CERMET COATINGS OF CHROMIUM CARBIDE–NICHROME SYSTEM PRODUCED BY SUPERSONIC PLASMA GAS AIR SPRAYING

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It is a well-known fact that application of supersonic methods of thermal spray deposition results in significant increase of service properties of parts. However, up to moment no trails were made on producing of carbide or cermet coatings with the help of supersonic methods of plasma spraying. Present work is dedicated to production of cermet coatings from chromium carbide–nichrome compositions using a method of supersonic plasma gas air spraying (SPGAS). SPGAS technology has series of advantages in comparison with well-known technology of HVOF spraying. First of all, it concerns efficiency, economy and characteristics (temperature, speed) of gas jet. Structure and phase composition of produced coatings were investigated. It is shown that spraying using supersonic gas jets promotes for increase of content of Cr_7C_3 carbide and reduction of NiCr in the coatings as a result of oxidation and formation of oxides. Coating from composite powder differs by higher level of density and homogeneity, has layered fine-laminated structure with inclusions of fine carbides, contains lower amount of oxide phase, but larger quantity of chromium carbide Cr_3C_2 in comparison with coating from mechanical mixture $Cr_3C_2 + NiCr$. These coatings can be recommended for application as wear-resistant at increased temperatures. 6 Ref., 6 Tables, 7 Figures.

Keywords: supersonic plasma gas air spraying, cermet coatings, chromium carbide, powders, microstructure, phase composition, microhardness

Plasma coatings based on chromium carbides are characterized by combination of such properties as resistance to wear by abrasive particles and hard surfaces at high temperatures (540–840 °C), high resistance under conditions of fretting-corrosion and aggressive media (for example, in liquid sodium at 200–625 °C), heat resistance at temperatures to 980 °C, radiation resistance [1].

 Cr_3C_2 mechanical mixtures (rarely its mixture with Cr_7C_3 or $Cr_{23}C_6$ carbide) with such metals as Ni, Co, Ni+Cr, NiCr at different combination of component content (amount of metallic binder can be from 6–8 to 45 wt.%) are used for spray deposition of cermet coatings with chromium carbide. Main methods, which are used for spray deposition of coatings with chromium carbides, are plasma, detonation and HVOF spraying [1–3].

It is a well known fact that application of supersonic methods of thermal coating deposition results in significant increase of their service properties. However, up to moment no trails were made on producing of carbide or cermet coatings with the help of supersonic methods of plasma spraying.

Present work is dedicated to production of cermet coatings from chromium carbide-nichrome compositions using a method of supersonic plasma gas air spraying (SPGAS), examination of structure and phase composition of produced coatings.

SPGAS technology has series of advantages in comparison with well-known technology of

Table	1.	Comparative c	haracteristics	of	HVOF	and	SPGAS	technologies	
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Technology		Gas consum	ption, m ³ /h		Powder consumption, kg/h		Coefficient	Jet characteristics	
	Propane	O_2	N_2	Air	Metallic alloys	Oxides	of material use, %	Speed, m/s	Temperature, °C
HVOF	3-4	15-21	1	_	Up to 23	_	40-75	1400-2700	2800
SPGAS	0.3-40	-	-	10-40	Up to 50	Up to 20	60-80	3000	3200-6300

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Table 2.	Composition	of powders
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Powder grade	Content of elements, wt.%									
	Cr	Ni	С	Mn	Fe	Si	Rest			
PP-53	71.10	17.10	9.49	0.036	1.75	0.065	0.41			
PP-53B	Base	20	9.40	Not indicated						

Table 3. Composition of particles of initial powders based on XSMA results

Powder particle	Content of elements, wt.%							
i owder particle	Cr	Ni	С	O^*	Additives			
Carbide (1 in Figure 1, a , c)	70.10-79.70	1.50-5.60	18.9-21	_	Fe - 0.73			
Metallic (2 in Figure 1, a, c)	52-71.10	24.23-24.39	-	_	W - 0.71; Fe - 1.45			
Cermet (3 in Figure 1, b , d)	30.77-68.10	10.55-49.81	9.17-13.60	6.2-7.7	Mg - 0.48-1.24; Al - 0.6; Fe - 0.55; W - 1.13-1.45			
Found in separate particles.								

HVOF spraying. First of all, it concerns efficiency, economy (cost of gases) and characteristics of gas jet (temperature, speed) (Table 1).

