The Structure-Phase Compositions of Powder Ni-based Coatings after Modification by DC Plasma Jet Irradiation

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Abstract. This paper presents the results of investigation of the structure-phase compositions of Ni-based coatings deposited by plasma jet on steel substrates after modification by direct current (DC) plasma jet irradiation. Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD) are used in the current study. The phase structures and morphology of precipitation of strengthening phases from solid solution are defined. The irradiation of the coatings leads to the evolution of the structural-phase state of coatings: an increase in the volume fraction of hardening intermetallic phases, the formation of sufficiently homogeneous fine-grained structure in the irradiated coatings. There is a mutual penetration of the substrate main element Fe into the coating and base coating elements Ni into the substrate as a result of the coating treatment by a pulse DC plasma jet.

1. Introduction
Surface modification by plasma jet has replaced other thermal treatments due to the short and efficient exposure time requirement [1,2]. The main problems of plasma sprayed protective coatings are their porosity, lack of homogeneity on account of poor agglomeration of powder particles, and high surface roughness. These result in insufficient corrosion and wear resistance of such coatings. To eliminate these drawbacks the coatings may be re-treated by application of electron beam, laser beam, or plasma jet [1,2]. In the current study, a novel choice of the DC plasma re-treatment modes has been used. This includes optimum choice of the power density of a plasma source on the coating surface and also an efficient speed of the source movement. A specific temperature field in the system of coating-substrate has been created. This is to provide the precipitation of hardening phases in the coating during the added treatment. Through this procedure the surface of the coating is melted, whereas the area of the interface of the coating with substrate is exposed to temperature of about 400°C for several minutes. In our previous study the temperature distribution in two-layer absorbers are calculated using both permanent linear case model and variable thermal parameters non-linear model [3,4]. On the basis of the model calculations we recommended the optimum irradiation modes. These modes ensure
temperature profiles which results in accelerated of diffusion process. Also they assist with precipitation of hardening intermetallic phases in protective powder coatings. The aims of the current research is to establish the regularities of the evolution of structural and phase composition and properties of Ni based powder coatings following additional treatment by DC pulse plasma jet. The behavior of these materials under irradiation will subsequently be experimentally verified.

2. Materials and Methods
Protective coatings of 100 -200 µm thickness were deposited on steel substrate. These were further processed by the “Impulse-6” plasma detonation unit. The substrate material was 10³ µm thick steel 3 (Fe – base, C - 0.25 %, Mn – 0.8 %, Si – 0.37 %, P < 0.045 %). PG-19N-01 Ni- based powders alloy with additives of Cr (8…14%), B (2.3%), Si (1.2…3.2%), Fe (5%), C (0.5%) were used for coating purpose. The powder fractions varied in size from 50 to 80 µm. The powder coatings were deposited in air. The modes of deposition of these coatings were described in detail in our previous papers [3,4]. The irradiation of the samples by DC plasma jet was carried out at power density of 1.9·10⁹ W/m² and travel speed of 0.006 m/s.

Experimental methods of analysis included Transmission Electron Microscopy (TEM) (JEM-2100 (“JEOL”, Japan) and TECNAI, (Phillips)), X-ray diffraction (XRD) (X’Pert PRO (“PANalytical”, the Netherlands)), Scanning Electron Microscopy (SEM) (JSM-6390LV (“JEOL”, Japan) with EDS (“Oxford Instruments”, Great Britain)) and Atomic Force Microscopy (AFM) (NT-206 (Belorussia)). M-691 Precision Ion Polishing System (“Gatan”, USA) was used to prepare TEM foils by the Ar ion sputter etching method. Microhardness test of the samples was performed using a digital microhardness tester (LM-700 (LECO, Russia)).

3. Results and Discussion
The untreated coatings showed a high surface roughness with Ra of approximately 70 nm (Fig.1a). They also displayed a sharp, structurally heterogeneous boundary with the substrate (Fig. 2a). According to the XRD data the PG-19N-01 coating before modification contains a Ni-based fcc-lattice phase with the parameter of a=3.525…3.540 Å. This is in accordance with the estimated electron-diffraction pattern of 3.53 Å.

