Studies of Structure and Properties of Coatings on Co-Cr BASE After Duplex Treatment

A.D. Pogrebnjak[1,2], Yu.A. Kravchenko[1,2], Sh.M. Ruzimov[3], V.V. Ponaryadov[4]

[1] *Sumy Institute for Surface Modification, str. 87, Romenskaya, Bldg. "M", 40002 Sumy, Ukraine*
[2] *Department Surface Beam Modification, Institute for Metal Physics, NAS Ukraine*
[3] *National University of Uzbekistan, Tashkent, Uzbekistan*
[4] *Belarus State University, Minsk, Belarus*

Abstract – Using X-ray structure analysis (XRD), scanning electron microscopy (SEM) with micro-analysis, measurements of friction wear and micro-hardness, we studied surface melting effects of powder coatings AN-35, which appeared as a result of action of concentrated energy flows (pulsed plasma flows). Plasma detonation deposition of a powder on a stainless steel substrate were accompanied by formation of an alloyed surface structure, which basic element was α(hcp) and β(fcc) cobalt. A temperature diapason chosen for coating formation (according to the XRD analysis) provided the formation of intermetallic compounds of cobalt and chromium of Co_xCr_y type. Pulsed-plasma surface melting of powder coatings also induced doping of the nearsurface layer by molybdenum atoms. We found that chosen methods of analysis and surface treatment regimes provided essentially decreased wear, as well as increased microhardness and nanohardness of the irradiated surfaces. It was demonstrated that a resulting increase in servicing characteristics was related to the processes of phase transformations occurring in the powder when it had been in a high temperature plasma-detonation flow as a result of pulsed plasma surface doping by molybdenum atoms, redistribution of the coating elements, appearance of micro- and nano-grain structure, as well as decreased coating porosity induced by thermal annealing by concentrated energy flows.

1. Introduction

One of the most promising ways to form protecting coatings are combined methods (a duplex and triplex) of alloy treatment [1–5], which allow one to improve a total spectrum of servicing characteristics of stainless steel tools. Recently industry pays very much attention to a practical application of high-velocity plasma-detonation technologies [6–8], which allows one to produce coatings from corrosion-resistant powder materials, ceramics and metal-ceramics [9]. One of the most promising powder materials possessing high plasticity and corrosion resistance to high temperatures (till 1500°) are alloys and core alloys on cobalt base. For example, the powder coatings of Al-Co formed by plasma detonation contained a total spectrum of intermetalloids, which, according to the performed studies, endured high temperatures and loads in aggressive media [6].

However, according to already obtained results [10–11], plasma, detonation and plasma-detonation treatment of powder coatings have a number of disadvantages as: formation of thin oxide layers in the treated surfaces and open pores occurring in the coating itself (from 0.5 to 1.8 %). To reach a decreased porosity of the powder coatings and improved cohesion and adhesion properties within the interface coating-substrate, in practice we melt the coating surface by pulsed plasma flows and electron beams of high energy density [6, 12, 13]. Treatment of a solid surface by concentrated energy flows resulted in absorption of some fraction of the incident energy, which activated various physical and chemical processes in the material surface layer and in the coating depth (heating, structure-phase transitions accompanied by changes in aggregate state, changes in the surface phase, plasma-chemical reactions, intensification of practically all diffusion mechanisms, etc.) [6, 13]. An important advantage of pulsed-plasma surface modification is a possibility to saturate near-surface coating layers by refractory doping elements.

In such a way, the goal of this work was to study the structure and properties of powder materials on AN-35 base deposited using the high-velocity plasma-detonation jet on the stainless steel substrate before and after this plasma jet treatment applying also coating surface layer melting.

