Structure and Properties of Ni–Cr–B–Si–Fe/WC–Co Coating Deposited to Steel and Copper Substrates[1]

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Abstract – A new kind of coating containing mechanical blend of the two powders (Ni–Cr–B–Si–Fe) and WC–Co (Hard Alloy) has been developed. The coating was deposited by two techniques using. Detonation technology and plasma-detonation technology, the thickness being of 150–200 μm on the steel 3 substrate (0.3 wt. % C) and technical copper 99.98/A part of samples with Ni–WC–Co(Cr, B, Si, Fe) coatings then we treated with plasma jet in the melting regime of 50–60 μm depth. The coating deposition was carried out on an Impulse-6 set with the parameters which have been well described.

The structure and properties study of the coating was carried out with the aid SEM microscopy with microanalysis (EDS), X-rays diffraction (XRD). The hardness was studied with nanoindentor (Nanoindentor-11, USA) and RBS of ions and protons (E-2.02 MeV). The following phases were found in the coating: CoCr, CoNi, Cr_3Ni_2, FeNi phase appeared after plasma jet treating. The additional effect on the coating with plasma jet results in more regular hardness distribution on the surface, less material ablation under friction and increasing hardness nearly of 50% compared with the PG-19N-01 coating. Redistribution of elements in the coating.

1. Introduction

Application of protecting coatings to improvement mechanical and physical-chemical properties of metals and alloys is now an actual problem of a material science. It is well known from [1–6] that the coatings of PG-19N-01, PG-10N-01, PGAN-33 (on Ni–Cr base and on the base of other additions such as Si, B, Fe, W, Mo can be applied to protect samples of steel [7–10] allowing one to increase their hardness, wear and corrosion resistance after melting these coatings by an electron beam or a plasma jet (see, for example, [10]). Other authors investigated the coatings on Ni–Al, Al–Co, Al–Mg–Cu, Al_2–O_3, $Al_2O_3 + Cr_2O_3$, WC–Co, Cr_3C_2–Ni, etc. base [7–10], which also played the role of protection for steels and alloys [11–14]. Detonation, plasma detonation, and a combination of various methods, for example, detonation with subsequent surface layer melting [2–6, 14] were used as deposition methods.

Works [15] show that alloys on Ni–Cr (Mo, Fe, Cu, etc.) have good anticorrosion properties, in particular, in acids HCl, H_2SO_4, $HNO_3 + HF_4$, etc. under higher temperatures. Nickel is able to dissolve high quantity of doping elements, as well as Cr, Mo, Fe, Cr + Mo, Cu. In the same works [2, 15], it was demonstrated that chromium in nickel alloys, molybdenum in nickel-molybdenum alloys decelerated an active dissolution of their nickel base, chromium providing its passive behavior, but molybdenum making it difficult. As a result, Ni–Cr(–Mo) alloys are resistant to acidic media. That is why application of these alloys for wear and corrosion protection today is a matter of current interest.

In such a way, the goal of this work was to investigate a structure and physical-chemical properties of the coatings manufactured on a base of two powders: Ni–Cr–B–Si–Fe/W–Co, which were deposited using a high rate plasma jet by detonation and plasma-detonation technologies.

2. Methods of analysis and coating application

To deposit the coatings, we applied a mechanical mixture of two materials: PG-19N-01 (Ni, Cr – 8–14%; B ~ 2%; Si ~ 2.5–3%; Fe > 5%), WC–Co of 28–63 μm dimensions for PG-19N-01 and of 42–65 μm – for WC–Co. The coating deposition was performed using a plasmatron "Impulse-6" with the following parameters: the powder expenditures ~ 23 g/min, a pulse repetition frequency – 4Hz, a condenser battery capacity – 800 μF. A distance to the sample was 55 mm, and the velocity of sample motion – 380 mm/min. The repeated melting of coating surface layer was performed using a plasma jet without powder at 45 mm distance from the nozzle shear. The sample motion velocity was 300 mm/min. Tungsten was used as an electrode material. WC was used as an eroding electrode. The coating thickness was not less than 150 μm.