Coating spray deposition in present work was carried out on «Kiev-S» installation, developed by Gas Institute and PWI of the NAS of Ukraine. Air mixture with addition of propane (around 4 vol.%) was used as plasma gas at following technological parameters: I = 260 A, U = 360 V, 180 mm distance, air pressure made 4 atm and consumption 20 $m^3/h.$

Powders of two types, namely PP-53 Cr_3C_225 (Ni20Cr) and PP-53B Cr_3C_2 (Ni20Cr) (Table 2) from «Bay State Surface Technologies, Inc.» (USA) were used as materials for coating spray deposition.

Powders of particle size $15-44 \ \mu m$ were applied for coating spray deposition.



Figure 1. Appearance (a, c) and microstructure (×800) of particles (b, d) of PP-53 (a, c) and PP-53B (b, d) powders: 1 - carbide; 2 - metallic; 3 - cermet particles





Figure 2. X-ray patterns of particles of Cr_3C_2 + NiCr powder: a - PP-53; b - PP-53B

Examinations of initial powders showed that they differ by appearance, microstructure, microhardness and phase composition. Thus, PP-53 powder consists of faceted particles (Figure 1 *a*, *c*) and being a mechanical mixture of carbide and metallic particles, which vary vastly on microhardness (13300 \pm 1500 and 1980 \pm 600 MPa, respectively).

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Powder PP-53B consists of spherical particles (Figure 1, b, d), and each particle, taking into account structure and microhardness, includes metallic as well as carbide phases (microhardness of particles is varied in 5000–10500 MPa range).

Examination of composition of powder particles using X-ray spectral microanalysis (XSMA) (Table 3) showed that nickel or carbon are virtually absent in PP-53 powder. According to



Figure 3. Microstructure of coatings from PP-53 (a, c) and PP-53B (b, d) powder (a, b – Neophot microscope, ×400; c, d – CamScan electron-probe analysis)



Powder grade	Microhard	ness, MPa	Phase composition wt %			
i owder grade	Average Most probable		Thase composition, we.76			
PP-53	8420 ± 1550	9000; 11500	$Cr_7C_3 - 26; Cr_3C_2 - 11; NiCr - 48; NiCr_2O_4 - 15$			
PP-53B	9960 ± 1400	10500	$Cr_7C_3 - 21; Cr_3C_2 - 15; NiCr - 53; NiCrO_3 - 11$			

Table 4. Characteristic of sprayed coatings



Figure 4. Microhardness variation curves of plasma coatings from PP-53 (a) and PP-53B (b) powders

carbon amount in the carbide particles (19-21 wt.%), they are close to Cr_3C_2 (19.34 vol. %) carbide on composition. Moreover, Cr_7C_3 carbide (9.01 wt.% C) (Figure 2, *a*) was found in powder using X-ray phase structural analysis (XPSA) method.

Particles of PP-53B powder contain all three elements (Cr, Ni and C) as well as additives of these elements such as small amount of Mg, Al,



Figure 5. X-ray patterns of sprayed coatings: a - PP-53; b - PP-53B powder

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W, Fe and Ca (see Table 3). Some particles have areas enriched by oxygen at the level of 6–7 wt.%.

At the same time, results of XPSA of PP-53B particles indicate that they do not differ from PP-53 powder (Figure 2, b) on qualitative content, and since each particle contains metallic as well as carbide phases, the powder can be considered as composite one, consisting from cermet particles.

Metallographic examination of sprayed coatings determined no fundamental differences in their structure depending on powder type (Figure 3). The only thing that can be noted is higher level of homogeneity of coatings from composite powder (PP-53B) in comparison with coatings from mechanical mixture (PP-53). Besides, some difference is observed in values of average microhardness of coatings and nature of microhardness variation curves (Table 4, Figure 4).

Thus, two most probable values of microhardness can be marked on microhardness variation curve of the coating, produced from PP-53 powder (mechanical mixture Cr_3C_2 and NiCr). This can be an evidence of presence in the structure, as in initial powder, of zones with harder carbide phases (HV = 11500 MPa) and metal enriched zones (HV = 9000 MPa). Microhardness variation curve of the coating from composite powder PP-53B has only one probable value of microhardness 10500 MPa, i.e. average between two indicated above.

