Cermet plasma coating TiC-Cr$_3$C$_2$-NiCr-MoC

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Abstract. The paper presents data on the effect of modes of plasma spraying on the concentration levels of carbon, oxygen, nitrogen in the TiC-Cr$_3$C$_2$-NiCr-Mo-C coating. It is determined that the microhardness of the coating reaches 27.1 GPa and the proportion of carbide phases in the coating is 82.9 %.

1. Introduction
Cermet coatings based on TiC have advantages in comparison with coatings based on WC-Co. They have lower density, higher operating temperature, and lower cost. But the carbides are partially dissolved in the liquid matrix during plasma spraying process [1, 2]. The amount of carbon in the carbide decreases due to the interaction with oxygen, and the hardness of the coating decreases. Losses of carbon can be reduced due to alloying of the carbide and matrix phases, as well as due to spraying in inert atmosphere.

The aim of this work is to study the carbon content in the TiC during the powder manufacturing and its plasma spraying. Mix of carbon and Cr$_3$C$_2$ was chosen to solve this problem. Cr$_3$C$_2$ was used to decrease the oxidation of the spraying particles. Also, the ring zone around the TiC contained Cr$_3$C$_2$, which reinforced the cermet. The powder of Mo was used to increase the wetting of TiC by matrix of Ni-20Cr. The ring zone also contained Mo [3].

2. Materials and methods
The composition of the powder was 45 wt. % TiC – 15 wt. % Cr$_3$C$_2$– 26.2 wt. % Ni-20Cr – 11 wt. % Mo and 2.8 wt. % C. The powder for spraying was obtained according to the following scheme. At the first stage, the feedstock powders were mixed in a ball mill. Further, the mechanical mixture was pressed into compacts. At the next stage, the compacts were being sintered in a vacuum furnace at a temperature of 1130 °C for 3 hours. Next, the compacts were crushed. After grinding the powders were dispersed on sieves. The fraction of 25–63 µm was prepared.

The UPU-3D with plasma spray gun PP-25 was used for plasma spraying. The diameter of the anode nozzle was 6 mm. The local protection of the spraying zone was carried out by a special water-cooled nozzle. The nozzle was developed in the IMET RAS; this device was described in the monograph [4].

Argon was used as plasma gas. Nitrogen was used as an additive gas for control of the arc power. During plasma spraying process the arc voltage was 50, 55, and 60 V. The magnitude of the current was a constant of 350 A. The total plasma gas flow was 36.5 l/min. For x-ray investigations the coating thickness of 0.3 mm was sprayed on the steel substrate with a thickness of 1 mm. For preparing metallographic specimens, the coating with a thickness of 1 mm was sprayed on a rotating...
steel shell with a diameter of 60 mm and a wall thickness of 4 mm. In addition, the plasma sprayed on the pre-heated up to 400° C substrate was carried out. The coefficient of the used powder in the experiments ranged from 52.5 to 74.8 %.

The bulk content of C, O, N was measured using the “Leco” CS-600 and TC-600. The standard deviation from the mean value did not exceed 1 % for carbon, 4 % for oxygen, and 6 % for nitrogen. The microhardness of the cross-sections of the coatings was being tested by a Vickers hardness indenter (PMT-3) with loads of 20 and 200 gf for 15 s. A total of 15 values was tested and averaged to determine the microhardness.

3. Results and discussions
The microstructure of the coating is shown in figure 1. The coating consists of disc-shaped particles, pores, and micro-cracks. The distribution of carbides is uniform. The distribution of carbides by size and relative area is bimodal (figure 2(a), (b)).

![Figure 1. The microstructure of the plasma sprayed coating from 45 wt. % TiC – 15 wt. % Cr₃C₂ – 26.2 wt. % Ni-20Cr – 11 wt. % Mo – 2.8 wt. % C powder.](image)

The size of the carbides in the initial powders was from 1 to 10 µm. Some carbides were dissolved in the liquid matrix phase during the deposition process. There were carbides with a size less than 1 µm in the cross-section of the coating. Probably these carbides were formed during the solidification. The total area occupied by the carbides with a size less than 1 µm was about 20 % (figure 2(b)).

