

PHASE COMPOSITION AND PHYSICAL PROPERTIES OF Co-Cr BASE COATING

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ABSTRACT

Coating structure was mainly composed of α -fcc- and β -fcc-cobalt. Selected temperature interval for coating formation, according to XRD analysis, allowed us to form inter-metalloid compounds of Co_xCr_y -type cobalt with chromium. Subsequent melting of a surface layer by a plasma jet resulted to doping of the coating surface by Mo atoms (compounds) from doping electrodes. It was demonstrated that essential improvement of servicing characteristics was due phase transformations induced by high-temperature plasma jet, Mo doping, redistribution of elements in the coating, and appearance of micro- and nano-grained structure, as well as decreasing porosity due to repeated melting.

Key words: coating Co-Cr, wear, hardness, corrosion resistance, plasma jet.

INTRODUCTION

The process named "Aero-Spray Supersonic" (in which a blend of an air and fuel is used) is an alternative to using a blend of a fuel and oxygen. Investigations have shown [1-7] that to form a dense coating which is closely bonded to a substrate, one needs a velocity of powder (usually an alloy on a metal base) of 600-1000 ms^{-1} before heating. Analysis of the efficiency of the different devices applied in high-velocity deposition shows [4] that to deposit 1 kg of coatings based on tungsten carbide, one needs least 10 m^3 of the combustible mixture and a 600-650 ms^{-1} maximum velocity of the powder (45-10) μm in size) to be accelerated in these devices. To form a high-velocity flow of the combustion products, 30-150 m^3 of the combustion mixture should be fired in the combustion chamber. However, the deposition efficiency and the resulting coating quality, as a rule, are not proportional to the increase of heat power [8].

In comparison with other methods of gas-thermal deposition, the advantages

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of high-velocity gas-plasma HVOF (High Velocity Oxygen Flow) are particularly its high particle velocity (up to 750m/s) and minimal porosity of its resulting coating of (1 to 4 %). Several commercial HVOF deposition systems as JP-5000/8000 (Tafa-Praxair, USA), DJ 2600/2700 (Zulser Metcom, USA), Intelli-Jet (Solid Spray Technologies, USA), HV 50 HVOF (Flame Spray Technologies, The Netherlands), etc. are in common use. TOPGUN AIRJET [9], which is able to sputter powders and wires, is an example of successful improvement of the HVOF device. The National Institute of Materials (NIM) of Japan developed a mouthpiece (an additional device) for HVOF [10], which is able to decrease the temperature of the working gas. Up to 30 m² per hour of nitrogen (N) can be feed to this mouthpiece. The most interesting mouthpiece for HVOF (Intelli-Jet) was presented by “Mashprom” (in Ekaterinburg, Russia) [11]. This mouthpiece needs more than 300 m³ of air and up to 16 m³ of propylene per hour. The mouthpiece was economically cooled by the combustion mixture components.

Disadvantages of the above HVOF devices seem to be their high energy expenditures and high pressure of the fed gases – 4 MPa. This complicates the gas control systems, increases safety requirements, and decreases the efficiency of the gas feeding systems. In practice, the cooling systems all HVOF devices consume 30 to 50 kW of electrical power.

Today, a new technology -- Cold-Spraying -- is developing very actively. Cold Spraying can deposit plastic materials using high-velocity inert gas or air jets. Gas is heated to increase its efficiency. In spite of high electrical power for gas heating of 10 to 35 kW [12], this technology is efficient for special applications and is being improved [13 – 15]. Cold spraying deposition systems provide high-velocity gas jets by compressing the gas to high pressures of 1 to 3 MPa and using a narrow nozzle.

Pulsed detonation systems, which can provide high-velocity gas jets with significantly lower heat flux is an alternative to Cold Spraying and HVOF technologies. High power of the gas jet in pulsed systems has a dominating kinetic component. Powders in these jets acquire high kinetic energy without powder overheating. This can form a lamella coating structure on a hard substrate. Low heat flux, and high gas and powder velocities, prevent overheating of the mouthpiece, increasing its life time by several orders of magnitude. Various detonation device configurations are known, but those featuring higher efficiency of detonation combustion of the gas mixtures are better. Aerostar Coatings, who employs high frequency devices HFPD [16] are among them.