2. Experimental Methods

We formed the protecting coatings of 300 to 500μm thickness from the powder alloy AN-35 on cobalt base with the following dopes: Cr (8 to 32 %); Ni (≤3 %); Si (1.7 to 2.5 %); Fe (≤3 %); C (1.3 to 1.7 %) and W (4 to 5 %) on the substrate of stainless steel 12X18M9 using the plasma-detonation facility "Impulse-6". The powder with fraction dimensions 56 to 260μm was used. Steel samples of 20×30×2 mm, which surfaces were preliminarily subjected to sand-blasting treatment, were used as the substrate materials. Plasma-detonation powder materials were deposited using the following regimes for pulsed-plasma deposition: a distance from the sam-

ple to the plasmatron nozzle was 60 mm, a velocity of sample motion was 360 mm/min. frequency of pulse repetition exceeded 4Hz, powder expenditure was 21.6 g/min, capacity of a condensation battery was 800 μF, and propane, oxygen and air were used as combustion and plasma-forming gases. We chose Mo for the material of eroding electrode. After cooling samples in the plasmatron chamber a half of the samples was covered, and the other half was treated by pulsed plasma flows till meting for one to three passes. Operation regimes of the plasmatron were the same as in the case of deposition, however, the pulsed repetition frequency was 2.5 Hz. After this the samples were spark cut into pieces, studied and subjected to different tests.

Surface morphology was studied using scanning electron microscopy with reflected and secondary electrons by means of a scanning electron microscope REM-103-01. To determine a chemical composition of the studied surfaces, we applied an X-ray wave microanalyzer EDS-2 (Selmi, Sumy, Ukraine) produced on a basis of semiconducting Si(Li) detector. The surface phase composition was analyzed by X-ray structure analysis using an X-ray diffraction facility DRON-2 in CuK_a emission under conditions of Bregg-Brentano focusing. The diffraction patterns were taken under the regime of uninterrupted surface scanning by an X-ray in the range 2θ angles from 20 to 100°. We interpreted diffraction peaks using a reference book [14] and a data base PCPDWIN.

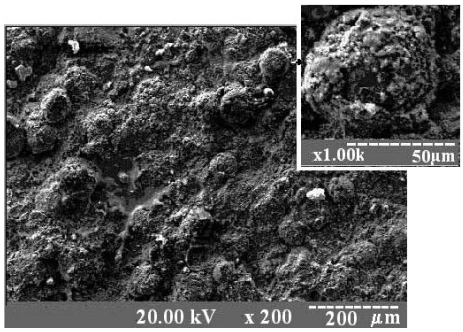
Microhardness measurements for plasma-detonation produced powder coatings were performed using a PMT-3(S-Peterbourg, Russia) apparatus with a diamond Vickers's pyramid under indenter load 10, 25, 50 g. Nanohardness tests were performed by a three-side Berkovich indenter of a nanohardness facility Nano Indenter-II (USA). These tests were performed in the following way: first, loading till 10mH, then stay during 20 sec, then the load was decreased to 80 %, stay under a constant load during 30sec to measure a heat drift, and finally we applied full indenter loading. To determine hardness and elastic modulus under maximum loading of the indenter, we used methods of Oliver and Pharr [15]. Wear resistance tests were performed using the apparatus SMTS-2 (Kiev, Ukraine) according to the scheme "plane-cylinder" in a medium of technical Vaseline. A criterion for evaluation of the samples' working ability in friction served the material volume ablated in the friction zone. The bulk wear was measured by microweighting in every 800 cycles. A total number of rotations (a counterbody or an engine) were about 10000. Corrosion resistance tests of am modified coating were performed using an electro-chemical equipment. We used a Bank-Wenking Potentio-Galvanostat PGS 81R and cells Princeton Applied research corrosion test. The tests were performed in sulphur acid solution 0.5 M under temperature till 200°. Potential from 1 to 1.3 V was applied to the facility electrodes. An area of corroding spot was equal to $8 \cdot 10^{-7}$ cm. Rate of material surface scanning was 15 mV/sec.

3. Investigation Results and Discussion

According to literature data, the technology of plasma-detonation deposition of powder coatings includes two main stages:

– the careful preparation of a tool surface before deposition (cleaning and thermal activation);
– the powder deposition onto the substrate surface by pulsed plasma flows [8, 10].

Figure 1, *a* shows that plasma-detonation modification of a stainless steel surface in the case we applied cobalt-based powder coating deposition was accompanied by formation of the strongly alloyed structure.



