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Developing a New Resource and Energy Saving Technology of Precision Application of Powder Coating Multifunctional Systems

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This paper presents new results of microhardness, corrosion resistance tests, and the structure-phase compositions study of the powder Ni-based coatings deposited by microplasma spraying onto the steel substrate. It is shown that the predicted specific structure with nanosized lamellas of intermetallic phases has been obtained due to the well-founded selection of energy saved modes of microplasma processing. The precision application of powder coating for protecting the surfaces of industrial products is achieved by using a material micro plasma processing unit which includes an industrial robot. The study showed that microhardness and corrosion resistance of the coated surface are significantly increased.

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PACS/topics: microplasma spraying (MPS), coatings, structure-phase compositions, microhardness

1. Introduction

Nowadays, various types of thermal spray coating processes for surface protection against temperature extremes, corrosion, and wear are widely used all over the world [1, 2]. Amongst different existing plasma spraying processes, the microplasma spraying (MPS) is particularly characterized by low plasma power, low plasma gas flow rate, small spray spot (1–8 mm). It also allows forming a laminar jet with the length of 100–150 mm, which heats the refractory material in a stream of Ar plasma. This provides low heat input into the substrate [3, 4]. These properties are very helpful for high accuracy deposition of coatings on small parts. However, there are still a number of challenges remaining in the area of microplasma coating. One of the major challenges is the formation of coatings with specified structure and properties. Most thermal spray powder coatings require additional processing such as heat treatment by irradiation after deposition of the coating [2]. Typically, additional processing of the powder plasma coatings by irradiation is used to melt the coating in order to reduce its roughness and increase the homogeneity of its structure, as shown in [1, 5, 6].

The authors of this work have had successful experience of plasma jet treatment of powder coatings. Their previous works in deposition by plasma detonation techniques on steel substrates have been reported in detail [7–9]. The selection of plasma irradiation processing modes (namely, the power density of the plasma jet on the coating surface, and the velocity of the plasma source) is based on the analysis the authors have done in their past works [10, 11]. They have shown when Ni-based alloys reach relatively low temperatures of the order of 300–400 °C due to irradiation, there can be radiation-enhanced diffusion. Additionally intermittent expulsion of chromium–nickel intermetallic compounds may take place with a short exposure time at a given temperature (several minutes).

Therefore, it is possible to ensure hardening of the surface due to the processing of coating with a moving radiation source at relatively low power density of the source. This hardening method is highly desirable. It provides the opportunity of using the same source for the coating deposition, and at the same time to reduce power consumption, needed for additional treatment. The results of additional processing of plasma-detonation coatings by the direct current (DC) plasma jet are discussed in our works [7, 9].

The purpose of the current study is to examine the effect of additional processing alongside MPS. Also it is our objective to form nickel based coatings with desired lamellas structure phase state. It is expected that this structure will improve the microhardness and corrosion resistance of the coated surface.

2. Materials and equipments

The 100 μm thick coatings from Ni-based powders were deposited on Steel 3 substrate by MPS with the help of "MPN-004" microplasma deposition unit (produced by E.O. Paton Institute of Electric Welding, Ukraine) mounted on the Kawasaki industrial robot arm (Kawasaki Robotics, Japan). The chemical compositions of Ni-based powders and steel substrate are given in Table I. The average diameter of powders particles is 40–45 μm. (The substrate surface has been cleaned by grit blasting before microplasma spraying of the powders.)

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TABLE I

The chemical composition of investigated materials.

Name Standard	Chemical composition [wt%]									
	Cr	B	Si	Fe	C	Al	Ni	Mn	P	S
PG-10N-01 powder GOST 21448-75	8.0–14.0	2.3	1.2–3.2	5.0	0.5	-	base	-	-	-
PT-19N-01 powder GOST 9722-97	3.9	1.7–2.5	1.2–3.2	1.2–3.2	0.3–0.6	0.8–1.3	base	-	-	-
Steel 3 GOST380-2005	-	-	0.17-0.37	base	0.25-0.35	-	-	0.5-0.8		

The modes of microplasma deposition were as follows: a laminar DC plasma jet; the Ar plasma forming and protective gas; 1–8 mm the diameter of the spray spot; 2 W the power of plasma source; 2 kg/h the powder flow rate; 0.008 m/s the travel speed of the plasma jet. The modes of additional irradiation were determined using the methodology described in our previous work [12]. This is based on the simulating temperature fields in the "coating-substrate" system when heated by a moving source of radiation. The numerical methods have been implemented for modeling of temperature fields raised by the radiation treatment of coatings. The software has been developed in Python [13]. The additional treatment of the samples by a plasma jet was carried out at power density of 2.0×10^9 W/m^2 with 0.006 m/s of the plasma jet travel speed. The main purpose of these microplasma deposited coatings is protection of surfaces of parts operating under conditions of increased friction, temperatures and aggressive environments: cylinder liners, shafts, etc.