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For analysis we applied the following methods: Rutherford back scattering of ions He^+ (2.035 MeV) and ions with $E = 2.012$ MeV energy, scanning electron microscopy with micro-analysis (SEM, EDS – energy dispersion spectrum, Selmilc, Sumy, Ukraine). For phase analysis, we applied a method of X-ray diffraction (XRD), DRON-3 device (St. Peterburg, Russia), as well as a method of sliding X-rays at 0.5° angle. To measure hardness, we applied nanoindentation with a three-face Berkovich pyramid (Nanoindentor-II, MTS Systems Corp., Oak Ridge, TN, USA). In the process of testing, we registered the dependence of Berkovich indenter top motion on a load with a high accuracy. The accuracy of indentation print depth was ~ 0.04 nm, that of the indentation load ± 75 nH. The device is able to do about three load motion measurements for a second. In every test, the indentor was loaded (unloaded) three times till higher load, which did not exceed 5 mHz at 150 mH depth. After the tests were over, we calculated the hardness over the indentation trace under the load, the elastic modulus being derived from analysis of the load curve [19].

A part of the samples with coatings was used to prepare transversal cross sections to analyze the coating composition and to measure hardness. Wear resistance was tested by a SMTS-2 device (Ukraine) using a scheme "plane-cylinder" in a technical Vaseline medium. A bulk wear was measured by weighting the samples through every 500 cycles. In our tests, a total number of cycles did not exceed 104 [13–14].

3. Experimental results and discussion

Figure 1 shows the fragments of diffraction patterns for the samples with Ni–Cr–B–Si–Fe–WC–Co coatings after coating deposition (*a*) and after plasma jet melting (*b*).

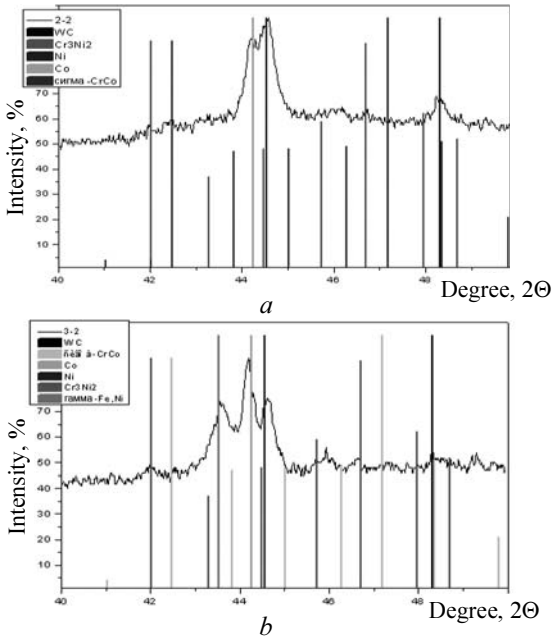


Fig. 1. Fragments of the diffraction patterns for the sample with Ni–Cr–B–Si–Fe/WC–Co coating (on the part of coating (*a*)), after subsequent melting by a plasma jet

Comparison of the spectra demonstrates that in the case of coating melting a phase γ (Fe, Ni) appeared and a ratio of intensities of other phases (WC, α-CoCr, Ni, Co, Cr_3Ni_2) changed.

Figure 2 shows the coating surface image (without plasma jet melting). The surface shows a typical relief with a high roughness resulting from deformation of a part of powder particles by a dynamical impact and plasma jet melting.

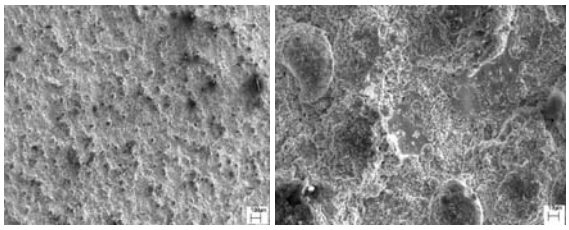


Fig. 2. An image of the Ni–Cr–B–Si–Fe/WC–Co coating region deposited to a steel 3 substrate using detonation: *a* – ×100 magnification; *b* – ×1000 magnification

These powder particles seem to be the hard alloy, i.e., a melting temperature of these powder particles is essentially higher than that of PG-19N-01. As a result of additional plasma jet action clearly pronounced powder particles were not found in the surface. The powder particles or regions stretching from the surface were melted due to high temperature, and as a result the surface roughness decreased approximately by 30 to 50%. And the coating elements were redistributed (Figs. 3, *a* and *b*).

