

Fine Structure Study of the Plasma Coatings B₄C-Ni-P

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Abstract. The article considers structure of coatings formed of the B₄C-Ni-P powder. The coatings were deposited using air-plasma spraying with the unit for annular injection of powder. The pipes from steel 20 (0.2 % C) were used as a substrate. The structure and phase composition of the coatings were studied by optical microscopy, scanning electron microscopy, transmission electron microscopy and X-ray diffractometry. It is shown that high-density composite coatings consisting of boron carbide particles distributed in the nickel boride metal matrix are formed using air-plasma spraying. The areas with round inclusions characterized by the increased amount of nickel, phosphorus and boron are located around the boron carbide particles. Boron oxides and nickel oxides are also present in the coatings. Thin interlayers with amorphous-crystalline structure are formed around the boron carbide particles. The thickness of these interlayers does not exceed 1 μm. The metal matrix material represents areas with nanocrystalline structure and columnar crystals.

1. Introduction

The topical problem of modern material science is the development of wear resistant materials. One of the most promising materials is the boron carbide (B₄C). Interest in this material is due to a complex of its unique properties: high microhardness (30...48 GPa) and wear resistance, low density (2.51...2.55 g/cm³), as well as high corrosion resistance [1-3]. Usually thin coatings of boron carbide are deposited on the already finished parts. The main methods of B₄C coatings deposition are considered to be the spraying techniques [3, 5-11].

Unfortunately, some difficulties connected with B₄C properties arise both at the deposition of coatings from boron carbide and at the formation of 3D materials. Low thermal conductivity of boron carbide does not allow to heat the powder particles fully and the high hardness does not allow plastic deformation on the substrate. The solution to this problem is addition of a binder: various metals or chemical compounds possessing higher ductility and thermal conductivity. Although the structure and properties of coatings formed of the blends of B₄C powders and various metals are well studied [4, 9, 11-15], there are few articles describing structural changes in the B₄C-Ni-P coatings [16]. In particular, there is no research relating to the formation features of these coatings using the air-plasma spraying with the unit for annular injection of powder. The purpose of this research is the study of the B₄C-Ni-P coatings fine structure formed using the air-plasma spraying with the unit for annular injection of powder.



2. Experimental

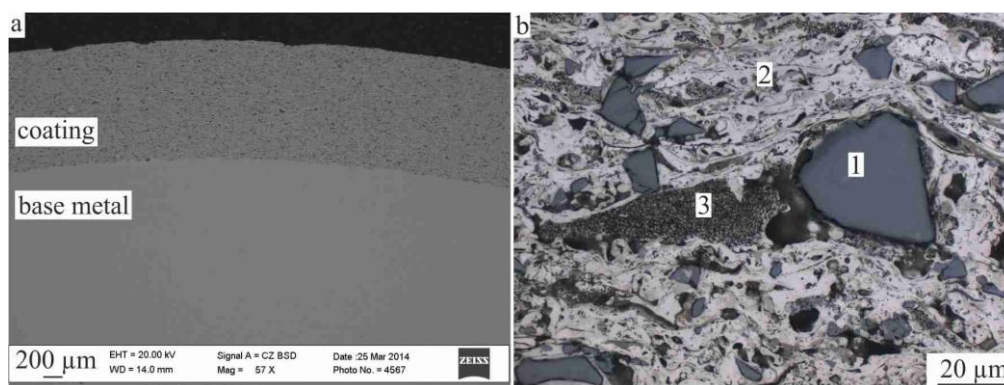
In this work the research objects were coatings formed from B_4C powder clad by Ni-P. The chemical composition of powder is 70 wt. % B_4C , 25.5 wt. % Ni, 4.5 wt. % P. The powder particles had irregular form.