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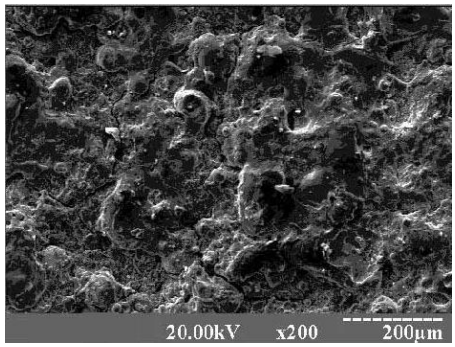

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Fig. 1. Surface morphology of plasma-detonation produced coatings of AN-35 powder: a) an initial surface state; b) coatings after HVPJ melting (two passes)

The surface structure of such coatings looked scaly and flaky. These coatings had highly pronounced relief without acute protrusions. Also we in the surface we observed many deformed protuberances, which looked as powder particles in-melted into the surface. First of all, we relate this to wide spread in powder particle dimensions – from 56 to 200 μm. That is why during their flying in the pulsed plasma flow small particles were totally melted, but those of bigger dimensions – only partially and being deformed in impacting formed the coating matrix. A

mechanism of powder coating formation was the following:

– the substrate surface treatment by high-energy plasma jet with high ion and electron density (1 to 5)·10^{17} cm^{-3} intensified electron heat conductivity and heating of an external substrate material layer.
– moving with high rate developed in the process of detonation of plasma-forming gases powder particles were melted in the high-temperature plasma flow of pulsed plasma. In a first pass when impacting the substrate they were deformed and filled in various micro-valleys in the substrate surface.

These photos show that both the transition region structure and that of the coating had a complicated character. As a result of mechanical and thermal treatment of a two-phase plasma-detonation flow by dynamical introduction of the powder material into the near surface substrate regions we succeeded to form a desired coating. After the transversal cross-sections were etched, along the contact boundary we found such white bands which were not able to be etched According to literature data [10], the look like finely dispersed oversaturated carbon solution in the substrate material. Its appearance was conditioned by a high contact temperature rose in the transition region and by fast substrate quenching occurring in the region being adjacent to the deposited coating. Since the powder coatings were formed for six passes, many-time layer deposition resulted in a partial or total destruction of such contact bands as far as moving deeper and deeper into the substrate surface (a region of h_2 thickness). Analysis of the coating surface structure demonstrated that it was composed of the regions of entire coating with in-melted powder particles and small in diameter cavities. The powder material filled in various valleys occurring in the substrate surface and powder coating after every subsequent pass. However, moving with high velocity the powder flow was saturated by elements of a plasmatron gas atmosphere, and some weakly melted particles "covered" various valleys conditioning occurrence of pores in the coating structure. The bigger the diameter of a particle, the lower it was heated in a plasma flow and impacting with the substrate surface it formed local regions of strengthened state in the surface, which we considered to be a good sign for forming strong adhesion power. The coating structure itself was such that those powder layers that were positioned closer to the substrate surface had much lower porosity than those of the near surface region. We assumed that probably with increased number of passes the lower positioned layers were hardened due to action of thermal and mechanical loads.

Also it is probable that after every subsequent pass of the plasmatron the deposited surface got cooled a little and the following powder layer, which was deposited, partially destructed the surface of the previous sublayer introducing in it powder particles. Metallography studies (Fig. 2) of detonation-produced coating structures demonstrated that the cobalt-based powder deposition process under chosen regimes was accompanied by the formation of a developed interphase boundary between the coating and substrate. As a result of this interaction some places in the substrate surface layer were deformed (the process of "micro-channeling" of powder particles). At the interphase boundary there are regions in which powder particles were introduced into the melted substrate surface at an initial stage of coating formation. Following the interphase boundary we found a region of a transition layer developing approximately to the coating depth. In the process of deposition his transition layer was subjected to high temperature action and mechanical hardening.

