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FEATURES OF THE STRUCTURE OF COATINGS OF TUNGSTEN AND CHROMIUM CARBIDES DURING DETONATION-GAS SPRAYING WITH ENERGY ACCUMULATION IN A MULTICHAMBER DEVICE

Ke Liming, P.D. Stukhliak, V.M. Mudrichenko

Scientific-Research Institute of Welding Technologies named after E.O. Paton in Zhenjiang Province
233 Yonghui Road, Xiaoshan District, Hangzhou City, Zhejiang Province, China

ABSTRACT

This paper presents the results of studies of the structure of coatings obtained from powders based on chromium ($75Cr_3C_2$ + 25NiCr) (wt.%) and tungsten carbides (WC+12Co) (wt.%) by detonation-gas spraying with energy accumulation in multichamber devices. It has been established that this technology provides high-density coatings with a thickness of 200–500 μm with porosity of less than 1 % and microhardness $HV_{0.5}$ = 1235 ± 80 (WC + 12Co) (wt.%) and 1547 ± 150 ($75Cr_3C_2$ + 25NiCr) (wt.%). A characteristic feature of these coatings is the formation of a substructure with the size of 1–8 μm and of carbide-type strengthening phases with dimensions of 100–800 nm, which are evenly distributed in the volume of the coating material. It was established that a high level of structural strengthening of these coatings is provided by formation of a material with a dispersed subgranular structure with a uniform distribution of particles of strengthening phases in it.

KEYWORDS: protective coatings, multichamber detonation-cumulative spraying, microstructure, microhardness, substructure, structural strengthening

INTRODUCTION

Improvement of operational reliability of the mechanisms of oil-pumping equipment in technological facilities envisages application of wear-resistant coatings, exposed to elevated temperatures in service. In this research area a promising approach is application of materials based on chromium and tungsten carbides. Formation of such composites and coatings on their base is performed by thermal spraying [1–3], including highly productive method of detonation spraying at process speed, exceeding the velocity of sound several times [4–7].

Compared to other methods of producing the coatings [8–12] such as flame, plasma or laser methods and hybrid technologies, the method of multichamber detonation spraying provides better technological effect of coating formation through realization of the cumulative energy effect in specially designed chambers [6, 7]. In this case, the pressure of pulsed gas flow rises that results in an increase of the velocities of detonation combustion products in the nozzle (1800 m/s) and velocity of powder transportation (1200–1500 m/s) to the surface to form the coatings. This method allows forming sound poreless nanostructured coatings, including those based on carbides, with high adhesion and cohesion characteristics and density [13–16].

Interesting from the scientific and practical viewpoint is application of dispersed WC–Co, Cr_3C_2–NiCr powder materials that have proven themselves well at formation of protective coatings on the surfaces of parts, and components of mechanisms and machines of different functional purposes. Selection of the abovementioned materials is due to the temperature conditions of their operation at 500–520 and 820–870 °C, respectively, under the conditions of erosion and cavitation wear and at dynamic alternating loads. Formation of WC- and Cr_3C_2-based materials with Co and Ni content leads to appearance of a nanocrystalline structure and zones with a non-crystalline structure in the coating material [3, 17, 18]. It allows improving the wear resistance and crack resistance due to strengthening on the interface and increasing the strength of adhesion bonding of the coatings with the base.

Application of the abovementioned materials is not limited by oil-transportation equipment. Particularly promising is application of such protective coatings in the mining industry, for equipment used in oil well drilling, agricultural machinery and for metal-cutting tools, and equipment repair by restoration of the wearing surfaces. Application for all the types of valves, water turbines, rolls for sheet steel rolling, shafts for protection of their working surfaces is promising.

At present insufficient attention is paid to studying the features of formation of the abovementioned coatings, produced by the method of multichamber detonation spraying and to determination of their structural-phase characteristics, influencing their service properties.

The objective of the work is investigation of the structure of coatings from powders of different systems: WC–Co; Cr_3C_2–NiCr, produced by the method of multichamber detonation spraying and of the influence of structural-phase characteristics on hardness values.

MATERIALS AND INVESTIGATION PROCEDURES

Coatings for investigation performance were deposited at the Scientific-Research Institute of Welding Technologies named after E.O. Paton in Zhenjiang Province (PRC) in a robotic detonation-gas spraying system developed at PWI (Figure 1).