The air-plasma spraying was performed at the Khristianovich Institute of Theoretical and Applied Mechanics of the SB RAS using PNK-50 plasmatron with the unit for annular injection of powder. The powder was deposited on the pipes from the low-carbon steel 20 (0.2 % C) 25 mm in diameter with 3 mm wall. The spraying regimes were: arc current is 180 A, voltage is 180 V. The spraying distance was 170 mm. The air was used as plasma-forming gas and carrier gas. The blend of air and propane-butane was used as shielding gas.

Structural investigations were conducted using the Carl Zeiss Axio Observer Alm optical microscope and Carl Zeiss EVO50 XVP scanning electron microscope with EDS X-Act microanalyser. The samples for the structural investigations were cut from pipes with coatings, pressed into the polymer matrix and then prepared by the standard method: mechanical grinding and polishing. We used 10 ml of HCl, 0.1 ml of HNO_3 and 10 g of $FeCl_3$ solution for etching of the coatings surface. More in-depth structure research was carried out using the Tecnai G2 FEI transmission electron microscope. Workpieces of 3 mm in diameter cut from the middle of the coatings were used as samples. They were mechanically thinned to the thickness of 90...100 μm . Gatan Dimple Grinder was used to obtain spherical dimples. The final operation was the processing of foil by an Ar-beam on Gatan PIPS until receiving a hole in the dimple. The phase composition was studied using ARL X'TRA X-ray diffractometer. The microhardness was estimated by Wolpert Group 402MVD microhardness tester at 100 N load.

3. Results and discussion

Figure 1a shows the cross section of plasma coating. The obtained coating thickness is 1200 μm . Figure 1b demonstrates that the coating material consists of dark particles with arbitrary form (area 1) equally spaced in a metal matrix (area 2). The etching of surface allows identifying areas with a eutectic structure (area 3) located predominantly around dark particles.



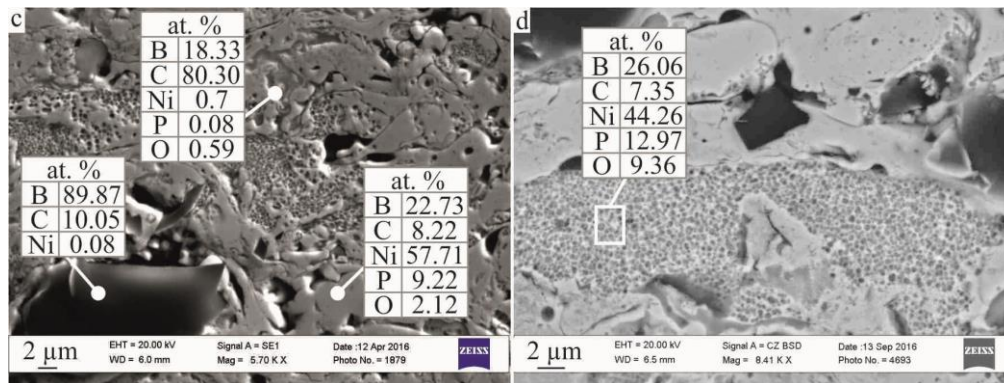


Figure 1. The structure and local chemical composition of coating: a) compound "base metal-coating"; b-d) coatings structure.

a, c, d – scanning electron microscopy; b - optical microscopy.

1 - boron carbide particles; 2 - metal matrix; 3 - eutectic areas.

According to X-ray phase analysis data (Figure 2) as well as micro-X-ray spectral analysis data (Figure 1c) the dark inclusions are the B_4C particles that unmelted in the plasma jet. A metal matrix consisting of various nickel borides (Ni_4B_3 , Ni_3B , NiB) is formed as a result of the interaction of Ni and B. High rates of mixing and solidification of the matrix material contribute to the nonuniform distribution of these elements in the coating, as evidenced by the results of micro-X-ray spectral analysis (Figure 1c). The areas with the eutectic structure are characterized by increased content of Ni, P and B. The scanning electron microscopy revealed that eutectic areas constitute round inclusions up to 500 nm located in the metal matrix (Figure 1d). X-ray phase analysis showed that reflections of boron oxide (B_2O_3) and nickel (NiO) are also observed in coatings.