XPSA of phase composition of sprayed coatings showed (Figure 5) that they contain chro-



Spectrum to be analyzed		Conte	ent of elements,	Supposed phase		
	Cr	Ni	С	0	Fe	Supposed phase
1 (a)	13.33	81.57	_	_	4.30	NiCr
2 (<i>a</i>)	81.82	1.45	16.72	-	-	Cr_7C_3
3 (<i>a</i>)	89.40	-	10.60	-	_	Cr_3C_2
4 (a)	56.41	18.50	4.87	20.22	_	Oxide
1 (b)	61.13	25.89	11.66	_	_	Zones of cermets (metal + carbide)
2 (b)	13.99	75.11	8.71	-	0.93	
3 (b)	26.50	61.97	8.89	_	0.79	
4 (b)	28.93	59.57	-	9.44	0.49	Oxide

Table 5. Content of elements, determined by XSMA method, in structural zones of coatings from PP-53 and PP-53B powders (acc. to Figure 6, *a* and *b*, respectively)



Figure 6. Zones of coatings from PP-53 (a) and PP-53B (b) powders examined by XSMA method

mium carbide Cr_3C_2 , Cr_7C_3 , nichrome (Ni₈₀Cr₂₀) and oxides NiCr₂O₄ (for coating from mechanical mixture) or NiCrO₃ (for coating from composite powder), the latter were not found in initial powders. Presence of indicated phased in the sprayed coatings conforms the results of local XSMA (Table 5) of separate structural elements of the sprayed coatings (Figure 6).

It can be noted when comparing intensity of X-ray reflections of separate phases in initial

Table 6. Results of XSMA of sprayed coating from PP-53B pow-der (acc. to Figure 7)

Spectrum	Composition, wt.%								
analyzed	С	Ο	Cr	Fe	Ni	W			
2	1.91	_	_	97.66	_	_			
3	9.10	6.10	52.61	2.62	29.58	_			
4	9.72	5.32	49.80	3.93	30.39	0.83			
5	8.56	6.55	55.21	2.23	26.75	0.68			
6	8.38	7.15	55.76	2.59	25.38	0.73			

powders (see Figure 2) and in sprayed coatings (see Figure 5) that spraying promotes increase of content of Cr_7C_3 carbide in the coating in comparison with Cr_3C_2 and NiCr content reduces as a result of oxidation and oxide formation. X-ray spectrum microanalysis of the sprayed coat-



Figure 7. Coating from PP-53B powder examined by XSMA method



ings (Figure 7, Table 6) showed that averaged composition (spectrum 3) and content of separate zones on depth (spectra 4–6) are somewhat differ from values of the initial powder (see Table 1). This takes place as a result of appearance of oxide phases in the coatings. At that, amount of oxygen in the case of PP-53B powder coating somewhat increases in direction from base interface to outer surface of the coating, while carbon content is reduced to the contrary.

The similar dependence is observed for PP-53 powder coating. This fact is related with rise of temperature of coating being sprayed in proportion to build-up of coating layer. Comparison of characteristics of sprayed coatings from PP-53 and PP-53B powders allows for noting that coating from composite powder differs by higher level of density and homogeneity, has layered fine-lamellar structure with inclusions of fine carbides, contains lower amount of oxide phase, but lager quantity of chromium carbide Cr_3C_2 in comparison with coating from mechanical mixture $Cr_3C_2 + NiCr$.

It is a well-known fact that refractory properties, stability and hardness of chromium carbides are reduced with decrease of carbon amount in them [4, 5]. Therefore, carbon loss is undesirable in the processes of thermal spraying of cermet chromium carbide based coatings. Review paper [6] dedicated to effect of thermal spraying methods (HVOF, air plasma spraying (APS), vacuum plasma spraying (VPS) and detonation spraying) on properties of the coatings from mechanical mixture Cr_3C_2 + NiCr indicates that hardness, abrasive wear resistance and thermal resistance of the coatings depend on carbon loss in spraying. Thus, for example, VPS coatings have higher hardness and abrasive wear resistance, but lower thermal resistance among others, and APS coatings with argon-helium plasma gas are superior on their properties to the coatings using argon-hydrogen mixture etc.

The results of present work allows for concluding that quality of Cr_3C_2 + NiCr composition coating can also be increased with the help of composite powder of the same compositions instead of mechanical mixture.

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