Experimental methods of analysis include transmission electron microscopy (TEM) by JEM-2100 (JEOL, Japan) with energy dispersive X-ray spectrometry (EDX) INCA Energy TEM 350 (Oxford Instruments, Great Britain), scanning election microscopy (SEM) by JSM-6390LV (JEOL, Japan), X-ray diffraction (XRD) by X'Pert PRO (PANalytical, the Netherlands). 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 with Durascan 10/20 digital microhardness meter (EMCO-TEST, Austria). The tests were carried out according to standard methods for the cross-section of a coated specimen. An indentation load of 1 N was applied with an average pitch of 25 μm in the coating and 40 μm in the substrate. Five measurements were performed and the statistical average was determined. Corrosion was tested using the potentiostatic method of recording polarization curves by PI-50.1.1 potentiostat (Ltd. ELINS, Russia) to measure the sea-water corrosion rate. The investigated samples have been used as a positive electrode — the anode. The NaCl 0.5H (3%) water solution simulated the sea water.

3. Results and discussion

XRD results clarify that the phase compositions of the initial powders and the microplasma coatings are different (Table II). The new $CrNi_3$ intermetallic phase appears in the coatings whereas the initial powders do not contain this phase. The volume fraction of Ni-based solid solution in the coatings is on average 5% higher than in the initial powders. At the same time, the phases of chromium oxide, nickel oxide, and $Cr_3Ni_5Si_2$ completely disappear in the coatings. This is the result of combined MPS of powders and additional treatment of coatings by plasma jet (Table II).

As TEM analysis demonstrates, the coating is mainly composed of crystallographically disoriented nanograins of Ni-based solid solution with the fcc type of crystal lattice (Fig. 1a), which precipitates nanoscale lamellae of the $CrNi_3$ intermetallic phase with the fcc structure (Fig. 1b and Fig. 2). The EDX spectrum shows the presence of elements such as Ni, Cr, Fe (Fig. 2). This is in a good agreement with the XRD results.

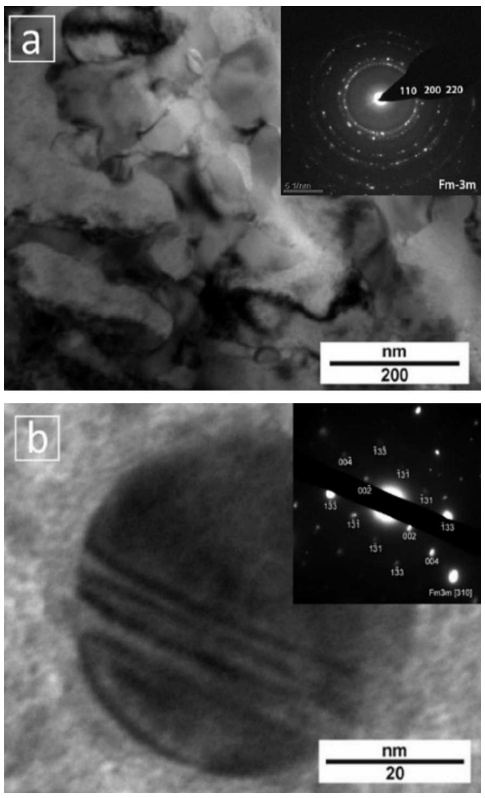

Fig. 1. TEM images of the PT-19N-01 coating with the corresponding microdiffraction patterns: (a) the nanograin polycrystalline structure, (b) the lamellas of intermetallic phases.

TABLE II

Phase composition of investigated materials.

