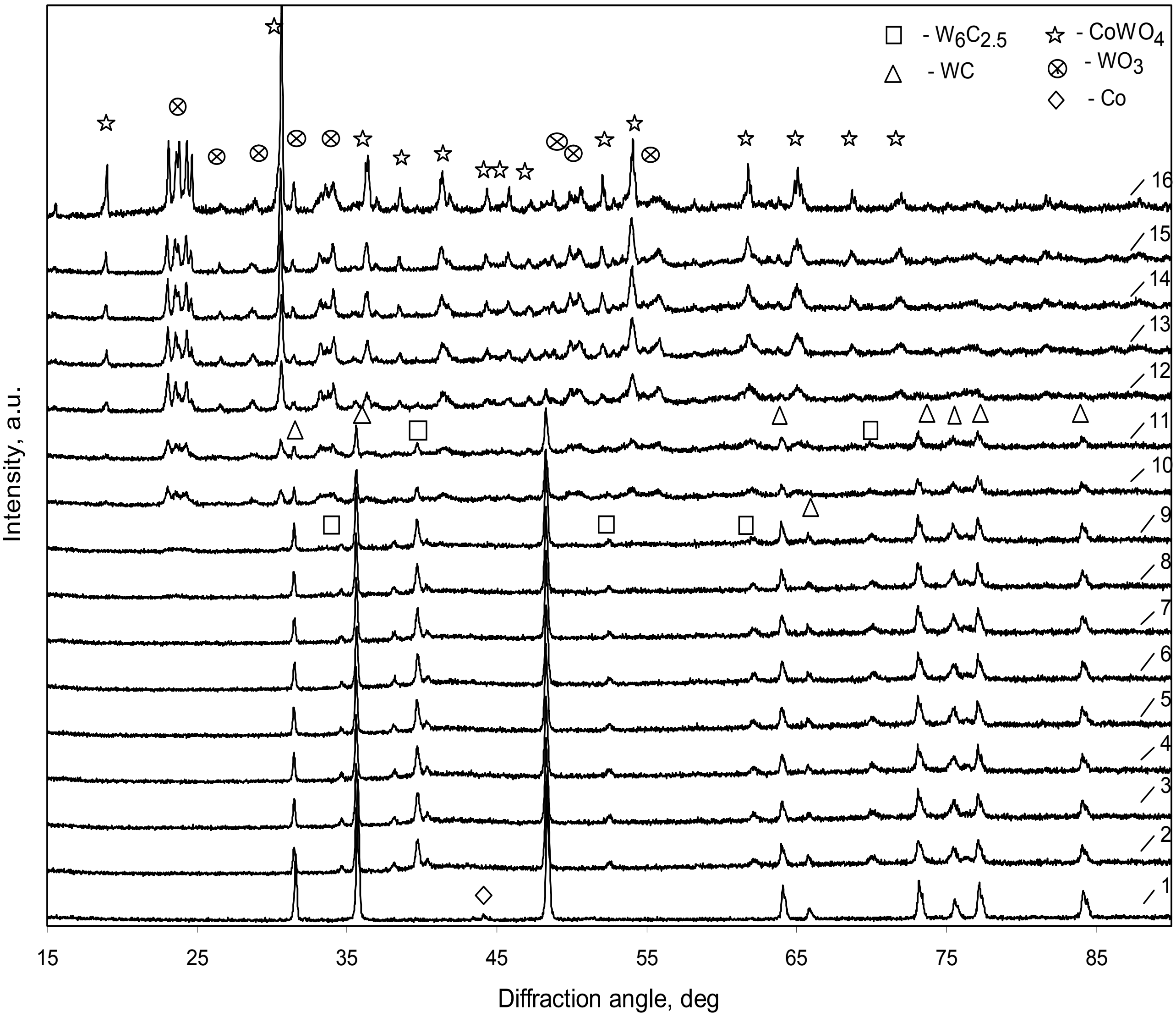

Fig. 3. X–ray diffractions pattern of WC – Co 12 % powders and as-sprayed coating after heat treatment from 200 °C to 1000 °C : 1 – powders, 2 – after spraying, 3 – 200 °C, 4 – 250 °C, 5 – 300 °C, 6 – 350 °C, 7 – 400 °C, 8 – 450 °C, 9 – 500 °C, 10 – 550 °C, 11 – 600 °C, 12 – 650 °C, 13 – 700 °C, 14 – 800 °C, 15 – 900 °C, 16 – 1000 °C

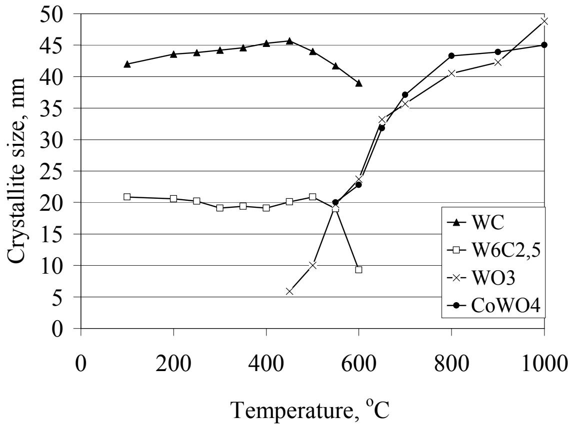

Fig. 4. WC, $W_6C_{2.5}$, WO_3 and $CoWO_4$ crystallite size dependence on the temperature

showed starting formation in the coating of WO_3 phase (Fig. 3, curve 8). After heat treatment at 550 °C started formation of $CoWO_4$ phase (Fig. 3, curve 10). As we see in Figure 3 that at the temperature 600 °C oxidation degree is very large and all phases of WC and $W_6C_{2.5}$ are transformed into WO_3 and $CoWO_4$ phases. When the temperature was increased up to 1000 °C the phases of oxides were the same as at the temperature 600 °C but peak intensity was higher.

Heat treatment from a temperature 200 °C up to 450 °C, resulted in WC crystallite size increase (Fig. 4). After oxidation process started at temperature 450 °C WC crystallite size quickly started to decrease. Sub - carbide $W_6C_{2.5}$ crystallite size up to the temperature 550 °C practically don’t change and after that quickly decreased. WO_3 and $CoWO_4$ crystallite size increased after temperature going up from 450 °C. At the temperature 900 °C coating separated from the substrate due to oxidation of substrate.

Mechanical properties of WC – 12 % Co coatings decrease with increasing temperature when oxidation process starting. The high volume expansion of tungsten carbide to tungsten oxide and the lack of Co due forming of $CoWO_4$ in the binderless material cause the coating to be more porous than the coating on Co – bonded material. This may explain decrease of carbides hardness, its lower adherence, cohesion and increased wear rate [12]. The temperature 550 °C is critical when oxidation process starts, so can say that WC – 12 % Co coating deposited with FVOF gun have good mechanical properties up to the temperature 550 °C.

4. CONCLUSIONS

Heat treatment of the WC – 12 % Co coating above 450 °C showed starting of the oxidation process and formation of WO_3 phase. At the temperature 550 °C formation of $CoWO_4$ phase started.

At the temperature 600 °C all phases of WC and $W_6C_{2.5}$ are transformed into WO_3 and $CoWO_4$.

After spraying WC particle lost a part of carbon and sub-carbides $W_6C_{2.5}$ appear in the coating.

No oxidation takes place during the spraying of WC – 12 % Co.

WC crystallite size increased till 450 °C and after oxidation process they started to decrease.

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