The Structure-Phase Compositions of Ni - Cr and Co–Cr Based Powder Alloys Coatings Deposited by Plasma-Detonation on Steel Substrates

Darya L. Alontseva[1], Alexander D. Pogrebnjak[2], Galina Klassen[3]

[1]East Kazakhstan State Technical University, 69 Protazanov St., 070004, Ust-Kamenogorsk, Kazakhstan, dalontseva@mail.ru

[2] Sumy State University, 2R-Korsakov St., 40007, Sumy, Ukraine, alexp@i.ua

[3]Technische Universitaet Dortmund, August-Schmidt-Str. 4, 44227, Dortmund, Germany

Key words: plasma detonation coatings, structure-phase composition, transmission electron microscopy

Abstract. This paper presents new results of transmission electron microscopy (TEM), X-ray diffraction (XRD) and atomic force microscopy (AFM) investigation of the structure-phase compositions of thick (150 μm) coatings on the base of Ni–Cr and Co–Cr deposited by plasma-detonation on steel substrates. The phase structures and morphology of precipitation from solid solution are defined. The microstructure model of a thick plasma detonation coating on steel substrate is developed. The main aim of carrying out these investigations is developing science based recommendations for modification of plasma-detonation coatings by plasma-jet or e-beam.

1. Introduction

The plasma detonation method is recent; it allows obtaining coatings from high-melting metal powder in air medium. One of the main problems of plasma detonated thick coatings (100-500 μm thick) is their porosity, lack of homogeneity on account of poor agglomeration of powder particles, high roughness of surface and low adhesion to substrate. These result in insufficient corrosion and wear resistance of such coatings. Practical experience of the use of combined technologies of coating deposition by plasma detonation with the subsequent modification by e-beam or plasma jet allows to claim that the mechanical properties of such coatings of metals and alloys (microhardness, nanohardness, wear resistance, and corrosion resistance) are very high. However, we should clearly constitute the structure-phase coating composition for coatings with expected properties by added irradiation. There are not enough published TEM data about structure-phase composition of coatings deposited by plasma detonation. The conditions of plasma-detonation depositing (heating at high speed, pressure, and short exposure to high temperatures) justify the formation of nanostructures and amorphous areas in coatings.

The goal of the research is to empirically establish the structure-phase compositions and mechanical properties of PG-19N-01 and AN-35 (Russia Industrial Standard) powder composite coatings deposited on steel by plasma detonation and to scientifically justify the modes of additional irradiation by plasma-jet or e-beam.

2. Materials and Experiment Methods

An “Impulse-6” plasma detonation unit was used to form 150 μm thick protective coatings of powder alloys on steel substrate (St 3: Fe – base, C - 0.25 %, Mn - 0,8 %, Si - 0,37 %, P < 0,045 %). For the coatings we used the PG-19N-01 Ni-based powder alloy with additives of Cr (8…14%), B (2,3%), Si (1,2-3,2%), Fe (5%), C (0,5%) and the 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%). The powder fractions varied from 56 to 260 μm in size. The substrates were 20x30x10 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 - 4 Hz; powder consumption – 21,6 g/min.. Pulse duration is 10^{-5} seconds, the shape of impulse is square, the diameter of a plasma jet on a sample is 25 mm. Propane, oxygen and air were used as combustible and orifice gases. Mo was selected as a plasma-jet eroding electrode material. The coating was deposited at the Sumy Institute for Surface Modification (Sumy, Ukraine).

Experimental methods of analysis: AFM by JSPM-5200 (“JEOL”, Japan) and by NT-206 (Belorussia), TEM by JEM-2100 (“JEOL”, Japan), SEM by JSM-6390LV (“JEOL”, Japan) with EDS

("Oxford Instruments", Great Britain), XRD by X'Pert PRO ("PANalytical", the Netherlands). The foils for TEM were prepared by the Ar ion sputter etching method using the PIPS facility ("Gatan", USA). For a more detailed analysis of the coating it was mechanically cut off the surface of the substrate to examine the structure at different distances from the coating surface. We used the method of arbitrary secant line to define the volume fraction of phases according to TEM-images and data [9-11] and Crystal Maker software to define the parameter of crystal-lattice according to TEM-diffraction pattern. Microhardness is measured on the coatings' angle laps by PMT-3 microhardness meter (LOMO, Russia) with an indentation load of 2, 5, and 10 N. Concurrently we measured the sizes of corresponding grains.