Coating deposition was performed by a multichamber detonation device (Figure 1), which includes: specially profiled forechamber which allows significantly shortening the section of transition from the arcing to detonation mode; main cylindrical chamber used for development of the detonation process, creation of the main gas-dynamic pressure of detonation combustion products, which accelerate and heat the powder; circular chamber, designed for forming an additional gas-dynamic flow, which "backs up" in the cylindrical barrel the detonation products from the second (main) chamber, and expands the powder heating and acceleration zone. Application of such a design of multichamber detonation device provides intensification of the detonation arcing mode, accumulation of detonation energy, and creation of the effect of detonation wave compression [6, 7].

The following powders were used for coating deposition: WC + 12Co (wt.%) (AMPERIT® 518.074); $75Cr_3C_2$ + 25NiCr (wt.%) (AMPERIT®585.003) with particle size of 15–45 μm, Abrasive-jet treatment of the base material surface (St. 3) with white electrocorundundum of F16 grade was performed (1–2 mm fraction) before spraying. Spraying mode was as follows: gun movement speed — 1500 mm/min; gun barrel length/diameter ratio (l/d) — 325/16 mm; oxygen flow rate — O_2 = 41 l/min (chamber 1), O_2 = 35 l/min (chamber 2); in each chamber the flow rate of air was 11 l/min and flow rate of C_3H_8 was 11 l/min; powder flow rate — 1600 g/h. Spraying distance (distance from the multichamber device nozzle to steel base surface) was 60–70 mm. Coating No. 1 (WC + 12 Co) was sprayed in three passes, No. 2 (WC + 12 Co) and No. 3 ($75Cr_3C_2$ + 25NiCr) were deposited in seven passes.

Microstructural studies of the coatings were conducted with application of light microscopy (Zeiss Axio Imager M2m microscope). Coating thickness (δ), microhardness (HV), dimensions of the structural components — lamel width (h_l) and their volume fraction (V_l, %), and porosity (P, %) were determined. Coating porosity and volume fraction of the lamels were determined using metallographic software with application of "Pro Imaging" software package (Zeiss Axio Imager M2m). Microhardness was measured in VH1102 instrument (USA) at 0.5 kg load.