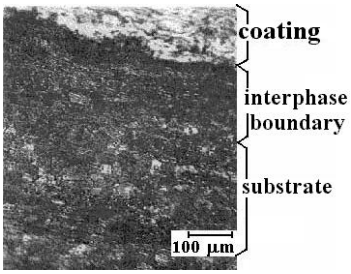

Fig. 2. Optical photo of AN-35 coating structure, that of the transition layer and substrate

To study the structure of such coatings and evaluate their element composition, we applied SEM and took imaged of their surface with secondary electrons.

It is shown that in the process of deposition a coating with a highly pronounced relief was produced. The surface of such coatings was composed of a great number of non-fully melted powder particles. We consider that pictures show round regions (≤50 μm in diameter), which seem to be centers of a hard powder matrix. Our studies of a local and integral element composition of the powder coatings demonstrated that their matrixes possessed high atomic concentration of Co (about 46 at.%) In addition we found about 28 at% of Cr; 10 at% of Fe, 3.2 at% of Si and 7.73 at% of Ni, carbon, molybdenum (the material of eroding electrode) and calcium playing a role of impurity elements.

It is known [5, 9] that mechanical and physical and chemical properties of plasma-detonation produced coatings depended on a relief of near surface regions, as well as on their element and phase composition, and their corrosion resistance – on pore concentration [6]. One of the ways to avoid porosity, to seal various coating non-uniformities and to increase coating to substrate adhesion power seems to be powder compaction by action of external thermal and mechanical loads. Improvement of mechanical characteristics of the treated surfaces is possible either by changed surface phase composition or by enrichment of the coating near surface layers by re-

fractory elements as a result of ion implantation or surface melting by pulsed plasma flows. According to performed studies of morphological features of the surfaces after their treatment by high-velocity plasma jet (HVPJ), they melted which resulted to essential smoothing of the relief and decreased roughness dimensions in the coating surface. However, some particles (depending on their initial dimensions), being treated by HVPJ for the second time, did not melt. They only sweated together with other non-uniformities. SEM analysis performed in some regions of the coating demonstrated that the same structure as in the case of concentrated energy flow (CEFT) treatment was formed in the surface [12]. Coating surface morphology studies demonstrated that some changes took place in the coating matrix under selected regimes of surface thermal modification. The obtained photos show that the HVPJ treatment was accompanied by through-melting of the surface since an amount of non-fully melted powder particles decreased essentially in the coating matrix. Traces of some powder particles remained in the photos, but they were significantly lower in diameter (Fig. 3, *a*), and the coating itself had higher degree of alloying. Surface melting by pulsed plasma flows provided also changed element composition of near surface coating layers.

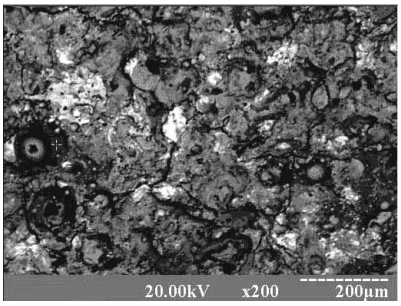

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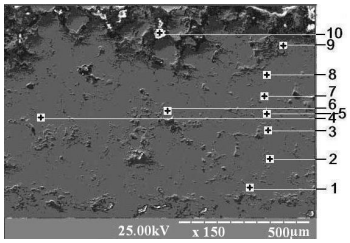
Fig. 3. Effect of high-velocity pulsed plasma flows on the structure and element composition of AN-35 powder coating surfaces: a) a general view of the surface obtained using secondary electrons; b) integral chemical composition of the surface region presented in Fig. 3, a

The photos of the near surface region demonstrate many brightly glowing areas of irregular forms (Fig. 4, *a*). Earlier we found that near surface coating regions formed without melting had a porous structure. But in the process of melting an amount and dimensions of these pores essentially decreased, and those which remained were filled-in by atoms of the eroding electrode.

Figure 4b demonstrates the structure of near surface regions of the resulting coating more clearly. Studies of the surface element composition by micro analysis demonstrated that these light aggregates by 95 % are composed of molybdenum atoms. Integral spectra of the coating surface element composition after melting demonstrated high intensity chromium, iron and cobalt peaks (Fig. 3, *b*). According to obtained result of analyses distribution of the coating composing elements practically does not change from point to point.

