FORMING THE STRENGTHENING NANOPARTICLES IN THE Co–Cr BASED COATINGS DEPOSITED BY PLASMA DETONATION ON A STEEL SUBSTRATE

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ABSTRACT

The investigation of structurally-phase compositions and properties of the plasma detonation coatings on steel substrates is carried out. These coatings are produced from industrial powders on the basis Co-Cr (Russia standard). An "Impulse-6" plasma detonation unit was used to form protective coatings 60 to 300 μm thick of powder alloys on construction steel (St3) substrate. Coatings are modified by pulse plasma jet at the SIMP (Ukraine).

Experimental methods of analysis: AFM, TEM, SEM with WDS and EDS, XRD X-Ray Photoelectron Spectroscopy. The foils for TEM were prepared by Ar ion sputter etching method using the PIPS facility. The micro- and nano-hardness measurement, and wear tests have done.

It has been proven that the plasma detonation coatings are a mixture of differently oriented nanograins in the size of 1-2 nanometers and lamels of intermetallic phases in length to 50 nanometers. Coatings have differences in phase composition, in a microstructure and in microhardness on depth. It is established that the roughness of the modified coatings decreases in 4-5 times, wear resistance increases in 6 time, hardness increases on the average by 15 %.

Key words: plasma detonation coating, pulse plasma jet, nanoparticles, hardness, wear resistance

INTRODUCTION

The peculiarity of plasma-detonation method of depositing powder coatings is the formation of reasonably heavy coatings (100-200 μm thick), as distinguished from PVD, CVD and PED methods that form thin films on a substrate. One of the main problems of plasma-jet deposited coatings is their porosity, lack of homogeneity on account of poor agglomeration of powder particles, low adhesion to substrate.

These result in insufficient corrosion and wear resistance of such coatings. The study [1] dealing with corrosion behavior of plasma sprayed metal and

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metal-ceramic coatings on steel AISI 304L describes the coatings of 150 to 500 μm. It states that the main reason for low corrosion resistance is high porosity of a coating.

To eliminate drawbacks the coatings may be irradiated by electron jet in vacuum or re-treated by pulsed plasma jet on the surface without powder coating in air (duplex treatment). In both cases we reach melting of the treated metal on the depth of the coating, and in most cases melting of the substrate 1-2, sometimes 3 times the depth of the coating.

Practical experience of the use of combined technologies of coating deposition by plasma detonation with the following modification by e-beam or plasma jet allows to claim that the mechanical properties of such coatings of metals and alloys (micro and nanohardness, wear resistance, and corrosion resistance) are very high [2-5].

Co based coatings, deposited by plasma detonation method, are not super hard; however their microhardness makes more than 5 GPa [3, 5]. It allows for hypothesizing nanostructure formation in them. Besides it is known that super hard PVD and CVD method deposited coatings may lose their properties a few hours after the coating deposition [6-9]. Plasma detonated coatings lack such drawback, and the conditions of their depositing: plasma jet temperature of a few thousand degrees Celsius, high speed of metal coatings' particles (from 600 to 1000 m/s [2]) in a plasma jet, short period of jet exposure (about 3 ms) justify for the formation of nanostructures and amorphous areas in them.

It is known that amorphous or nanostructure states are especially effectively received at high speed heating, pressure, and short exposure to high temperatures [10]. The studies [11 - 14], which deal with the study of structure and properties of the coatings deposited by a plasma jet, note the formation of nanostructures in them after e-beam irradiation.

However it has some problems with using of a duplex treatment. First, we should to clear perceive the structure-phase consist of coatings for the making of coatings with expected properties by duplex treatment. There are not enough publicized TEM-dates about structure-phase consist of coatings deposited by plasma detonation. Second, in reason of more thickness of these coatings we shouldn't indentify their properties with properties of coatings with analogy chemical consist but made of other methods. Third, we need to provide the choice of duplex treatment mode: the energy of plasma jet, current density, time of action on surface et al. Therefore we need of a model correct for a structure-phase consist of coating before duplex treatment. The setting of certainly modes could be used for the power-saving and automation of duplex treatment.