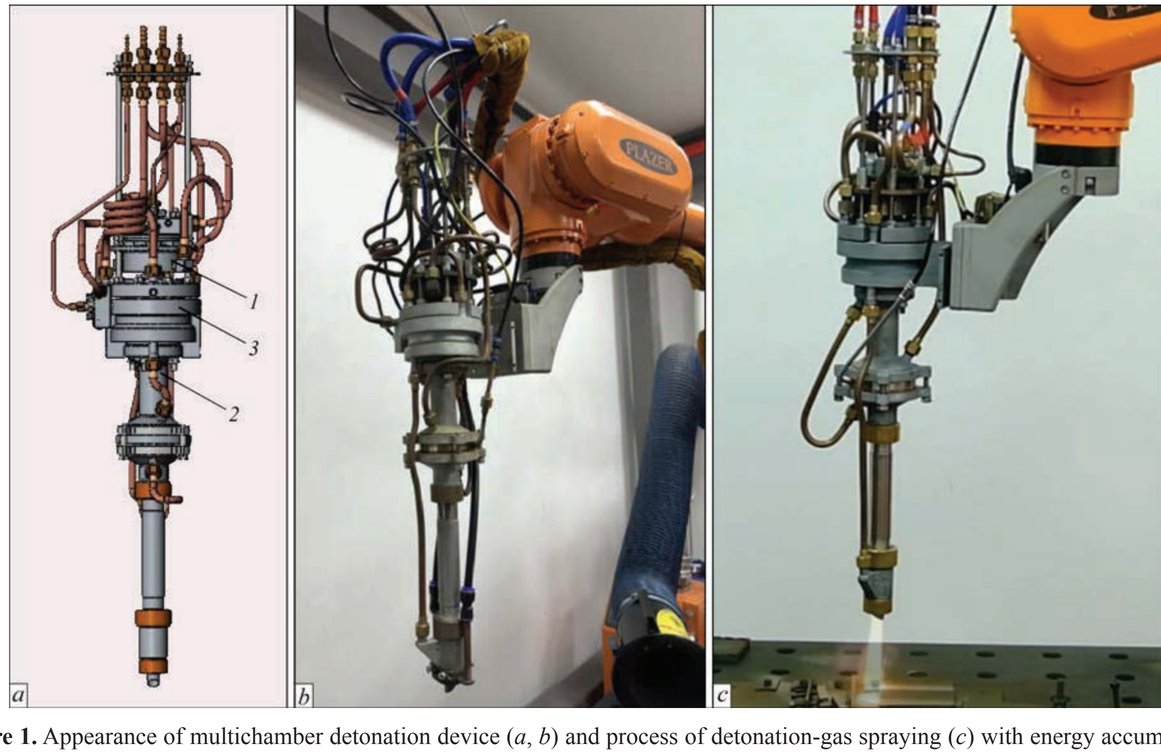

Figure 1. Appearance of multichamber detonation device (*a*, *b*) and process of detonation-gas spraying (*c*) with energy accumulation in the multichamber device: *1* — forechamber; *2* — main chamber; *3* — cylindrical chamber

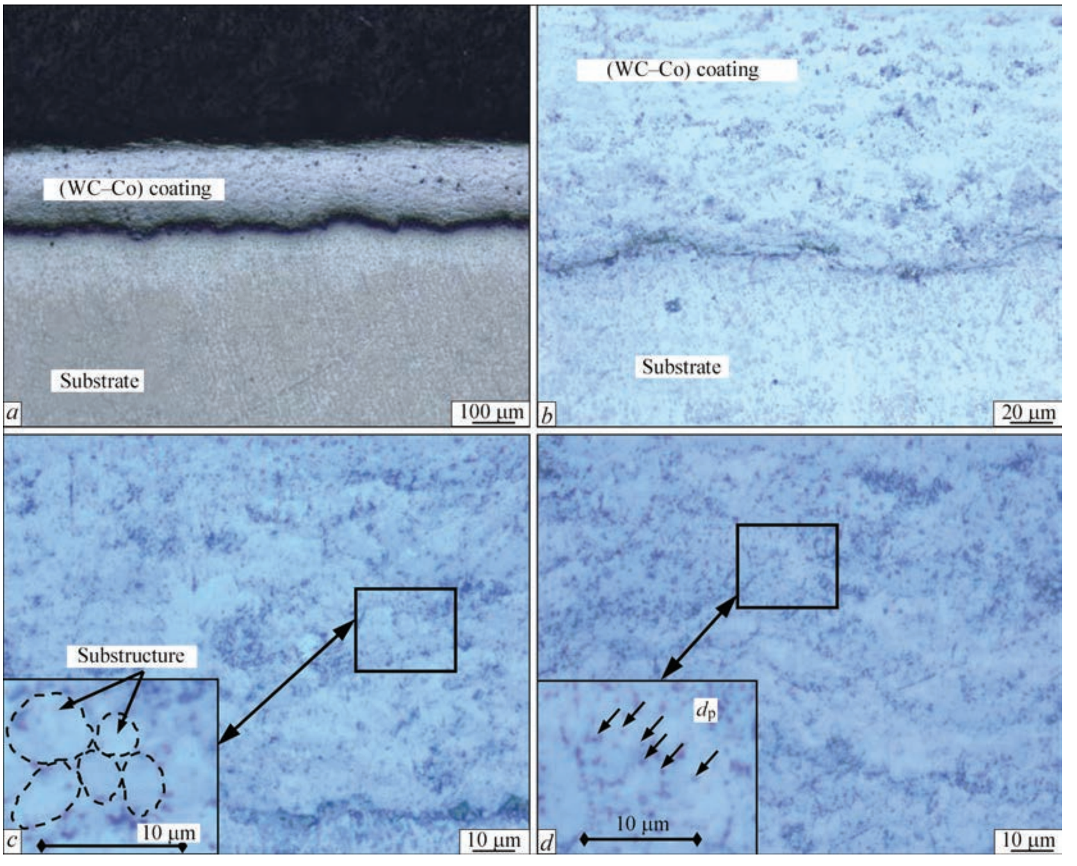

Figure 2. Microstructure of coating No. 1 from (WC + 12Co) powders (*a* — ×100; *b* — ×500; *c*, *d* — ×1000)

INVESTIGATION RESULTS

Three types of coatings were produced from the initial powders: No. 1 — from (WC + 12Co) powder of thickness δ = 200 μm (Figure 2, *a*); No. 2 — (WC + 12Co) of thickness δ = 520 μm (Figure 3, *a*); No. 3 — ($75Cr_3C_2$–25NiCr) of thickness δ = 500 μm (Figure 4, *a*). Coating materials differ by the volume fraction of the lamels (Table 1).