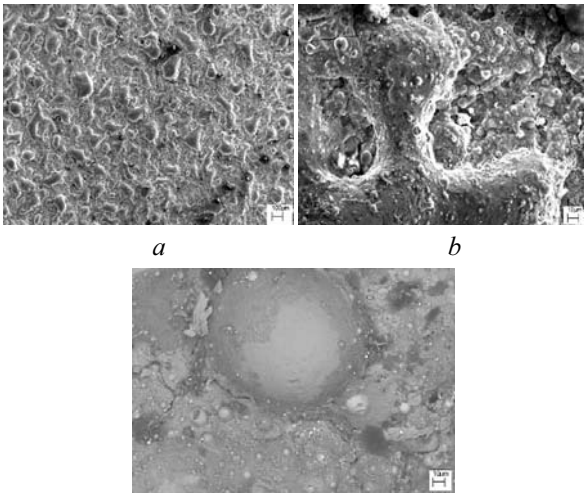


Fig. 3. An image for the Ni–Cr–B–Si–Fe/WC–Co coating region deposited to a steel 3 by a detonation method after subsequent melting by a plasma jet to a depth 40–60 μm: *a* – ×100 magnification; *b* – ×1000 magnification and in the element contrast (*c*)

To investigate the coating element composition over its depth, we prepared the cross sections. Figure 4 shows a surface image of such a cross section. It is seen that the coating-substrate boundary has a "wavy"

character and has not cavities or voids, which indicates good adhesion of the coating with the substrate.

Figure 5 shows the results of microanalysis for the surface regions demonstrated in Fig. 4. Results of this microanalysis show that the highest concentration of (Ni ~ 76%, Cr ~ 13%, W ~ 3.56%, Si ~ 2.6%, Fe ~ 3%, Co ~ 0.9%) was observed near the surface. In the region of a point 2 (Fig. 5, *b*) the element concentration changed: the nickel concentration decreased to about 58.6%, Cr concentration increased to 19.98%, Co ~ 3.21%, Si ~ 2.31%, and W concentration increased to 9.71%, Fe being ~ 4%, C ~ 1.1%. Near the interface "coating-substrate" the concentration of elements composing the powder changed also: Ni ~ 25%, Cr ~ 8.77%, W ~ 7.06%, Co ~ 1.85%, Fe ~ 1.55%, Al ~ 1.42%, Si ~ 0.84%. At the same time, the Cu concentration was even about 50%, and about 100% in the substrate.

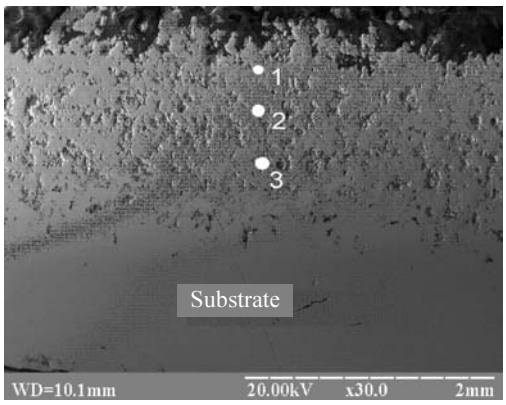
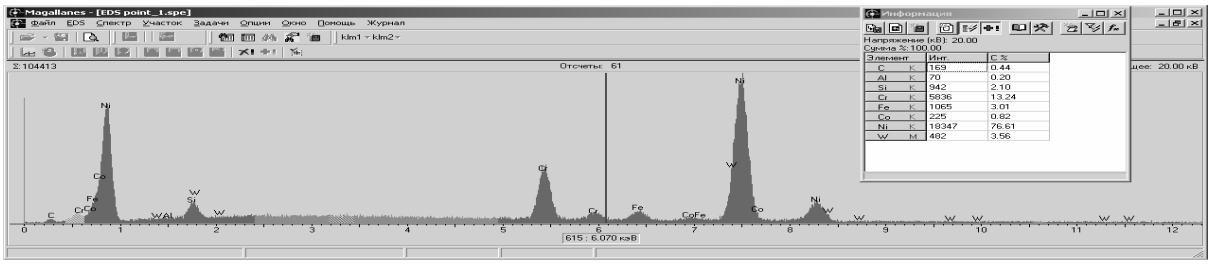
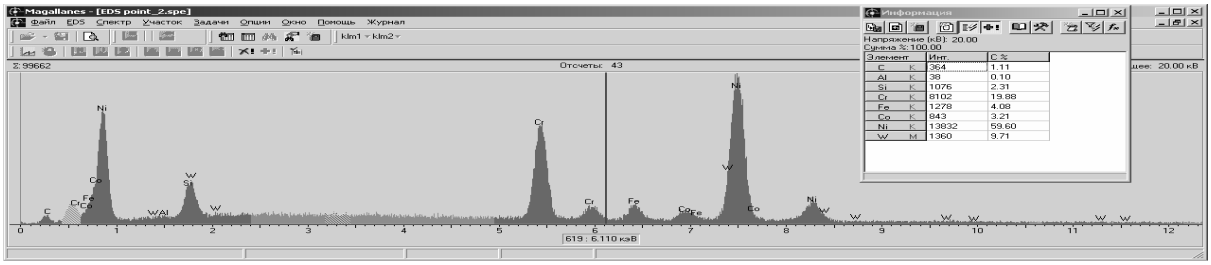