The goal of the research is to empirically establish the structure-phase state and mechanical properties of the AN-35 (Russia Industrial Standard) powder composite coatings deposited on steel by plasma detonation. On the

basis of the analysis of the experimental dates to offer the model of coatings' consist. To establish the structure-phase and mechanical differences the coatings before and after plasma treatment and to give recommendations for industrial application of such coatings.

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

An Impulse-6 plasma detonation unit was used to form protective coatings 80 to 300 μm thick of powder alloys on stainless steel 3 substrate (Fe – base, C - 0.25 %, Mn - 0,8 %, Si - 0,37 %, P < 0,045 %). For the coatings we used the Co-Cr based powder: AN-35 Co-based powder alloy with additives of Cr (8…32 %); Ni (≤ 3%), Si (1,7…2,5%), Fe (≤ 3%); C (1,3…1,7%) and W (4…5%). We used the powder with fractions from 56 to 260 μm in size. The substrates were 20x30x2 mm^3 steel samples with the surface pre-treated by sandblasting.

Plasma-detonation powder coatings were deposited in air using the following modes: the distance from the sample to the plasma jet nozzle edge – 60 mm; sample travel speed – 360 mm/min; pulse frequency – more than 4 Hz; powder consumption – 21,6 g/min; capacitor bank – 800 μF. Pulse duration was 10^{-5} second. Propane, oxygen and air were used as combustible and orifice gases. Mo was selected as plasma-jet eroding electrode material.

After cooling in the plasma-jet chamber, the samples were exposed to pulsed plasma jet in the melt mode (from 1 to 3 exposures). Plasma jet operating parameters were the same as at deposition, but with the pulse frequency equal to 2,5 Hz. The coatings was made and melting at at the Sumy Institute of Surface Modification (Sumy, Ukraine).

Experimental methods of analysis: AFM by JSPM-5200 ("JEOL", Japan), TEM by JEM-2100 ("JEOL", Japan), SEM by JSM-6390LV ("JEOL", Japan) with WDS and EDS ("Oxford Instruments", Great Britain), XRD by X'Pert PRO ("PANalytical", the Netherlands), X-Ray Photoelectron Spectroscopy by SRV-1 spectrometer ("Technoanalyst", Kazakhstan), metallography by Neophot-21 ("Carl Zeiss", Germany). The foils for TEM were prepared by Ar ion sputter etching method using the PIPS facility ("Gatan", USA).

The micro- and nano-hardness measurement, wear tests have done.

Microhartdness was measured with a PMT-3 microhardness meter (LOMO, Russia) with an indentation load of 2, 5, and 10 N.

There have also been performed nano-hardness tests. The tests were conducted with Berkovich triangular indenter on Nano Indentor II nano-hardness tester, (MTS Systems Corporation, Oak Ridge, USA). The accuracy of print depth measured ± 75 mN. To define nanohardness and elasticity modulus at the peak load on indenter there was used Oliver and Farr procedure [15].

Wearability was measured with a SMTS-2 (Ukraine) using a plane-cylinder scheme in technical petroleum jelly. Wear rate was measured by mi-

croweighing every 500 cycles; the total number of revolutions was 10 000. The length and width of the fret originating from the counter-object contact with the test sample was measured in relation to the number of counter-object revolutions.

For a more detailed analysis of the AN-35coating deposited by plasma detonation method, it was mechanically cut off the surface of the substrate to examine the structure and content from both sides (the side of the surface and the substrate). We used of data [16] to define the parameter of crystal-lattice t according to TEM-diffraction pattern.