Coating from (WC + 12Co) powder is characterized by volume fraction of the lamels (V_l) of 5–10 % (coating No. 1) and of 10–15 % (coating No. 2) in the matrix, respectively (Figures 2, *b*; Figure 3, *b*). Spraying of Cr_3C_2–NiCr ensures lamellation with V_l = 25–30 % (Figure 4, *b*).

At application of Cr_3C_2–NiCr powder in the material of coating No. 3 the lamel width is h_l = 1–20 μm (Table 2). Here, formation of the grain structure at D_{gr} = 10–20 μm (Figure 4, *b*) and of a substructure with size d_s = 2–8 μm (Figure 4, *c*, *d*) with microhardness $HV_{0.5}$ = 1417 ± 67 MPa (across coating thickness) and $HV_{0.5}$ = 1547 ± 150 MPa (along the thickness of the coating middle zone) (Table 2) was observed. Presence of particles of dispersed phases with size d_p = 0.15–0.3 μm is also characteristic with their uniform distribution at distances λ_p = 0.2–0.45 μm (Figure 4, *c*).

In case of producing coating No. 2 from (WC + 12Co) powder the lamel width h_l = 20–30 μm, grain size is D_{gr} = 10–20 μm at microhardness $HV_{0.5}$ = = 1235 ± 80 (across coating thickness) and $HV_{0.5}$ = = 1209 ± 80 MPa (along the coating middle zone length), Table 2. Also observed was formation of a substructure with size d_s = 1.2–3.0 μm (Figure 3, *c*) in the presence of dispersed phase particles of size d_p = 0.15–0.45 μm at distances λ_p = 0.25–0.6 μm (Figure 3, *d*).

Material of coatings No. 1 sprayed using (WC–Co) powder is characterized by formation of grain and subgrain structures with sizes D_{gr} = 10–20 μm (Figure 2, *b*) and d_s = 2–5 μm (Figure 2, *c*, *d*) with microhardness $HV_{0.5}$ = 1120 ± 100 MPa (across the thickness) and $HV_{0.5}$ = 1184 ± 66 MPa (along the length of the coating middle zone), Tables 1, 2. The size of dispersed phase particles is d_p = 0.1–0.8 μm, distance between them is λ_p = 0.16–1.0 μm (Figure 2, *d*). The main phases forming in the material of coatings from

Table 1. Structural parameters of the coatings

Coating	δ, μm	$HV_{0.5}$		V_l, %
		Across the thickness	Along the length	
No. 1 (WC–Co)	200	1120±100	1184±66	5–10
No. 2 (WC–Co)	520	1235±80	1209±80	10–15
No. 3 (Cr_3C_2–NiCr)	500	1417±67	1547±150	25–30