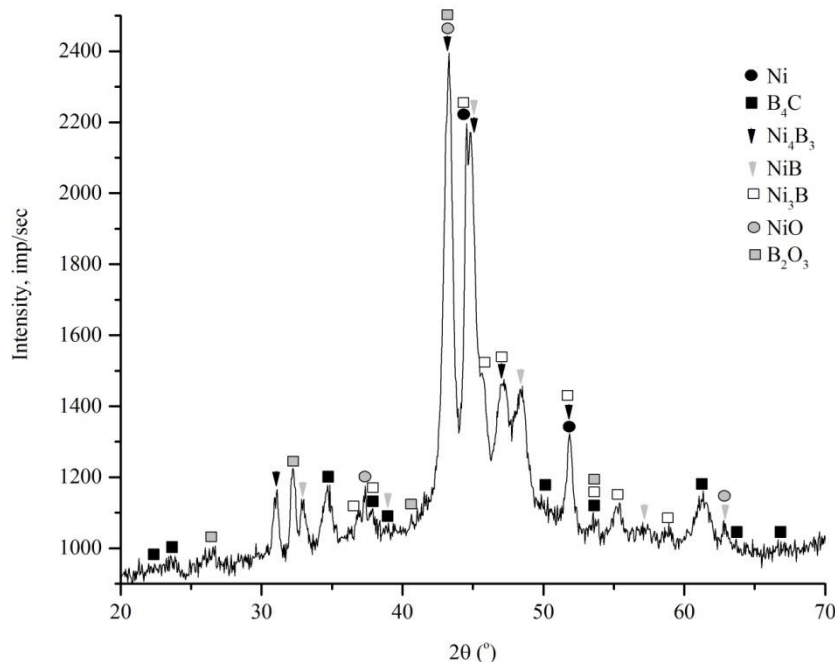


Figure 2. XRD patterns of the coatings.

Studies of the coatings fine structure were carried out using the method of the transmission electron microscopy. Figure 3 shows the coating material. It is clearly seen that there is an interlayer about 1000 nm between the boron carbide particles and the metallic matrix (Figure 3a). The presence of the

interlayers is the evidence of high level cohesion between the ceramic particles and the metallic matrix. Figure 3b shows more detailed picture of this interlayer. It is seen to be characterized by an amorphous-crystalline structure, as evidenced by the microdiffraction pattern. The metal matrix is the areas with nanocrystalline structure (Figure 3c) and the columnar structure (Figure 3d). The packets of columnar crystals formation up to 20 nm in width are associated with high degrees' deformation of the sprayed particles upon the concussion with the solidified material. The analysis of the metal matrix allows revealing that areas with a nanocrystalline structure and columnar crystals are randomly distributed within the volume of the coatings.