3. Experiment Results

The roughness of plasma-detonation coatings is very high. The average number of roughness coefficient Ra is 100 nm for AN-35, and 121nm for PG-19N-01. We observed X-Ray halo in the field of low-angle area at the X-ray diffractogram, which allows assuming surface amorphization. The XRD analysis results of coating phase structure are presented in Table 1.

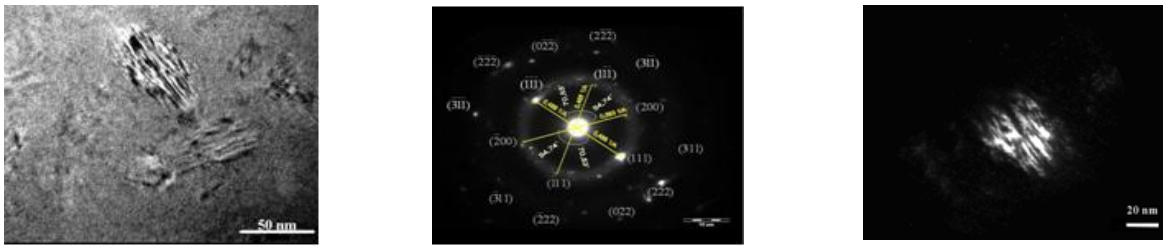
Table 1. Phase composition of the Ni-Cr and Co-Cr based coatings (the thickness of analyzed layer is about 50 μm)

Material and the field of analysis	Volume concentration. Chemical formula. Crystal system. Space group. Space group number. Parameters (Å)
Ni-Cr based coating	
PG-19N-01 base powder	75 % - solid solution on Ni-base (γ-phase) - Cubic, Fm3m, 225, *a* =3,55 25% - Cr_{13} Ni_5 Si_2- Cubic, Pm-3m, 221, *a* =6,1180
coating PG-19N-01, 0-50 μm from the surface	60 vol. % -solid solution on Ni-base (γ-phase) - Cubic, Fm3m, 225, *a*=3,535..3,540 15 vol. % Cr_3 Ni_5 Si_2 – Cubic, Pm-3m, 221, *a*=6,1180 15 vol. % Cr Ni_3 -Cubic, Fm-3m, 225, *a*=3,552 10 vol. % NiO_2 - Cubic, Fm-3m, 225, *a*=4,2
coating PG-19N-01, 150-200 μm from the surface	70 vol. % - solid solution on Ni-base (γ-phase) - Cubic, Fm3m, 225, *a*=3,525...3,500 10 vol. % Cr Ni_3 -Cubic, Fm-3m, 225, *a*=3,552 20 vol. % Fe_7Ni_3 – Cubic, Im-3m, 229, *a*=2,861
Co-Cr based coating	
AN-35 base powder	20 vol.% - Co –based solid solution, hexagonal (hcp) 70 vol% - Co –based solid solution, Cubic (fcc) 10%- $CoCr_2O_4$, Cubic (fcc), Fm-3m (225), *a*=8,2990
coating AN-35, 0-50μm from the surface	60 vol. % - Co-based solid solution, Cubic (fcc), Fm-3m, 225, *a* =3,55…3,54 20 vol. % - $Co_{0.8}Cr_{0.2}$, hexagonal, P63/mmc,194 , *a* =2,52; *в* = 2,52; *c* = 4,062 10 vol. % $FeCr_2O_4$- Cubic (fcc), Fm-3m, 225, *a* =8,3780 10 vol. % $CoCr_2O_4$ - Cubic (fcc), Fm-3m, *225*, *a*=8,2990
coating AN-35 150-200 μm from the surface	50 vol. % - Co-based solid solution, Cubic (fcc), Fm-3m, 225, *a* =3,52-3,53 15 vol. % - Co0.8Cr0.2 , hexagonal, P63/mmc,194, a =2,52; в = 2,52 ; c = 4,062 35 vol. % CoFe– Cubic, Pm-3m, 221, *a* =2,8570

The coatings have differences in the phase structure with depth (see table 1).We noted the reduction of γ-phase parameter *a* in the coatings and relative increase of the γ-phase peak (220), (422), (440) intensity with depth. In general the γ-phase peaks spread. In the coating layers that contact substrate the volume concentration of Fe–based phases rises (Fe is the basic component of a substrate), and the oxides disappear.