Volume concentration [%]	Chemical formula	Crystal system	Space group	Space group number	Parameters [Å]
PG-10N-01 base powder					
75%	solid solution on Ni-base (γ-phase)	cubic	Fm-$3m$	(225)	$a = 3.52$
5%	Ni_3Fe	cubic	Pm-$3m$	(221)	$a = 3.55$
10%	$CrO_{0.87}$	cubic	Fm-$3m$	(225)	$a = 4.04$
10%	$Cr_3Ni_5Si_2$	cubic	P213	(198)	$a = 6.12$
PG-10N-01 coating					
80%	solid solution on Ni-base (γ-phase)	cubic	Fm-$3m$	(225)	$a = 3.52$
5%	Ni_3Fe	cubic	Pm-$3m$	(221)	$a = 3.55$
15%	$CrNi_3$	cubic	Fm-$3m$	(225)	$a = 3.55$
PT-19N-01 base powder					
80%	solid solution on Ni-base (γ-phase)	cubic	Fm-$3m$	(225)	$a = 3.52$
7%	FeNi	tetragonal	$P4/mmm$	(123)	$a = 3.53$, $b = 3.53$, $c = 3.58$
10 %	NiO	cubic	Fm-$3m$	(225)	$a = 4.20$
3%	Cr_3O	cubic	Pm-$3n$	(223)	$a = 4.54$
PT-19N-01 coating					
85%	solid solution on Ni-base (γ-phase)	cubic	Fm-$3m$	(225)	$a = 3.52$
5%	FeNi	tetragonal	$P4/mmm$	(123)	$a = 3.53$, $b = 3.53$, $c = 3.58$
10%	$CrNi_3$	cubic	Fm-$3m$	(225)	$a = 3.55$

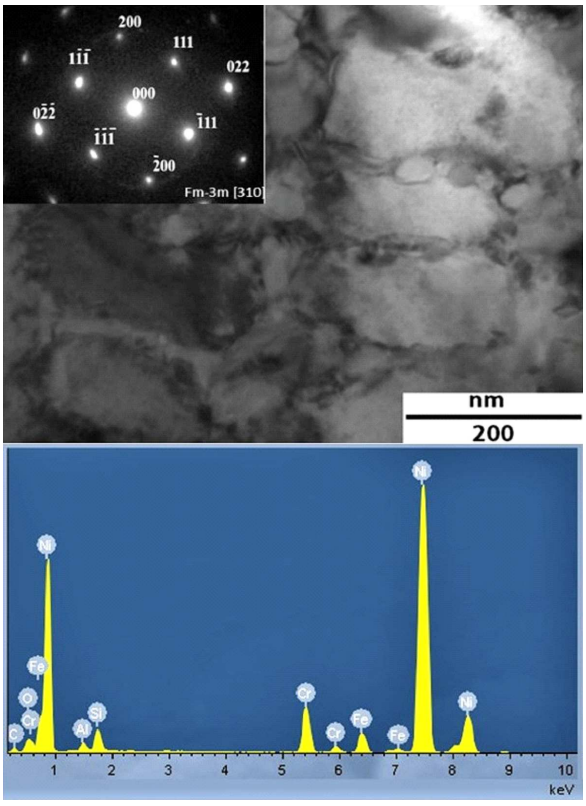

Fig. 2. TEM and STEM images (with corresponding diffraction pattern and EDX-spectrum) of lamellas of $CrNi_3$-phase in the PG-10N-01coating.

The average microhardness of the PG-10N-01 coating is 7.3±0.5 GPa (Fig. 3a), the average microhardness of the PT-19N-01 coating is 3.5±0.5 GPa (Fig. 3b) and that of the substrate is 1.4 ±0.1 GPa (Fig. 3a and b). Thus, on average the microhardness of the PG-10N-01 coating is 4 times higher than the substrate, and that of the PT-19N-01 coating is only twice higher. These results are confirmed by the higher volume concentration of the strengthening phase in PG-10N-01 coating. According to our findings the volume concentration of the strengthening $CrNi_3$-phase in the PG-10N-01 coating is 5% higher than its volume concentration in the PT-19N-01 coating (Table II).

The results of corrosion resistance test in sea water confirm the considerable improvement in corrosion resistance for the coated samples compared to unprotected substrate (Table III). We believe that the high corrosion resistance of coated samples is due to improved homogeneity of the coating and its adhesion to the substrate. The additional microplasma processing of the coatings has resulted in enhancing the quality of the coatings.

The high corrosion resistance of the coated samples has been caused by improved homogeneity of the coating. Moreover the adhesion of the coating to the substrate has been enhanced due to the additional processing of the microplasma coating.