“Grom” device of OAO Khimmash, Novosibirsk, Russia, “Perun” device, Ukraine are employed for deposition of coatings of hard alloys and metal ceramics. Low productivity and limitations in components of a combustion mixture seem to be disadvantages of the detonation technology.

Devices, where products of detonation combustion of gas mixtures imparted additional kinetic energy, were developed. For this purpose, high-power trans-

former of an electric energy of up to 20kW, which was switched into a special electrode occurring in a detonation chamber [17], was used. It should be noted that the Stellite 6 was used in studies in high power laser cladding, Hot Isostatically Pressed [18].

METHODS OF SAMPLE MANUFACTURING AND ANALYSIS

We formed the protecting coatings of 300 to 500 μ m thickness from the powder alloy STELLITE-6 on cobalt base with the following composition: Cr (8 to 32%); Ni (\leq 3%); Si (1.7 to 2.5%); Fe (\leq 3%); C (1.3 to 1.7%) and W (4 to 5%) on the substrate of stainless steel 12X18M9 (321 stainless steel with doped Mo 6-9 at%). Using the plasma-detonation facility "Impulse-6". The powder with fraction dimensions 56 to 200 μ m was used. Steel samples of 20x30x2 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 sample to the plasmatron (detonation gun for deposition) nozzle was 60 mm, a velocity of sample motion was 360 mm/min. frequency of pulsed repetition exceeded 4 Hz, powder expenditure was 21.6 g/min, capacity of a capacity battery was 800 μ F, and propane, oxygen and air were used as combustion and plasma-forming gases. We chose Mo for the material of doping 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.

The surface morphology was studied using scanning electron microscopy with reflected and secondary electron modes a scanning electron microscope REMMA-103-01, (Selmi, Sumy, Ukraine) and optical profiler VEECO WYKO NT 1100 (AZ 85706 USA) To determine a chemical composition used energy dispersive X-ray spectroscopy (EDS). The surface phase composition was analyzed by X-ray structure analysis using an X-ray diffraction facility DRON-2 (St.-Peterbourg, Russia) in $Cu_{K\alpha}$ emission under conditions of Bregg-Brentano focusing. The diffraction patterns were taken by an continues X-ray scan in the range of 2θ angles from 20° to 100° . We interpreted diffraction peaks using a reference book and a data base PCPDWIN.

Microhardness measurements for plasma-detonation produced powder coatings were performed using a PMT-3 (St.-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 10mN, then hold during 20 sec, then the load was de-

creased to 80%, stay under a constant load during 30 sec 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. Wear resistance tests were performed using the apparatus SMTs-2 (Kiev, Ukraine) according to the set-up “plane-cylinder” in a medium of technical vaseline. A criterion for evaluation of the samples’ friction performance was the material volume ablated in the friction zone. The bulk wear was measured by microweighing every 800 cycles. A total number of rotations (a counter body or an engine) were about 10000. Corrosion resistance tests of a modified coating were performed using a Bank-Wenking Potentio-Galvanostat PGS 81R and cells Princeton Applied research corrosion test. The tests were performed in sulphuric acid solution 0.5M under temperature up to 200°. Potential from 1 to 1.3V was applied to the facility electrodes. In all cases the sample surface exposed to the corroding medium was 1 cm². The test in 0.5 M H₂SO₄ solution were carried out in the potential region – 1000 to + 1500 V at ambient temperature. Five rapid scans (scan rate = 25 mV/s) followed by one slow scan (scan rate = 0.25 mV/s) were performed on specimen.

RESULTS AND DISCUSSION

Figure 1a taken from the optical microscopy, 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. 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.