RESULTS AND DISCUSSION

It has been proven that the plasma detonation coatings are a mixture of differently oriented nanograins in the size of 1-2 nanometers and lamels of intermetallic phases in length to 50 nanometers Figure 1 presents a TEM - images and microelektronogramme of the nanostructured AN-35 coating.

Electronic diffraction microscopy of thin foils established that the middle part (in depth) of AN-35coating deposited by plasma detonation method onto the steel 3 substrate is a mixture of nanograins of varied orientation with separate crystalline particles. We didn't note ordering in distribution crystalline elements; their linear size varies from 30 nm (width) to 50 nm (length); the particles are unequiaxial. The morphology of new phase particles found in the coating suggests that it is cellular precipitation. The $Co_{0.8}Cr_{0.2}$ phase is distinguished in the form of lamels. Lamels are structurally unhomogeneous to a Ni-base and gleam in a dark field. Electron diffraction pattern of particles is typical for crystals different from ring electron-diffraction pattern of Co-base. According to the data of the XRD the material contains a Co-based fcc-lattice phase with the matrix a=3,543 Å (*Table 1*). In accordance with the estimated electron-diffraction pattern this parameter makes 3,5 Å. The volume ratio of microcrystallines in the coating material, as defined by TEM images, makes about 20%. The XRD analysis results of d Co-Cr-based coating phase structure are presented in the *Tables 1*. After duplex treatment the coatings become multiphase. In Co-Cr-based-coated the Mo bcc-phase is formed (Table 1).

The diffractograms reveal a great number of low-intensity peaks, which are supposedly connected to the formation in the process of fusion MoO_2 и MoO_3 Molybdenum oxide films on the surface of coatings. We are supposed that Mo was penetrated in coating from electrode.

Coatings have differences in phase composition, in a microstructure and in microhardness on depth. It is established that the roughness of the modified coatings decreases in 4-5 times, wear resistance increases in 6 time, hardness increases on the average by 15 %.

The nanohardness of the coating was specified as 8,7 hPa, and that of the substrate as about 3 GPa (substrate elasticity modulus makes about 210 GPa).

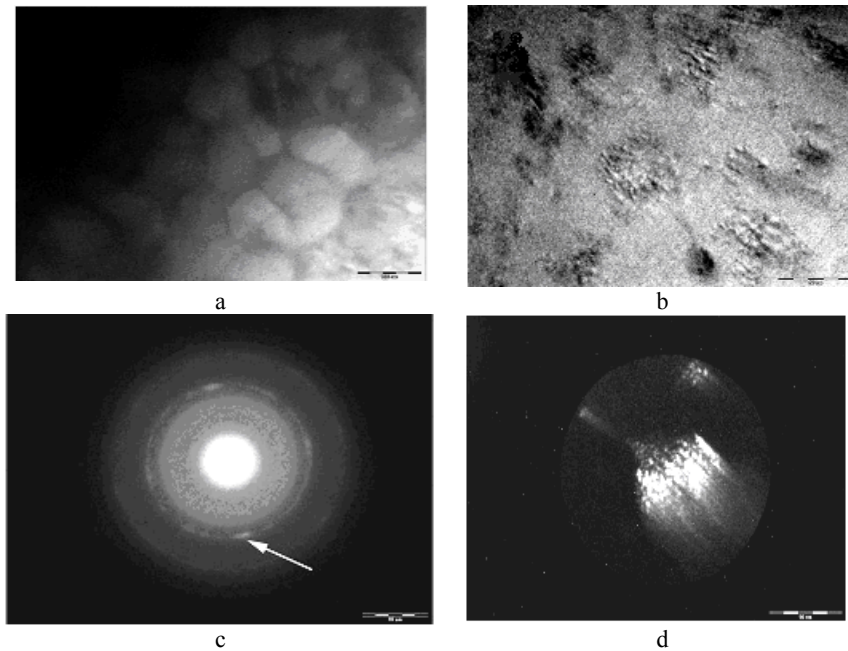

Fig. 1 – TEM - images the middle layer of AN-35 powder coating: nanoparticles (a), lameles of $Co_{0.8}Cr_{0.2}$ phase (b), electron diffraction pattern (c), dark field, shot in point reflex (d)