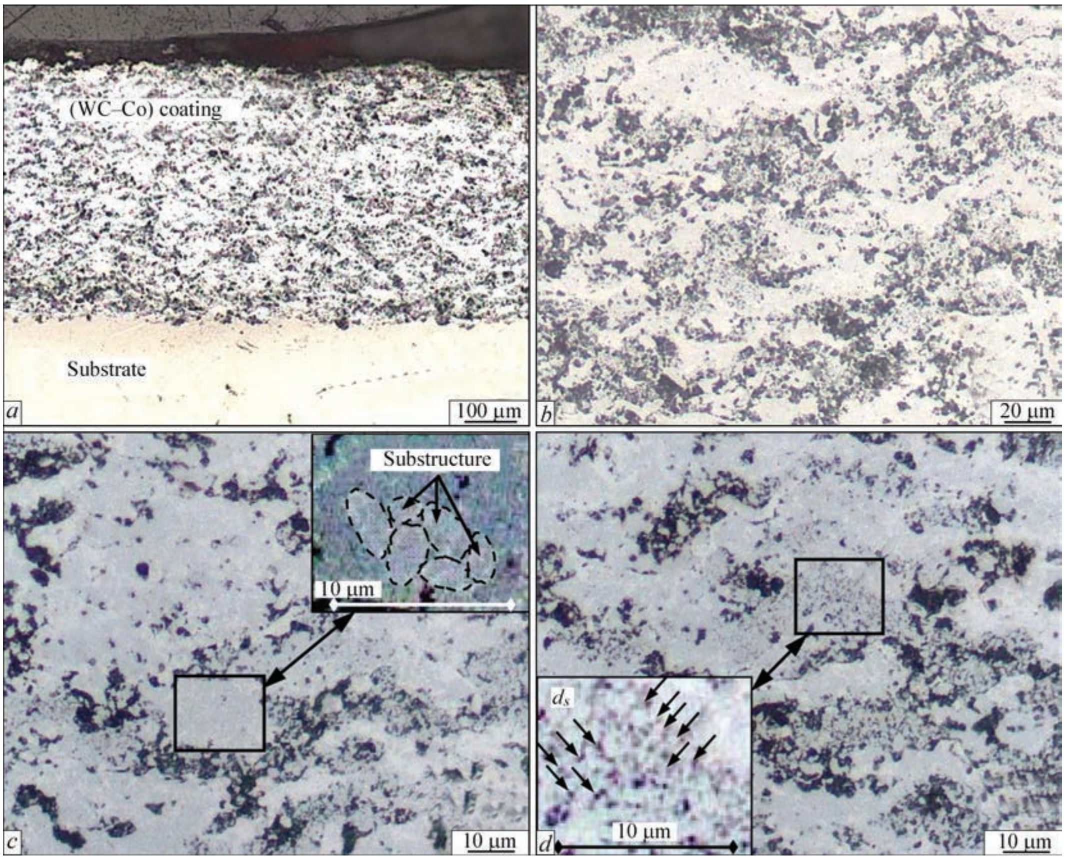

Figure 3. Microstructure of coating No. 2 from WC–Co powder (*a* — ×100; *b* — ×500; *c*, *d* — ×1000)

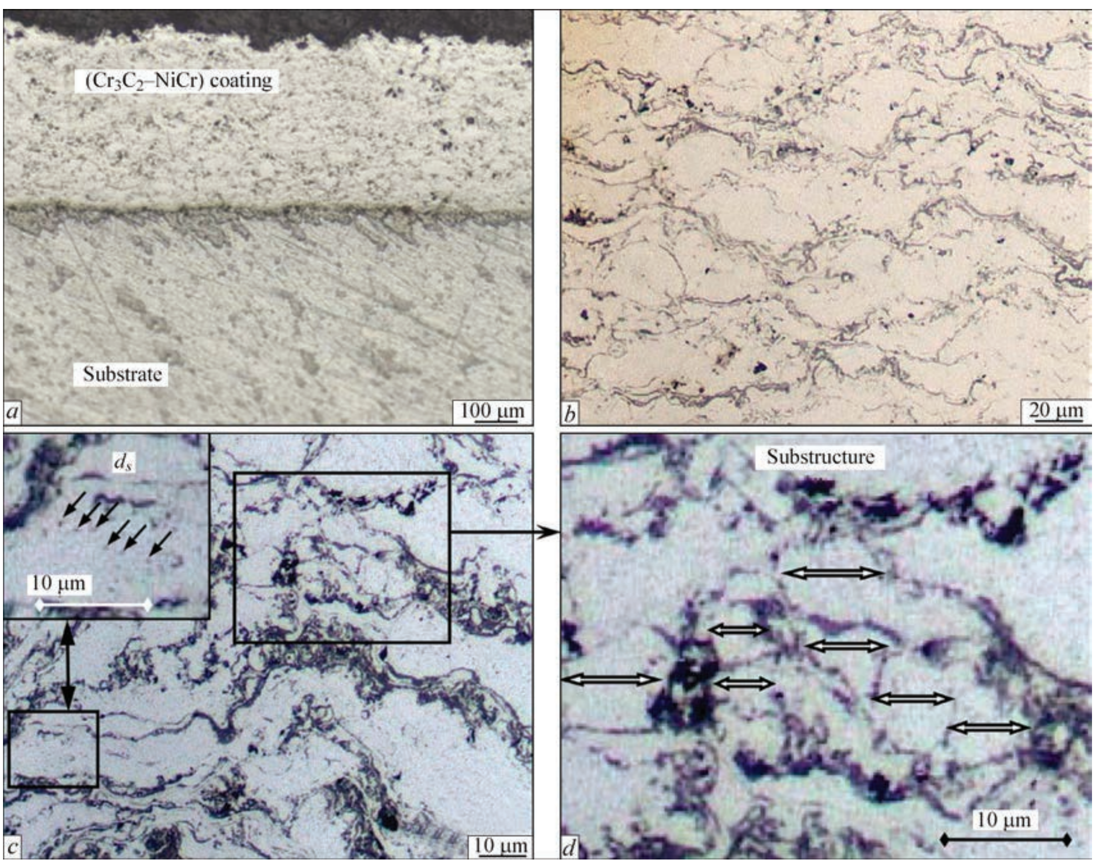

Figure 4. Microstructure of coating No. 3 from (Cr_3C_2–NiCr) powder: *a* — ×100; *b* — ×500; *c*, *d* — ×1000 (*d* — enlarged fragment from Figure 4, *c*)