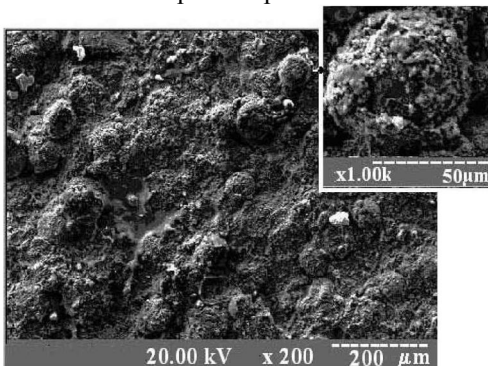


Fig. 1 – Surface morphology of plasma-detonation produced coatings of STELLITE-6 powder an initial surface state

plasma jet with high ion and electron density (1 to 5) $\times 10^{17}$ cm⁻³ intensified

First of all, we relate this to wide spread in powder particle dimensions – from 56 to 200 μ m. During their flight in the pulsed plasma jet small particles were totally melted, but those of bigger dimensions – only partially and being deformed on 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) $\times 10^{17}$ cm⁻³ intensified

electron heat conductivity and heating of an external substrate material layer.

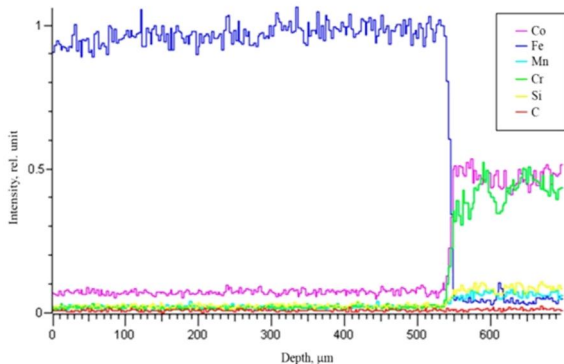


Fig. 2 – Cross-sectional images of the sample coated with STELLITE-6, obtained in secondary electron mode. The specified markings shooting for microanalysis

Fig. 2 shows the contents of chemical elements: for each item - a line of color. It is evident that iron (blue) penetrates the coating layer (top) to a small thickness. To understand how much interest has changed the iron content, the analysis on several points. Choose three of them: on the surface, the transition layer substrate-coating and the substrate itself.

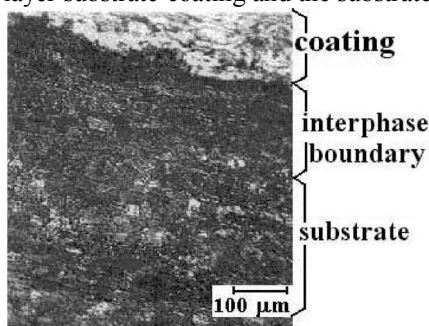


Fig. 3 – Optical photo of STELLITE-6 coating structure, that of the transition layer and substrate

(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 this transition layer was subjected to high temperature action and mechanical hardening. To study

Moving with high rate developed in the process of detonation of plasma-forming gases powder particles were melted in the high-temperature plasma jet of pulsed plasma. In a first pass when impacting the substrate they were deformed and filled in various micro-valleys in the substrate surface.

Metallography studies (*Fig. 3*) 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 structure of such coatings and evaluate their element composition, we applied SEM and took images of their surface with secondary electrons.

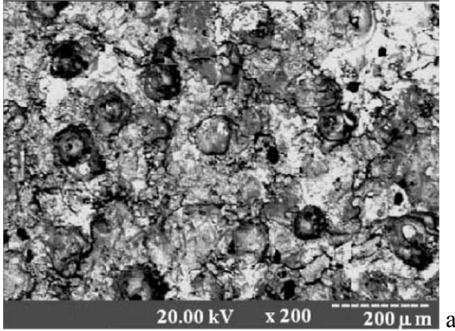
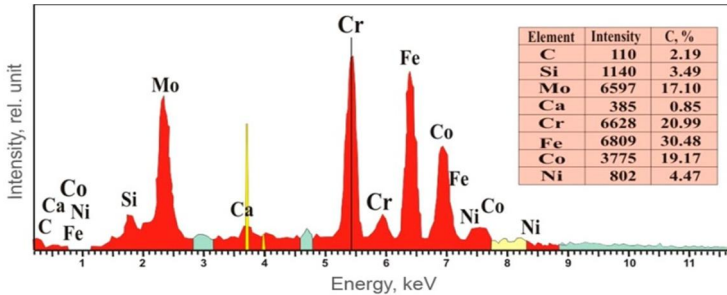