Table 1. XRD phase structure analysis of Co-Cr based coatings

Material	Phase Structure. Chemical formula. Parameters (Å).
AN-35 base powder	100 weight % - solid solution α - Co(hcp) + β-Co(fcc)
AN-35 plasma detonated coating	60 weight % - solid solution β-Co - Cubic, Fm-3m *a* =3,545 30 weight % - $Co_{0.8}Cr_{0.2}$, hexagonal, P63/mmc , *a* =2,52; *в* = 2,52 *c* = 4,062 5 weight % $Fe Cr_2 O_4$- Cubic, Fm-3m , *a* =8,3780 5 weight % $Ni Cr_2 O_4$ - Cubic, Fm-3m , *a*=8,2990
AN-35 coating treated by plasma jet at a depth of 45÷60 μm	70 weight % - solid solution β-Co - Cubic, Fm-3m *a* =3,545 20 weight % - $Co_{0.8}Cr_{0.2}$, hexagonal, P63/mmc, *a* =2,52; *в* = 2,52 *c* = 4,062 10 weight % - Mo Cubic, Pm-3m *a*=3,130 Å ($a_{tab\ Mo}$=3,147Å)

We hypothesize that the structure-phase pattern of Co-Cr based coatings deposited by the plasma-detonation method has common characteristics. We consider that the nanocrystalline pattern found AN-35 coating is distinctive for

all the coatings deposited by plasma detonation method, and partially characteristic for the substrate layer next to the coating. One of the reasons is high micro structure defectiveness conditioned by the plasma jet impact action on the surface and steep temperature gradient in the coating, which may lead to a great deformation in a coating. As a result, in order to remove the strains in a coating there forms a substructure of nanograins of different crystal lattice orientation with high and continuous disorientation, which is proved by distinctive ring electron-diffraction patterns. When the foils in a goniometer are oriented randomly, the characteristic of polycrystals features of diffraction contrast are absent, namely, the changes of its intensiveness on the boundaries, necessary for defining grain edges. We assume that we observe the pattern similar to a fragmented one, with fragment – nanograin – disorientation being analogous to the one of crystal polygonization. The validation of this assumption for the coatings is some diffusion of the peaks and lowering of their intensiveness on the diffractograms.

Due to considerable depth of the coating (150 μm) there is no problem of conjunction of high-duty and brittle surface film with the main material that possesses much lower strength and high plasticity. The process of deformation has a consistent structure rate on all the coating and the substrate intermediate layer. We think that the structure-phase state of a coating is defined by the following factors: deformational impact of a plasma jet, temperature profile distribution in the coating material, and inhomogeneous concentration of elements in the coating.

The fact of nanostructure formation in the coatings deposited by plasma detonation method is new, although it has been hypothesized before. The formed structures are stable at room temperature, no reduction of strength properties is observed.

The structure-phase state of Co-Cr based coatings deposited by plasma-detonation method and exposed to duplex treatment also has common characteristics.

First, forming multi-phase dense coatings with intermetallic strengthening compounds and increasing of Fe mass fraction in the coatings are typical for such coatings. We are supposed arising of deformations waves during impulse plasma treatment and penetration Fe from substrate in results of melting and interfusion.

We indubitably stated the layered structure of the coatings deposited by the plasma detonation method. On the surface of the coatings is formed a thin layer (not more than 5 μm) which contains oxides, C, or carbides, as well as phases with the elements of the coating, that are poorly soluble at high temperatures (Cr in this case). The new experimental results can be used for the model of Co-Cr-base coating development. This model will be used as base for the

estimate of temperature profiles under duplex treatment for the choice of its parameters.