Table 2. Microstructural parameters of coating material

Coating	Structural parameters				
	h_l, μm	D_{gr}, μm	D_s, μm	d_p, μm	λ_p, μm
No. 1 (WC–Co)	20–30	10–40	2.0–5.0	0.15–0.45	0.25–0.60
No. 2 (WC–Co)	8–20	10–20	1.2–3.0	0.10–0.80	0.16–1.00
No. 3 (Cr_3C_2–NiCr)	2–20	10–20	2.0–8.0	0.15–0.30	0.20–0.45

powders based on tungsten carbide are WC and W_2C [19, 20].

Thus, metallographic studies of material structure in coatings produced by the method of multichamber detonation spraying of powders based on tungsten and chromium carbides, showed the following. The coatings are characterized by porosity of less than 1 %, and differ by microhardness and lamellation. The level of material microhardness is without significant gradients. Microhardness is practically the same in coatings of different thickness (Nos 1 and 2), sprayed from WC-based powder (Figure 5).

The highest microhardness was observed in Cr_3C_2–NiCr coating (Figure 5). At detailed measurements of $HV_{0.5}$ of different structural components, such as unmolten particles (Figure 6, *a*), light (Figure 6, *b*) and dark lamels (Figure 6, *c*) it was established that their microhardness was found to differ as follows: $HV_{0.5}$ = = 579–1147 (unmolten particles); $HV_{0.5}$ = 826–1776 (light lamels); $HV_{0.5}$ = 1039–1573 (dark lamels). This is indicative of the activity of phase formation process when producing the coatings. Application of Cr_3C_2–NiCr powder for spraying of coatings led to appearance of particles of Cr_3C_2 (30–50 %) and Cr_7C_3 + Cr_2O_3 phases (30–40 %) [13, 21–23].

Compared to Cr_3C_2–NiCr coating in coatings from WC–Co powder the microhardness decreases 1.2 times on average. At spraying of (WC-Co) powder in the material of coating No.1 (of thickness δ = 200 μm) the lamel width and grain size increase 2.2 times at substructure coarsening 2.6 times.

Measurements of phase particle size and distribution in the coating matrix were conducted. Software for metallographic microscope Zeiss Axio Imager M2m was used. Analysis of microstructure fragments obtained at magnifications of ×1000 (Figure 2, *d*; Figure 3, *d*; Figure 4, *c*) further magnification of the images 10–15 times was performed.

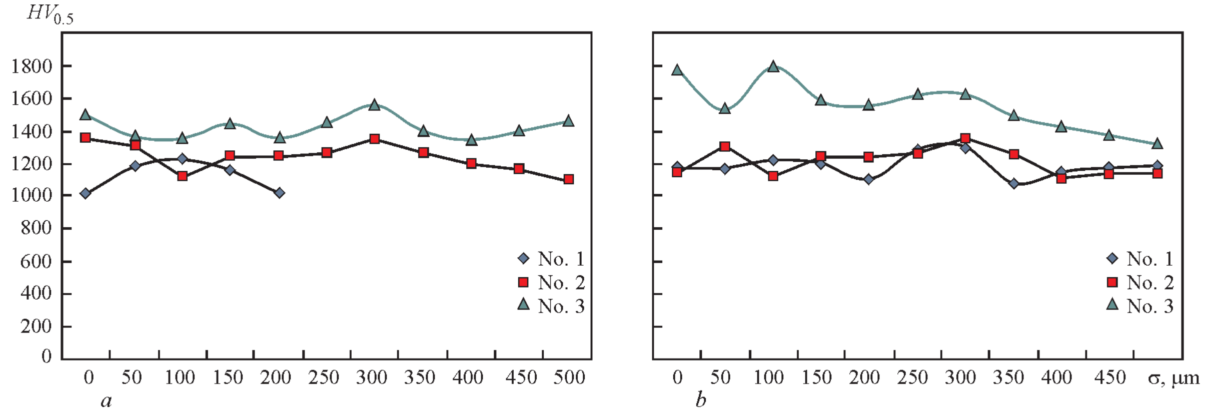

Figure 5. Change of microhardness across the thickness (δ) of coatings and length (*L*) of middle zone of coatings produced from WC–Co (Nos 1, 2) and Cr_3C_2 + NiCr (No. 3) powders