We assume that presence of molybdenum atoms in powder coatings was due to its presence in the plasmatron gas atmosphere and the result of deposition process, since distribution of molybdenum atoms over the coating depth and width shows uniform character.

However, physical and mechanical surface properties are determined not only by its morphology and elements composition. When the coating porosity is low their hardness will be dependent on the surface phase composition. Using X-ray analysis we found that the powder which was used for deposition was composed of a solid solution α- and β-Co. We assumed that Ni, Si, Fe, Cr and W played a role of substitution atoms. In spite of significantly high chromium content occurring in the powder, its peaks in the diffraction image are absent



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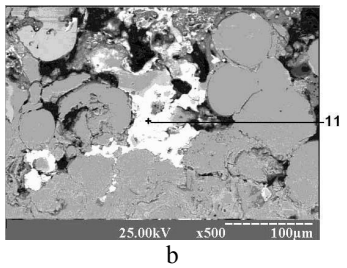

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Fig. 4. Results of studies for distribution of coating element composition over depth after HVPJ treatment (crosses mark the points of local element analysis): a) photos for some region of the powder coating cross-section; b) the structure of powder coating near surface regions after melting (under secondary electron regime conditions)

This means that all the chromium atoms have chemical bonds with those of cobalt. As a result of plasma-detonation coating deposition induced by the pulsed plasma flow an initial powder material underwent a number of phase transformations.

Also a solid cobalt solution α(fcc) and β(hcp) are a part of the coating surface. As one can see in a diffraction pattern, after coating deposition the peaks corresponding to X-ray reflection from cobalt lattice planes broadened significantly and became lower intensive. We assume that their broadening was due to atomic regrouping in the initial material induced by high temperatures. According to a phase diagram Co-Cr, in addition to α-cobalt a phase $Co_{60}Cr_{40}$ must be formed in the coating. Therefore basing on the data of this phase diagram and table data [14], we relate this background increasing in the region of angles 2θ from 37 to 42° and from 43 to 47° to the formation of cobalt chemical compounds with chromium in the surface. Calculation of a per cent phase ratio in the coating demonstrated that 65 volume % was occupied by cobalt solution, and the rest was for an intemetallic compound of cobalt with chromium.

After melting of the coating surface by pulsed plasma flows to the depth till 45 to 60 μm the its near surface region also was composed of α- and β-Co. As for the intermetallic compound CoCr, it was at the lowest limit of detection (≤5 volume %). X-ray analysis confirmed that thermal activation of a surface by high-velocity pulsed plasma flows provided saturation of near surface coating layer by molybdenum atoms. The diffraction patterns show well pronounced intensity peaks corresponding to reflections of (110), (200), and (211) planes for (bcc)-phases of molybdenum According to performed calculations the molybdenum lattice parameter was equal to 3.13 (a table (Mo)=3.147Å [14]. We found in these diffraction patterns many peaks of low intensity, which we related to the formation of oxide molybdenum films formed in the coating surfaces in the process of melting. These peaks we explained as a result of formation of MoO_2 and MoO_3 oxides in the treated surfaces. Calculations of a per cent ratio of phases composing the near surface regions of powder coatings demonstrated that their matrixes are composed by 30 volume % of a solid solution on cobalt base and 20 volume % of molybdenum. The rest 50 % are molybdenum oxides and inter metallic compounds of cobalt with chromium.

Microhardness measurements performed for HVPJ- produced coatings after their modification, in which we used transversal cross-sections allowed us to obtain the following results:

– microhardness in the coating near surface region reached 4.55±0.35 GPa;
– maximum value of 6.25±0.34 GPa was found near the plasma jet melted zone.
– microhardness measurements, which we performed at the half-depth of the coating (120 μm, which corresponded approximately to the interface of melting depth) demonstrated some average value of 4.20±0.25 GPa.
– In a contact region "coating-substrate" an average value of microhardness was about 3.14±0.23 GPa.
– In the process of our studies we also found that an average value of microhardness decreased with increased coating thickness.