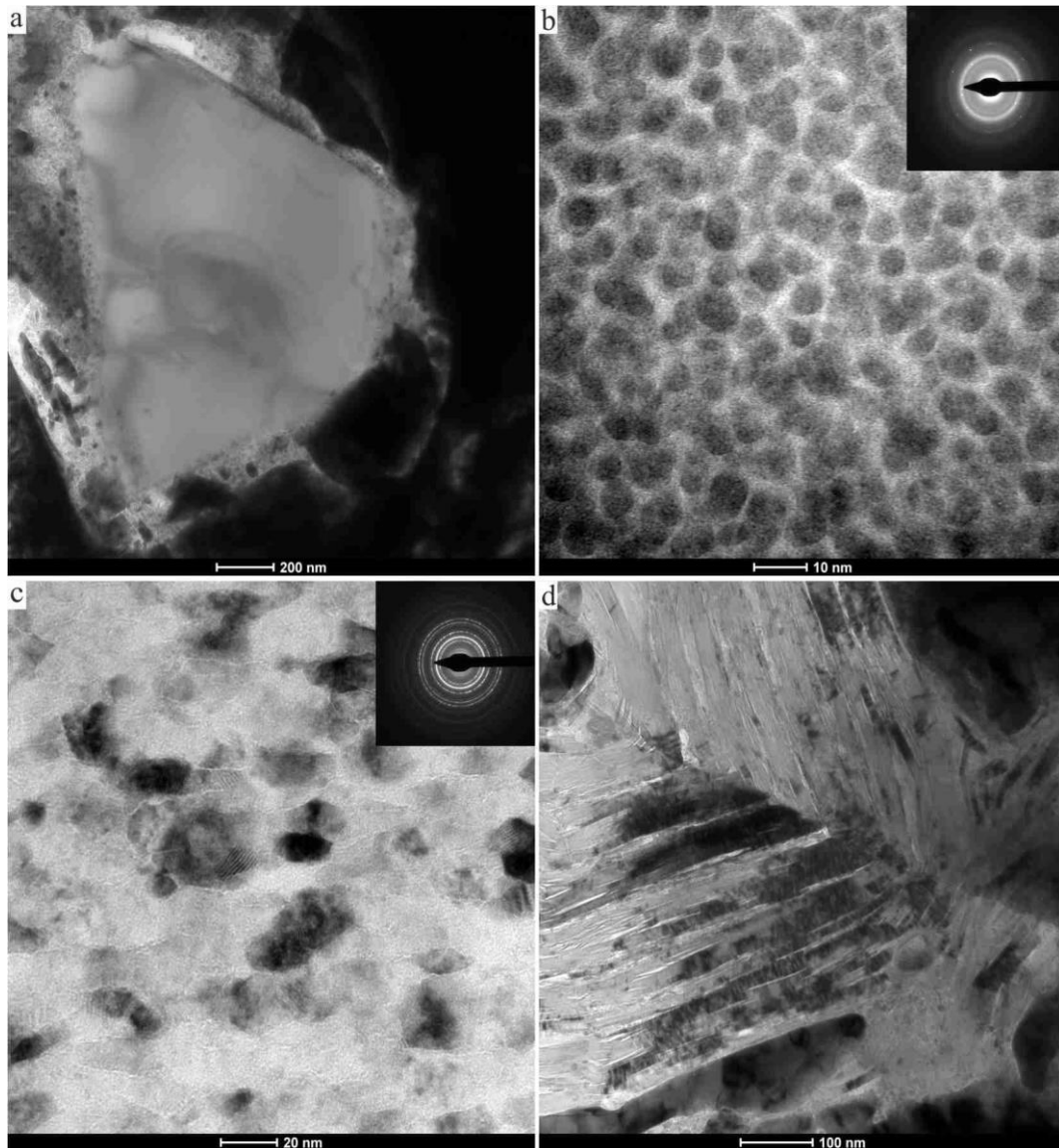


Figure 3. The boron carbide particle and the interlayer between the ceramic particle and the metallic matrix (a); the interlayer structure and microdiffraction pattern (b); the nanocrystalline structure of the metal matrix and the microdiffraction pattern (c); columnar structure of the metal matrix (d).

4. Conclusions

1. The B₄C-Ni-P dense composite coatings can be formed using air-plasma spraying.

2. The optical microscopy and scanning electron microscopy showed that the plasma coating material consists of the boron carbide particles equally spaced in the metal matrix. The metal matrix material is nickel borides. The areas with round inclusions were formed around the particles. These areas are characterized by increased content of nickel, phosphorus and boron. There are boron oxides and nickel oxides in the coating.

3. The transmission electron microscopy showed that thin interlayers with amorphous-crystalline structure up to 1 μm in thickness are formed between the boron carbide particles and the metal matrix in the process of plasma spraying. The metal matrix is the areas with a nanocrystalline structure and columnar crystals.