These results are of significance. They indicate that the coating consists of the ductile base with fcc lattice type which is reinforced by lamellas of hard intermetallic phase. These are shown in Figs. 1 and 2. Such structures are very promising in developing new advanced metal materials with increased fracture toughness. Full description of mechanism has been reported by the authors in their past research [14, 15]. Secondly, we proposed an alternative approach to the choice of modes of additional processing compared to the past researches [5, 6]. In the previous studies either laser [5] or pulse plasma jet [6]

has been used to reduce the roughness and increase the structural homogeneity of the coatings. This approach suggests that by using low power densities of a plasma source, it is possible to harden the coating. This hardening effect is due to the phase transformations which take place at lower temperatures. However, our proposed approach is not general. It requires a thorough analysis of the coating material and the potential for desirable phase transformations.

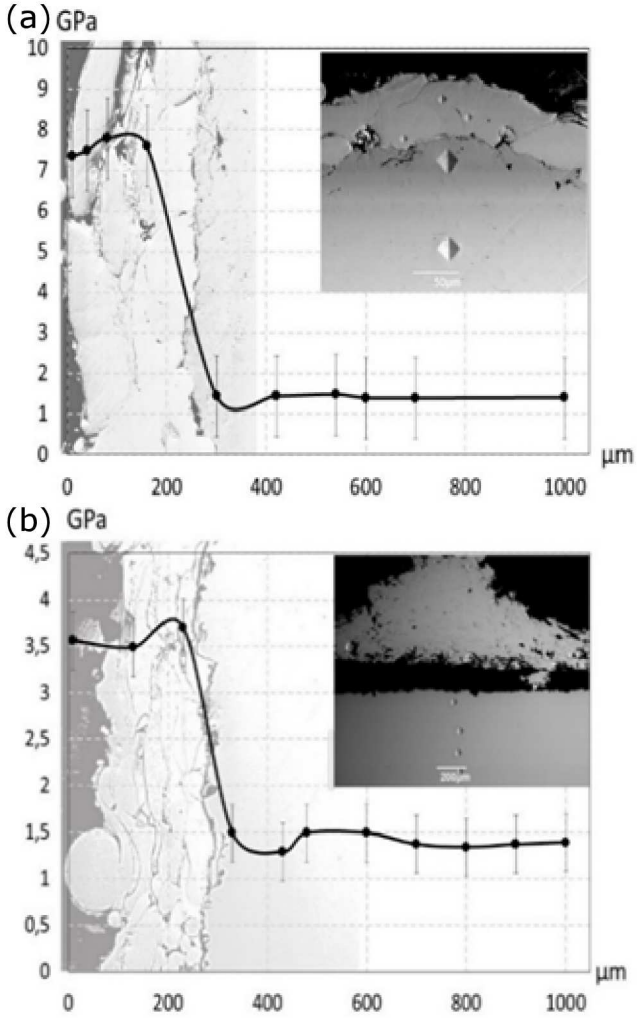

Fig. 3. The curves of distribution of microhardness in the plasma sprayed coatings and substrates in depth from the surface and SEM-imagines of the cross-sections of the substrate with the (a) PG-10N-01 and (b) PT-19N-01 coatings.

TABLE III

The results of corrosion resistance test in seawater.

Material	Corrosion	
	potential [V]	rate [mm/y]
Steel 3 (substrate)	–0.28	3.9
PG-10H-01 coating	-0.30	2.5
PT-19N-01 coating	-0.35	2.7

4. Conclusion

The laboratory samples with protective powder coatings deposited by the microplasma according to the recommended modes onto steel substrates have been obtained. The TEM and XRD results indicate that the coatings have the predicted structure-phase composition, namely the nanograin Ni-based solid solution with precipitations of strengthening intermetallic lamellas of $CrNi_3$-phase. It is established that on average the microhardness of the PG-10N-01 coating is 5 times higher than that of the substrate, and the microhardness of the PT-19N-01 coating is 2.5 times higher than that of the substrate. The XRD results have established that the volume concentration of the $CrNi_3$-phase which enhances the microhardness in the PG-10N-01 coating is 15% whereas the volume concentration of this intermetallic phase in the PT-19N-01 coating is 10%. The corrosion tests showed that an average corrosion rate of the PG-10N-01 coating in sea water was 1.56 times lower and that rate of the PT-19N-01 coating was 1.44 times lower than that of the substrate. Therefore, the current research provides evidence for effectiveness of surface modification technology by microplasma exposure. The technology is energy efficient. This is due to the fact that the structural phase transformations and heating affect only a small surface layer of modified material. Therefore no bulk heating is required. The estimation of exposure modes assists with avoiding energy waste. The technology involves the replacement of long-term heat treatment by short-term high-energy impact to achieve the desired structural phase state. The technology is resource-saving as the modifications only takes place on the surface. Therefore volumetric material alloying is not required.

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