According to the data of the XRD the material of the substrate contains a Fe -based bcc-lattice phase (cubic, Im-3m, 229) with the parameter *a*=2,8662 Å. It was proven by TEM that the base through-thickness layer of plasma detonation coatings is a mixture of crystallographically differently oriented nanograins of austenitic γ-phase with the size of 1-2 nanometers and lamellas of intermetallic phases up to 50 nanometers long (Fig. 1a, Fig. 2a). Though in electron diffraction pattern all reflexes of face-centered cubic lattice are observed, yet the planes with zone axis <111> give brighter reflexes. It is indicative of texture. Every indexed reflex of intermetallic phases (Fig. 1b and Fig. 2b) was tested by the dark field method (Fig. 1c and Fig. 2c). According to the XRD data the PG-19N-01 coating contains a Ni-based fcc-lattice phase with the parameter *a* = 3,525…3,540 Å (Table 1). In accordance with the

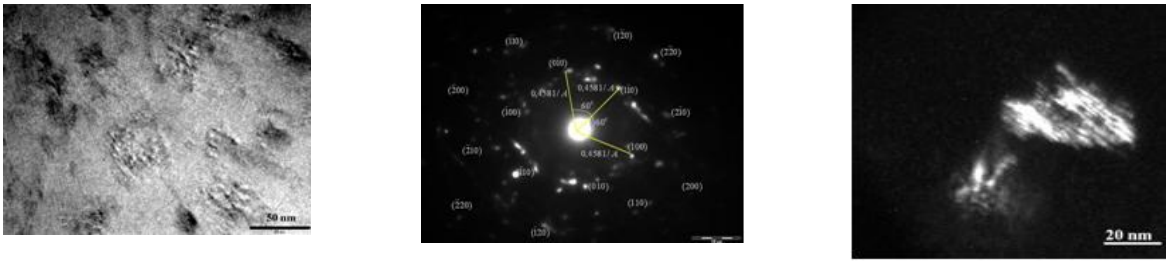
estimated electron-diffraction pattern this parameter makes 3,53 Å. The estimated fcc-lattice parameter of $CrNi_3$ (Fig. 1b) in the coating made a= 3,58 Å (the interplane distance is 2,05 Å), which is very close to the XRD data (Table 1). The volume ratio of $CrNi_3$ in the coating PG-19N-01, as defined by TEM images, makes about 20%.



(a) (b) (c)

Fig. 1. TEM - images of PG-19N-01 coating: the $CrNi_3$ particle (bright field) (a); the electron diffraction pattern of a $CrNi_3$ particle, the zone axis is $[0\bar{1}1]$ (b); the $CrNi_3$ particle (dark field) shot in point reflex (111) (c)

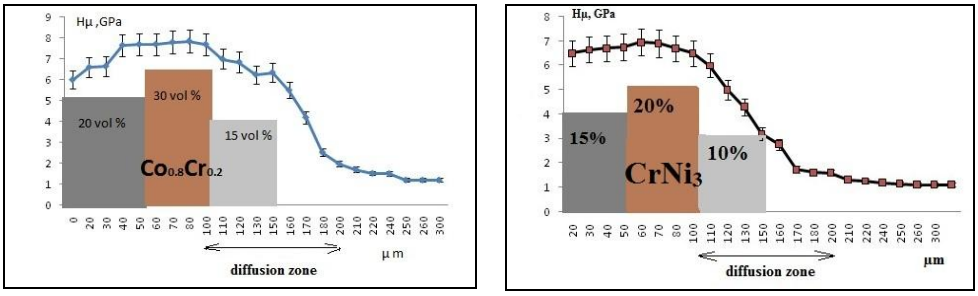
In accordance with the estimated electron-diffraction pattern (Fig. 2b) the parameters of $Co_{0.8}Cr_{0.2}$ - phase are: a =$в$ = 2,5 Å and c = 4,0 Å. The volume ratio of $Co_{0.8}Cr_{0.2}$ in the coating AN-35, as defined by TEM images, makes about 30 %. These nanosize intermetallic phases ($CrNi_3$ and $Co_{0.8}Cr_{0.2}$) may be called strengthening as the highest microhardness of a coating corresponds to those places where the volume concentration of these phases is the highest (Fig.3). In the contact with the substrate layer the coatings are deformed.