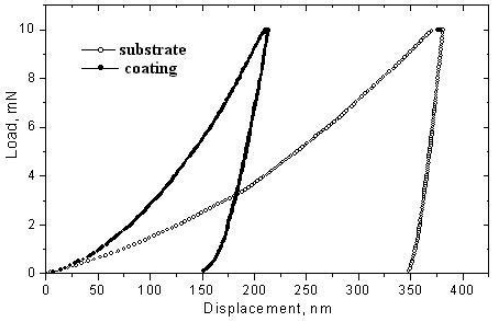

Fig. 5. Loading curves taken in substrate nanohardness measurements (light circles) and the AN-35 coating (dark circles) after pulsed plasma flow treatment

At the same time we performed measurements of the produced coating nanohardness. Figure 5 shows curves of loading for the substrate and AN-35 coating after melting by a high-velocity pulsed plasma jet. These data evidence that the coating hardness is 8.7 GPa and that of the substrate reached 3 GPa (the substrate elastic modulus was about 210 GPa).

Figure 6 shows dependences of wear curves obtained for initial coatings and for those after pulsed plasma modification.

From these dependences one can see that the highest wear was observed in the stainless steel substrate. Plasma detonation deposition of powder coatings decays essentially wearing of a treated surface.

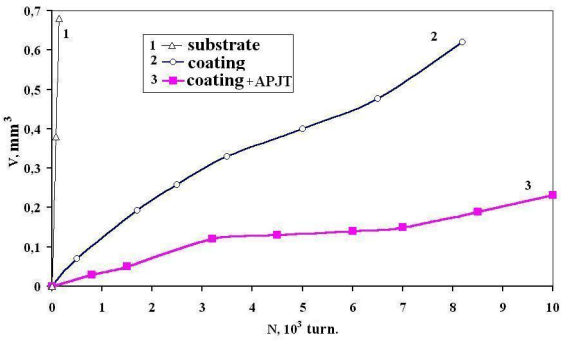

Fig. 6. Dependence of surface wear for powder coatings on cobalt base during dry friction on the number of rotations: 1 – the substrate material (stainless steel); 2 – wearing of plasma-detonation produced coatings (240 μm thick); 3 – effect of coating surface melting as a result of pulsed plasma flow action (2 passes) on wear resistance

Thermal coating hardening by pulsed plasma flows allows one to have the most optimum combination of hardness and plasticity. Tests of sample sur-

faces for wear resistance in technical Vaseline medium demonstrated that:

- the deposition of powder coatings on cobalt base under above mentioned regimes resulted in a factor of 12 increase in their surface wear resistance in comparison with substrate material;
- the repeated HVPJ treatment of surfaces was accompanied by a factor of 25 decrease of wear (which was likely to be related to Mo oxide formation).

Preliminary tests of workpieces with such protecting coatings under temperature increasing 200 °C in acid medium demonstrated very good corrosion resistance. Therefore from this point of view application of the presented technology may attract high interest.

4. Conclusions

In the process of powder deposition in a high-temperature plasma flow the initial material underwent a number of phase transformations after which we found a solid substitution solution of cobalt and intermetallic CoCr compound in the content of produced plasma detonation coatings. Also we should like to note that in the process of powder deposition we succeeded to develop highly a transition region "coating-substrate" with a greatly hardened coating occurring in the vicinity with this zone. Thermal coating modification using a high-velocity plasma jet resulted in a decreased surface relief due to melting of various non-uniformities and filling of valleys in the surface by this liquid material We also found a decreased porosity of near surface layers by local saturation and simultaneous filling-in of pores by molybdenum atoms.

We conclude that namely this change in the element and phase composition (appearance of molybdenum oxide films in the surface), the decrease in porosity and surface relief occurred in the process of thermal treatment by high-velocity pulsed plasma treatment resulted in increased nano- and microhardness, as well as higher coating wear resistance and their long life in aggressive media.

Acknowledgements

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