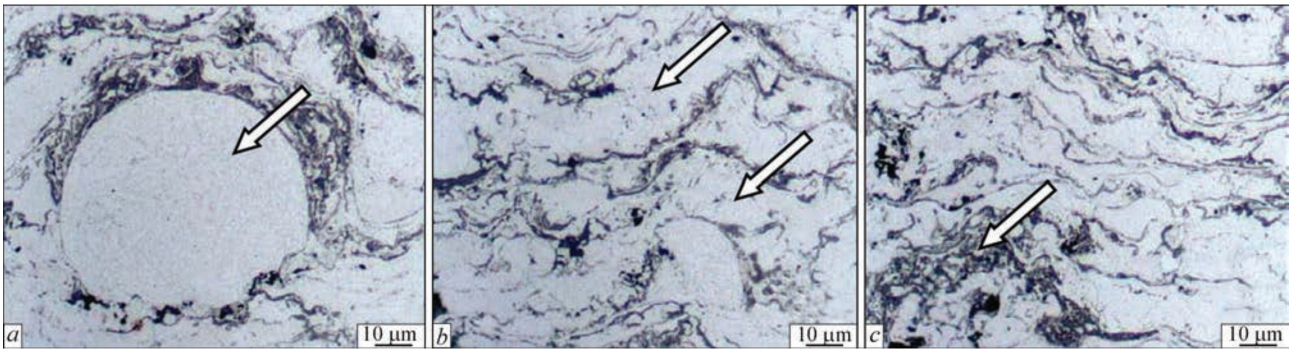

Figure 6. Different structural components in coating No. 3 (Cr_3C_2–NiCr): unmolten particles (*a*), light (*b*) and dark lamels (*c*)

Table 3. Calculated values of coating material structural strengthening

Coating	Structural strengthening				
	$\Delta\sigma_0$	$\Delta\sigma_{gr}$	$\Delta\sigma_s$	$\Delta\sigma_{d.s}$	$\Sigma\Delta\sigma_y$ (average)
No. 1 (WC–Co)	46	17–5* 128–181**	291–460	1341–1849	2208
No. 2 (WC–Co)	60	10–16* 135–192**	375–593	811–2159	2206
No. 3 (Cr_3C_2–NiCr)	34	32–3* 75–150**	230–460	750–1812	1809

*Lamels. **Grain.

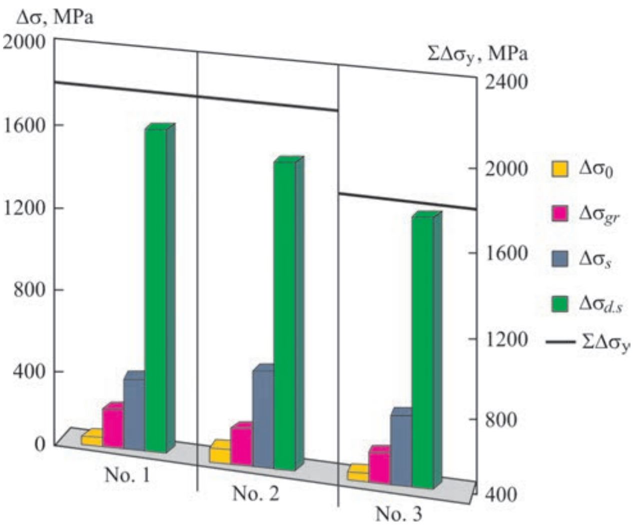

Figure 7. Histograms of the contribution of average values of structural strengthening of coatings from the following powders: Nos 1, 2 — (WC–Co); No. 3 — (Cr_3C_2–NiCr): — lattice friction ($\Delta\sigma_0$), grain ($\Delta\sigma_{gr}$), subgrain ($\Delta\sigma_s$) and dispersion ($\Delta\sigma_{d.s}$) strengthening

In case of application of (Cr_3C_2–NiCr) powder, the size of dispersed phase particles d_p = 150–300 nm in the coating matrix is negligibly small compared to coatings No. 1 (WC–Co), where d_p = 150–450 nm (Table 2). Distance (λ_p) between the particles is also reduced, which is characterized by increase of their volume fraction in the coating matrix up to 30 %. However, in coating No. 2 (WC–Co) at minimal sizes of dispersed phases (d_p = 100 nm) and distances between them (λ_p = 160 nm) their volume fraction in the coating matrix rises up to 43 %. This will ensure a high level of dispersion strengthening of the coating material [13, 15, 21–24].