Figure 1. AFM-images of the surface of PG-19N-01 coatings before (a) and after (b) irradiation by DC Plasma Jet

TEM results indicate that the base through-thickness layer of coatings is a mixture of crystallographically differently oriented nanograins of the fcc-matrix with the size of 1-2 nanometers, and lamellas of intermetallic phases up to 50 nanometers long (Fig. 3a). The indexed reflex of intermetallic phases (Fig. 3b) was tested by the dark field method (Fig. 3c).
Figure 2. SEM - image of the non-modified sample cross section (the coating at the top of the image) with a line of spectrum (a) and the corresponding distribution of elements (b)

Figure 3. TEM - images of PG-19N-01 coating: the CrNi$_3$ particle (bright field) (a); the electron diffraction pattern of a CrNi$_3$ particle with the zone axis [111] (b); the CrNi$_3$ particle (dark field) shot in point reflex (220) (c)

The type of crystal lattice and the interplane distances matches the experimentally observed ones for CrNi$_3$. According to the database of “2011 International Centre for Data Diffraction” (the PDF Card No 01-071-7595) for the CrNi$_3$ phase (Chromium Nickel, Cubic, Fm-3m, 225), its crystal lattice parameter is 3.552 Å. In the current coating, the estimated fcc-lattice parameter of CrNi$_3$ is $a = 3.6$ Å (fig 3b). This is very close to the data obtained by XRD which is ($a = 3.555$ Å). The TEM images indicate that the volume ratio of CrNi$_3$ in the coating PG-19N-01 before irradiation is about 20%. These nanosize intermetallic phases are highly strengthening. It has been shown that the greatest microhardness of the coating occurs at locations of high volume concentration of these phases.$^{[3,4]}$. The maximum microhardness of the coating PG-19N-01 before modification is 6.0 GPa. The microhardness at some distance from the surface shows that the coating has considerably higher hardness compared to the steel substrate. The average microhardness of the steel is about 1.4 GPa. The microstructure of the coating in this case could be compared to composite material with nanosized reinforcement.

After modification by DC plasma jet the roughness decreases in average by 3.5 times (from Ra = 70 nm to Ra = 20 nm). This is due to the melting of the surfaces of coatings through additional treatment (Fig 1 b). TEM and XRD examinations reveal that the volume concentration of the CrNi$_3$ phase in the coatings is increased to about 25%. This is about 5% higher than the untreated coatings. Correspondingly, an increase of about 1 GPa in microhardness was observed. At the same time, additional processing does not affect the particle size, particle morphology, and the crystal lattice parameter (Fig.4 c, d). The matrix structure of the coating is also unaffected by irradiation (Fig.4 a, b). However, the microstructure of the coatings after irradiation has changed to a fine-grained homogeneous microstructure (Fig.5 a). Also SEM with EDS indicates more than 100 microns penetration of Ni from the irradiated Ni-based coatings into the substrate (Fig. 5b). Also penetration
of Fe from the substrate into the irradiated coatings could be clearly observed (Fig 5c). Both observations suggest the development of radiation-enhanced diffusion in the absorbing materials during irradiation.

![Figure 4](image_url)

**Figure 4.** TEM images of the Ni-based irradiated coatings (a), corresponding diffraction pattern (b) the CrNi$_3$ particle (c) and its diffraction pattern (d)

![Figure 5](image_url)

**Figure 5.** SEM image of modified Ni-based coating (the left part of the image) on steel substrate (the right part of the image) (a), corresponding map of Ni distribution (b) and the map of Fe distribution (c)

4. Conclusions

The irradiation of the coatings by a DC pulse plasma jet according to the recommendations of model calculations modes leads to the evolution of the structural-phase state of coatings: This results in an average of 5% increase of the volume fraction of hardening intermetallic phases. It also leads to the formation of a sufficiently homogeneous fine-grained structure in the irradiated coatings. The strengthening particles of intermetallic phases are precipitated in the form of nanosized lamellae. SEM observations show redistribution of the elements of the coating into the substrate. This indicates the acceleration of diffusion processes during irradiation.

5. Acknowledgment

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6. References

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