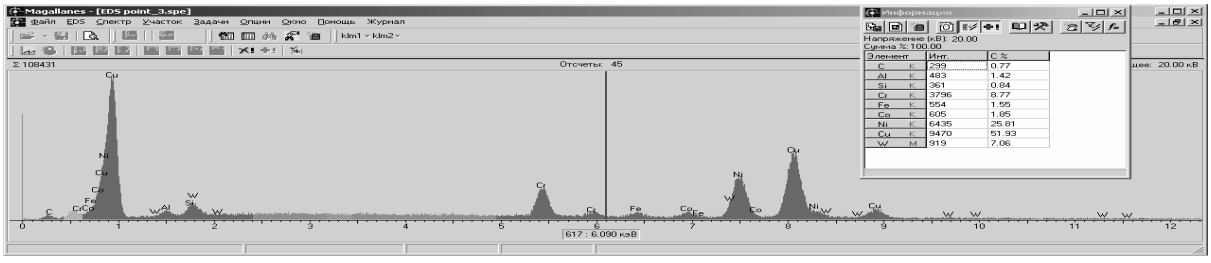
Fig. 4. An image of the cross section region taken at 15° angle for a copper sample with a deposited Ni–Cr–B–Si–Fe/WC–Co coating using detonation method. The points show regions of EDS and WDS microanalyses



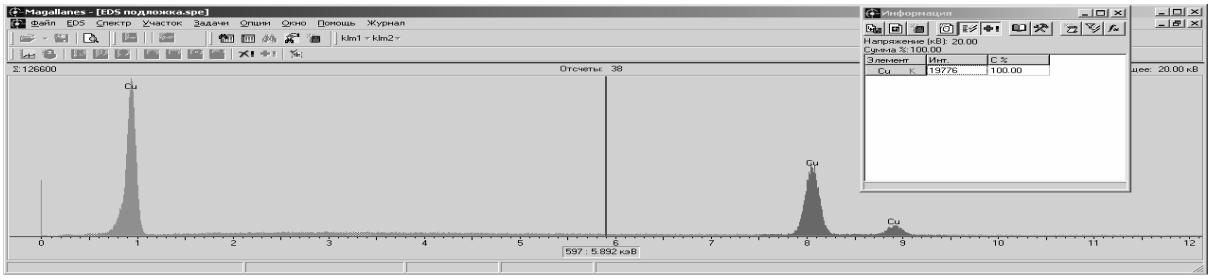
a



b



c



d

Fig. 5. X-ray energy dispersion spectra taken for the cross section demonstrated in Fig. 4, for the regions marked by points 1, 2, 3, 4, respectively

The Cu substrate is more plastic in comparison with the coating, and adhesion between the coating and substrate is very high.

Figure 6 shows the element distribution over the coating depth (the transversal cross section).

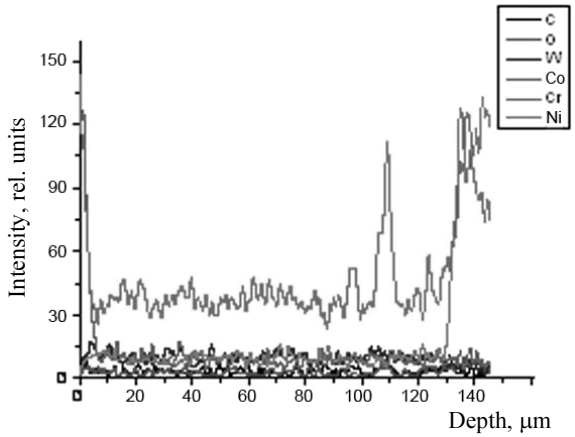


Fig.6. Distribution of the characteristic X-ray element emission over this cross-section (A–A') in a combined composite coating (a thick coating was melted by a plasma jet).