Second, smoothening of the surface relief and forming the microstructure with micrograins and high micro and nano hardness, and wearability are typical for such coatings. The microhardness increase in number 1 GPa in comparison with microhardness Co-Cr –base coating before duplex treatment. The intermediate layer depth 150 μm with improved microhardness is formed. We are supposed that main reasons of improvements of the properties after duplex treatment are phase modifications and smoothening of rough coating surfaces and homogenization of coatings at melting by a plasma jet.

CONCLUSIONS

TEM and XRD allowed detecting the formation in the material of AN-35 coating before duplex treatment nanocrystalline Co-based γ-phase. It has been proven that the plasma detonation coatings are a mixture of differently oriented nanograins in the size of 1-2 nanometers and lamels of intermetallic phases CoCr in length to 50 nanometers. We suggested that the nanostructure of crystallographically disoriented nanograins is formed to remove mechanical strains in a coating.

After duplex treatment all the coatings become multiphase, with intermetallic strengthening compounds. The coatings are characterized by high microhardness (8,7 GPa) and nanohardness (in order 7,0 GPa), high wearability. It is established that the roughness of the modified coatings decreases in 4-5 times, wear resistance increases in 6 time, hardness increases on the average by 15 %. The improvements of the properties after duplex treatment are reached on account of phase modifications and smoothening of rough coating surfaces at melting. Therefore the Co-Cr coatings after duplex treatment can be used for protection of valves and other components working in aggressive environments and in condition of high friction.

REFERENCES

[1] Celik E., Ozdemir I., Avci E. and Tsunekawa Y.Surface and Coatings Technology, V. 193, No 1, (2005), P. 297 -302
[2] Kadyrzhanov K.K., Komarov F.F., Pogrebnyak A.D. et al. Ion-beam and Ion-plasma Modification of Materials. Moscow: MGU, (2005), 640 pp.
[3] Pogrebnjak A.D. Kylyshkanov M.K., Alontseva D.L.. Structure and properties of materials and composite coatings before and after exposure to concentrated energy flow. Ust-Kamenoogorsk: EKSTU, (2008), 296 pp.
[4] Pogrebnjak A.D., Alontseva D.L. et al. Technical Physics Letters, Vol. 30, No. 2, (2004), P. 164-167.
[5] Pogrebnjak A.D., Alontseva D.L. et al. Vacuum 81, (2007), P. 1243-1251
[6] Musil J. Surface and Coatings Technology, V. 125 (2000), P. 322–330.
[7] Musil J. Proceeding of the Euro powder metallurgy pm 2005. Congress and Exhibition, Prague, (2005), P. 476 – 488

[8] Musil J., Dohnal P., and Zeman P. Vac.Sci.Technol. B 23(4), (2005), P. 1568 – 1575
[9] Musil J., Jirout M. The 5th Asian-European International Conference on Plasma Surface Engineering, invited paper, Qmgdao City, China, (2005)
[10] Pought J., Foty G., Jackobson. D. E-beam and Ion Beam Modification and Doping of Surfaces M.: Mashinostroenie, 1987. - 424 pp.
[11] Ivanov Yu.F. et al. Russian Physics Journal, No. 8/2, (2009), P.402-404
[12] Ivanov Yu.F., Koval N.N. et al. Izvestiya VUZov. Fizika, No11/3,(2008), P.17-21.
[13] Pogrebnjak A.D.,Kravchenko Yu.A. et al. Surface and Coatings Technology, V. 201, (2006), P. 2621–2632.
[14] Pogrebnjak A.D., Il'jashenko M. et al. Vacuum, V. 62, (2001), P. 21–26.
[15] Oliver W.C., Pharr G.M. J. J. Matter. Res., V.7, No 6, (1992), P.1564-1583
[16] Gorelik S.S., Skakov Yu.A., L.N. Rastorguev. Moscow: MISIS, (2002), 360 pp.