In the initial mixture the calculated content of the carbon was 12.81 % (10.01 % in the carbides and 2.8 % as carbon) and the content of the oxygen was 0.85 %. After mixing the powders in the mill, the content of the carbon was 12.6 % and the content of the oxygen was 0.81 %. After pressing, sintering
and crushing, the content of the oxygen in the powder decreased to 0.15%, and the content of the carbon was 12.5%.

![Graph](image)

**Figure 2.** Relative distributions of the carbide particles in the coating by quantitative composition (a) and the total areas occupied by the carbide phases (b).

After plasma spraying, the average content of the carbon in the coating decreased to 4.8%, and the total loss of the carbon relative to the original mixture was 5.6%. The average content of the oxygen in the coating increased by 3.8 times to 0.58%, relative to the powder for the plasma spraying.

After sintering, crystal size of TiC was reduced from 0.4327 to 0.4324 nm. Metal Mo formed the phase (Mo,Cr)2C. Pure graphite was detected. The Mo part may also be present in (Ti,Cr)C and as a ring zone around the carbide TiC [2, 4].

During plasma spraying with minimum power the content of the TiC was practically unchanged, but the crystal size was reduced to 0.4321 nm. As the plasma power increased and the substrate temperature increased, the content of the TiC was decreased to a minimum value of 38.4%, and the crystal size remained almost the same, 0.4322 nm.

Cr3C2 phase of a different structural type compared to the initial one was detected during plasma spraying. The content of this phase was from 6.3 to 8.5%. We assume that the change in the type of crystal lattice in Cr3C2 carbide occurred by the mechanism of its dissolution in the liquid matrix phase and subsequent crystallization.

The content of (Mo,Cr)2C in the coating was reduced to 0.2–1.2%. The content of the new carbide (Ti,Cr)C increased significantly with the power of the arc from 14.6 to 28.8%, the size of the crystal size increased, too.

For plasma sprayed coating the volume of the carbide phases TiC, (Ti, Cr)C, Cr3C2 and (Mo, Cr)2C was 82.9 vol.%, and for the initial mixture of powders the volume of carbide phases was 70%.

The content of the matrix phase Ni-20%Cr in the coating was not changed. The crystal size after mixing the cermet powders did not change and it was 0.3547 nm. But crystal size increased to 0.3551 nm after sintering pressing and had a maximum value in the coating of 0.3609 nm. The microhardness of the coating had high value. The average microhardness of the coating at the load of 200 gf was 15.1 GPa. The average microhardness of the coating at the load of 20 gf was 27.1 GPa.

Such values could be explained by the formation of nanosize carbides based on titanium, molybdenum chromium. The carbides were formed from the liquid and reinforced the matrix phase. We assume that the mechanism of dispersion hardening was realized. This was facilitated by the additional introduction of carbon into the powder to compensate its losses. Carbon minimized the loss of carbides in their interaction with oxygen during plasma spraying process.
4. Conclusions

Determined that the carbides were dissolved in the liquid matrix during the plasma spraying of the cermet 45 % TiC – 15 % Cr₃C₂ – 26.2 % (80 % Ni – 20 % Cr) – 11 % Mo – 2.8 % C, then on the cooling cycle the dispersion carbides were precipitation. Bimodal distribution of the carbides was detected. Content of TiC with the size more than 1 micron was 53.7 vol. %. Volume of the (Ti,Cr)C, Cr₃C₂, and (Mo,Cr)₂C carbides of the small size was from 23 to 38.4 vol. %. The volume of the carbides was being increased with the increase of the plasma power.

The content of the carbon was 12.81 mass. % in the initial mixture of the powders and 11.9 mass. % in the coating. The relative loss of the carbon was 7.1 mass. % during the experiment. The loss of the carbon was 4.8 mass. % after plasma spraying.

Decrease of the crystal size of TiC from 0.4327 to 0.4321 nm and increase of the crystal size Ni-20% Cr matrix from 0.3547 to 0.3609 is evidenced by redistribution of the carbon. For this reason, new carbide phases (Ti,Cr)C, (Mo,Cr)₂C were obtained. Also, stoichiometry of the initial phases was changed because of quenching from liquid.

The high value of the microhardness of the coating was 27.1 GPa due to saving the content of the carbon in the initial carbides and formation of the new carbides of the small size. The new carbides of the small size were obtained because of reaction between the carbon and matrix and quenching.

Acknowledgments

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