It should be noted that a characteristic feature of the produced coatings is presence of dispersed phase particles (Figure 2, *d*; Figure 3, *d*; Figure 4, *c*) of the size from 100–150 up to 300–800 nm at substructure formation (Figure 2, *c*; Figure 3, *c*; Figure 4, *d*).

In order to study the influence of the structure on the mechanical characteristics of the coating material the structural strengthening index ($\Sigma\Delta\sigma_y$) was analytically assessed, allowing for the contribution of each of the structural parameters (size of lamels and grains — D_{gr}, subgrain — d_s, dispersed phase particles — d_p and distances between them λ_p) [21–24]. Calculation of the structural strengthening components σ_0; σ_{gr}; σ_s; $\sigma_{d.s}$ was performed (Table 3, Figure 7). A similar approach was also tried out on other materials, where significant results were obtained as regards the experimental values of mechanical properties in the structure of different materials — steels of different class, aluminium and titanium alloys, tungsten single-crystals, protective coatings, etc. [25–27].

As a result it was established that the average integral values of strengthening ($\Sigma\Delta\sigma_y$) for (WC–Co) coatings No. 1 (thickness δ = 200 μm) and No. 2 (δ = 500 μm) are equal to $\Sigma\Delta\sigma_y$ = 2208 MPa and $\Sigma\Delta\sigma_y$ = 2206 MPa, respectively (Figure 7, Table 3). A slight reduction of $\Sigma\Delta\sigma_y$ is observed in the material of (Cr_3C_2–NiCr) coating. In all the cases, the maximal contribution (up to 70 %) into the total strengthening value is made by strengthening of the coating matrix due to dispersed particles of nanosized phases (Orowan dispersion strengthening): $\Delta\sigma_{d.s}$ = 1595 MPa (coating No. 1); $\Delta\sigma_{d.s}$ = 1485 MPa (coating No. 2): $\Delta\sigma_{d.s}$ = 1281 MPa (No. 3). Here, the contribution of grain and subgrain strengthening for the studied coatings is equal to 8–9 % ($\Delta\sigma_{gr}$) and 17–22 % ($\Delta\sigma_s$), respectively.

Thus, the high level of structural strengthening of coatings from powders based on WC and Cr_3C_2 at application of the method of multichamber cumulative-detonation spraying is ensured predominantly due to dispersion strengthening by phase particles at their uniform distribution in the coating material.

CONCLUSIONS

The structural features were revealed in coatings from (WC + 12Co) (wt.%) powders deposited on the steel surface by the method of multichamber cumulative-detonation spraying. A high density coating of 200–500 μm thickness was produced with less than 1 % porosity, with a gradientless microhardness level.

A characteristic features of the coating microstructure formed at multichamber cumulative-detonation spraying, is formation of a dispersed substructure of 1–8 μm size and carbide-type strengthening phases of 100–800 nm size, evenly distributed in the coating material volume. Such submicron and nanosized substructure of the carbide phases provides higher values of coating microhardness $HV_{0.5}$ = 1014–1352 for (WC + 12Co) (wt.%) coating and $HV_{0.5}$ = 1256–1785 for ($75Cr_3C_2$ + 25NiCr) (wt.%).

It was found that the high level of structural strengthening of the produced coatings is ensured due to dispersion strengthening by submicron and nanosized carbide phases at their uniform distribution in the coating material.

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ORCID
P.D. Stukhliak: 0000-0001-9067-5543,
V.M. Mudrichenko: 0009-0005-8311-2685

CONFLICT OF INTEREST
The Authors declare no conflict of interest

CORRESPONDING AUTHOR
P.D. Stukhliak
Scientific-Research Institute of Welding Technologies named after E.O. Paton in Zhenjiang Province
233 Yonghui Road, Xiaoshan District, Hangzhou City, Zhejiang Province, China.
E-mail: stukhlyakpetro@gmail.com

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