(a) (b) (c)

Fig. 2 TEM - images of AN-35 coating: the $Co_{0.8}Cr_{0.2}$ particle (bright field) (a); the electron diffraction pattern of a $Co_{0.8}Cr_{0.2}$ particle, the zone axis is [001] (b); the $Co_{0.8}Cr_{0.2}$ particle (dark field) shot in point reflex $(0\bar{1}0)$ (c)

The analysis of dependence of microhardness at some distance from the surface shows that the coating microhardness is considerably higher than that of the steel substrate (fig.3). The steel microhardness on the average is 1,4 GPa. The maximum microhardness of AN-35 is 8,0 GPa and of PG-19N-01 is 7,0 GPa. It is observed in the coatings at the depth of 60 μm from the surface. The width of the transitional from a coating to a substrate layer with the increased microhardness is estimated as 100 microns, the analysis of its structurally-phase composition (Tab. 1) allows to name it a diffusion zone.



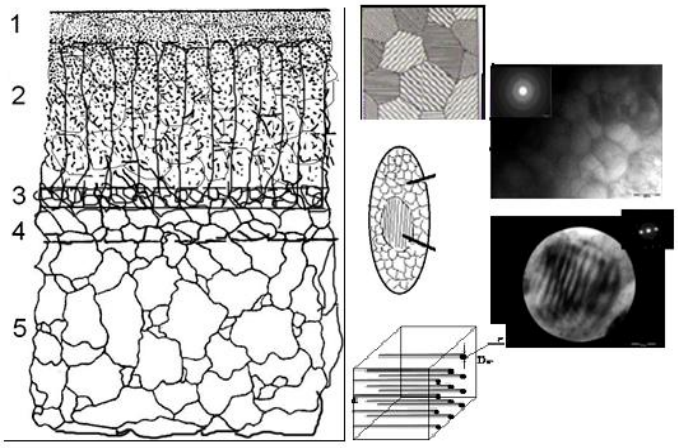
(a) (b)

Fig. 3 Coating microhardness variation according to the distance from the surface and to the volume concentration of the intermetallic phase: AN-35 (a), PG-19N-01 (b)

4. Discussion

We think that the structure-phase state of a coating is defined by the following factors: the deformational impact of a plasma jet, the temperature profile distribution in the coating material, and the inhomogeneous concentration of the elements in the coating. The formed structures are stable at room temperature, no reduction of strength properties is observed.

We consider that the nanocrystalline patterns found in these coatings are distinctive for all the coatings deposited by the 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 relieve the stresses in a coating there is formed a substructure of nanograins of a 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 characteristics of polycrystal 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 X-Ray diffractograms. Occurrence of a fiber texture with the zone axis perpendicular to the coating surface is connected with the direction of a heat current at heating by a plasma jet at deposition and the subsequent cooling of the coating. The results of research of the microstructure, phase structure and the microhardness of plasma detonation coatings at depth from the surface helped to develop the scheme of their structure (Fig.4).



(a) (b)

Fig. 4 The scheme of the structure of coatings on Ni - Cr and Co–Cr based powder alloys deposited by plasma-detonation on the steel substrates (a) with explanatory drawings and images: the nanograins and intermetallic phase precipitation with their electron diffraction pattern and the scheme of cubic grain (b), where: 1- amorphous layer with oxides and carbides; 2 - textured layer (solid solution on Co-base or Ni-base with an intermetallic phase) and unmelted particles of the coating powder; 3 - intermediate coating layer (coating-substrate) with deformed and broken particles of coating; 4-intermediate substrate layer with the fine-grained microstructure; 5-substrate with large grains. The strokes (a) show precipitation of lamellas of the intermetallic phase in the cubic grains of the γ-phase (b).

This scheme was used at working out the model of the temperature profile distribution in these coatings under irradiation by a plasma jet or an e-beam. The choice of additional irradiation modes is based on the calculations of irradiation modes leading to heating of the upper thin layer of a coating to the Co or Ni melting point, respectively, and heating the coating across the entire thickness with the aim of its homogenization. The numerical experiment to determine the temperature profiles during irradiation was carried out by mathematical simulation methods.