The demonstrated profiles show that C, W, Co, Cr, Ni and O form a part of the coating. We found a significantly high oxygen concentration in the coating, which indicated high oxidation ability of the powder in its initial state.

Measured hardness of this coating composed of a composite (a mechanical mixture of PH-19N-01 and WC–Co powders) using nanoindentation demonstrated that in the coating there were found not only regions of 7.9 to 9 GPa hardness, but also those of 16 to 18 GPa, and the hardness of (7.9 ± 1.1) GPa related to the regions with PG-19N-01 structure. The hardness of 9 GPa related to the melted regions, and non-melted regions of the same materials demonstrated (7.8 ± 0.4) GPa. The regions of high hardness seem to be related to formation of a hard alloy WC–Co (exactly, with tungsten carbide formation).

4. Conclusions

The work presents investigation results for structure and element composition of Ni–Cr–B–Si–Fe/WC coating, which was deposited to steel 3 and copper substrates. The following phases were found in this detonation-deposited coating: WC, α-CrCo, Co, Ni, Cr_3N_2, and after melting of this coating by a plasma jet till 40 to 60 μm depth we found a formation of an additional phase γ-(Fe, Ni). The coating hardness for PG-19N-01 and WC–Co combination for 70 : 30% ratio was (16 ± 2) GPa, its wear resistance increased by 1.7 to 2.2 in comparison with substrate of PG-19N-01 coating and by 4.5 to 5.2 in comparison with the steel substrate.

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References

[1] P. Misaelides, A. Hatzidimitou, F. Noli et al., Surf. And Coat. Tech. **180–181**, 290–296 (2004).
[2] A.D. Pogrebnjak, V.V. Vasilyuk, D.L. Alontseva et al., J. Tech. Phys. **30**/2, 164–167 (2004).
[3] A.D. Pogrebnjak, O.P. Kul'ment'yeva, V.S. Kshnyakin et al., FMM **24**/47, 44–52 (2004).
[4] A.D. Pogrebnjak, V.V, Vasilyuk, Yu.N. Kravchenko et al., Trenie I Iznos (Wear and Friction), Mogilev **25**, No. 1, 71–78 (2004).
[5] A.D. Pogrebnjak, E.A. Bazyl, and N.V. Sviridenko, Usp. Fiziki Metallov **5**, 257–281 (2004).
[6] A.D. Pogrebnjak, Yu.N. Kravchenko, V.V. Vasilyuk et al., FHOM 11, 35–41 (2005).
[7] A.D. Pogrebnjak, M.V. Illyashenko, O.P. Kul'ment'yeva,et al., Zh. Tekh. Fiz. **71**/7, 111–118 (2001).
[8] Yu.N. Tyurin, M. Zhadkevich, A.D. Pogrebnjak, O.V. Kolisnichenko, and E.I. Likhachiov, *in Proc. IV Int. Congree on "Mechanical Engineering Technologies'04"*, Varna, Bulgaria, 2004, pp. 21–24.
[9] A.D. Pogrebnjak, and Yu.A. Kravchenko, Poverhnost' **11**, 1–23 (2006).
[10] A.D. Pogrebnyak, Sh.M. Rusimov, D.L. Alontseva et al., Vacuum **81**/10, 1243–1251 (2007).
[11] A.D. Pogrebnjak, and Yu.N. Tyurin, Usp. Fiz. Nauk **125**/5, 514–543 (2005).
[12] A.D. Pogrebnjak, O.P. Kul'ment'yeva, and V.S. Rusakov, et al., Physical Surface Ingeneer **3**, Nos. 3–4, 137–184 (2005).
[13] K.K. Kadyrzhanov, F.F. Komarov, A.D. Pogrebnjak et al., *Ion Beam and Ion-Plasma Modification of Materials*, Moscow, MSU, 2005, 640 pp.
[14] N.A. Azarenkov, V.M. Beresnev, and A.D. Pogrebnjak, *Structure and Properties of Coatings and Modified Layers of Materials*, Kharkov, Kharkov Nation. Univ., 2007, 565 pp.
[15] W.Z. Friend, *Corrosion of nickel and alloys*, Vol. 14, New York, Wiley, 1980, 459 pp.