Fig. 4 – Structure and chemical composition of the plasma-detonation produced coating: a) a photo for the surface region subjected to element analysis (under secondary electron regime conditions); b) integral element surface composition



b

The pictures (*Fig. 4a*) show 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 ($\leq 50 \mu\text{m}$ in diameter), which seem to be centers of a hard powder matrix. Our studies of a local and integral element composition (*Fig. 4b*) of the powder coatings demonstrated that their matrixes possessed high atomic concentration of Co (about 19.17 wt.%) In addition we found about 21wt% of Cr, 30.5wt% of Fe, 3.5wt% of Si and 4.7wt% of Ni, carbon, molybdenum (the material of doping electrode) and calcium playing a role of impurity elements. 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 treatment (CEFT) was formed in the surface [27,29,33]. 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 essen-

tially in the coating matrix. Traces of some powder particles remained in the photos, but they were significantly lower in diameter (*Fig.5a*), 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. To evaluate parameters of relief roughness for Co-Cr coating surface after plasma jet melting, we additionally employed an optical microscope with laser attachment VEECO.

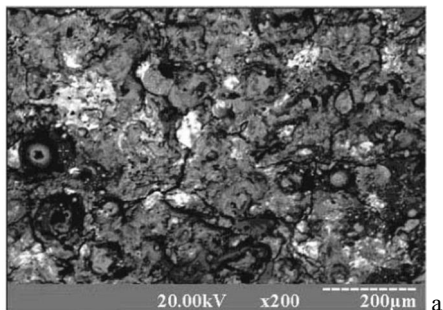
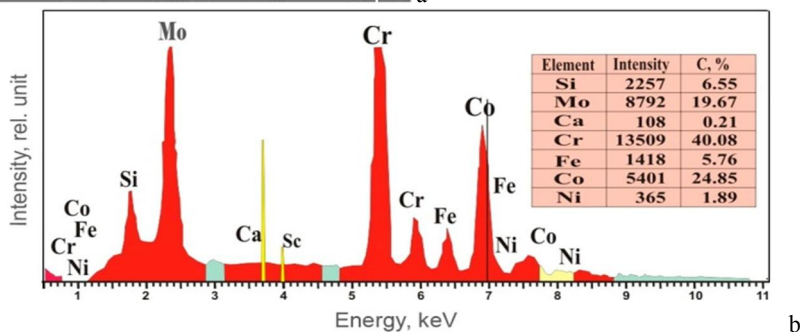


Fig. 5 – Effect of high-velocity pulsed plasma flows on the structure and element composition of STELLITE-6 powder coating surfaces: a) a general view of the surface obtained using secondary electrons; b) integral chemical composition of the surface region presented in Fig.4a



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. 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. 5b*).

CONCLUSIONS

Plasma detonation deposition of powder coatings on cobalt base was accompanied by formation of an alloyed powder structure with a highly developed relief. Basic matrix components of these powder coatings were cobalt,

chromium, nickel, iron, molybdenum (the eroding electrode element) and carbon (a component of the plasmatron gas atmosphere). In the process of powder deposition in a high-temperature plasma jet 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. In the process of powder deposition we succeeded to develop out of place, 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-in 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 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 micro-hardness, as well as higher coating wear resistance and their long life in aggressive media.

Acknowledgements

This work was partly funded by ISTC Project K-1198, as well as by the Project "Nano-Materials, Nano-Films, Nano-Systems, New Physical Principles of Nano-Film Production, Nanotechnologies and Coatings" NAS of Ukraine.

The authors acknowledge Dr. Sc V.N. Radziyevskiy and Dr. Ph. G.G.Tkachenko (Concern "UkrRosMetal"), Dr. Ph S.N.Dub (Institute for SuperHard Materials NAS of Ukraine) for their help in performance of these experiments, and prof. E.A. Levashov from MISA (Moscow) for their help in performance (Measurement parameters for Wyko Optical Profiles Veeco).

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