Reference

- [1] Risovany V, Zakharov A, Klochkov E and Guseva T 2011 *Bor v Yadernoi Tekhnike* [Boron in Nuclear Engineering] (Dimitrovgrad: «GNTs NIIAR») p 668
- [2] Alekseev A et al. 1986 *Svoystva, Poluchenie i Primenenie Tugoplavkikh Soedineniy* [Properties, Production and Using of Refractory Compounds] (Moscow: Metallurgiya Publ.) p 928
- [3] Zhu H, Niu Y, Lin C, Huang L, Ji H and Zheng X 2012 Fabrication and Tribological Evaluation of Vacuum Plasma-Sprayed B_4C Coating *Journal of Thermal Spray Technology* **21** 1216-23
- [4] Sarikaya O, Anik S, Aslanlar S, Okumus S and Celik E 2007 Al-Si/ B_4C Composite Coatings on Al-Si Substrate by Plasma Spray Technique *Materials and Design* **28** 2443-49
- [5] Feng C, Guipont V, Jeandin M, Amsellem O, Pauchet F, Saenger R, Bucher S and Iacob C 2012 B_4C /Ni Composite Coatings Prepared by Cold Spray of Blended or CVD-Coated Powders *Journal of Thermal Spray Technology* **21** 561-570
- [6] Cao Y, Huang C, Liu W, Zhang W and Du L 2014 Effects of Boron Carbide Content on the Microstructure and Properties of Atmospheric Plasma-Sprayed NiCoCrAlY/ Al_2O_3 - B_4C Composite Coatings *Journal of Thermal Spray Technology* **23** 716-724
- [7] Zeng Y, Lee S and Ding C 2002 Study on Plasma Sprayed Boron Carbide Coating *Journal of Thermal Spray Technology* **11** 129-133
- [8] Zeng Y, Feng J and Ding C 2000 Microstructure and Properties of Plasma Spraying Boron Carbide Coating *Journal of Materials Science and Technology* **16** 63-66
- [9] Moradi M, Moazeni M and Salimijazi H 2014 Microstructural Characterization and Failure Mechanism of Vacuum Plasma Sprayed Ti-6Al-4V/ B_4C Composite *Vacuum* **107** 34-40
- [10] Salimijazi H, Coyle T, Mostaghimi J and Leblanc L 2005 Microstructure of Vacuum Plasma-Sprayed Boron Carbide *Journal of Thermal Spray Technology* **14** 362-368
- [11] Zhu H, Niu Y, Lin C, Huang L, Ji H and Zheng X 2012 Microstructures and Tribological Properties of Vacuum Plasma Sprayed B_4C -Ni Composite Coatings *Ceramics International* **39** 101-110
- [12] Rafiei M, Salehi M, Shamanian M and Motallebzadeh A 2014 Preparation and Oxidation Behavior of B_4C -Ni and B_4C - TiB_2 -TiC-Ni Composite Coatings Produced by an HVOF Process *Ceramics International* **40** 13599-609
- [13] Mao Z, Ma J, Wang J and Sun B 2009 Comparison of the Coatings Deposited Using Ti and B_4C Powder by Reactive Plasma Spraying in Air and Low Pressure *Journal of Materials Science* **44** 3265-72
- [14] Lin C, Kong M and Zhu H 2016 Tribological Behavior of Vacuum Plasma Sprayed B_4C -Mo Composite Coating *Journal of Inorganic Materials* **31** 100-106
- [15] Rafiei M, Salehi M and Shamanian M 2014 Formation Mechanism of B_4C - TiB_2 -TiC Ceramic Composite Produced by Mechanical Alloying of Ti- B_4C Powders *Advanced Powder Technology* **25** 1754-60
- [16] Ebrahimian-Hoaeinabadi M, Azari-Dorcheh K and Moomir-Vaghefi S 2006 Wear Behavior of Electroless Ni-P- B_4C Composite Coatings *Wear* **260** 123-127