Electric spark alloying with ZrN-based electrode material

A.V.Paustovsky, V.I.Novikova, N.M.Mordovets

I.Frantsevich Institute for Problems of Materials Science,National Academy of Sciences of Ukraine,3 Krzhizhanovsky St., 03680 Kyiv, Ukraine

Received May 25, 2005

Dependences of erosion characteristics have been studied for ZrN-(Cr, Ni, Al₂O₃) electrode material and relations have been established between the phase composition, structure, and tribotechnical properties of coatings formed by electric spark alloying techniques.

Исследованы зависимости эрозионных характеристик электродного материала ZrN-(Cr, Ni, Al₂O₃) и установлены связи между фазовым составом, структурой и триботехническими свойствами электроискрового покрытия, полученного методом ЭИЛ.

Novel electrode materials are required to provide high anti-friction characteristics of electric-spark coatings. The electric-spark alloving (ESA) is used to enhance the reliability and durability of machine details [1]. The ESA is one of the coating laying techniques and belongs to technological processes of good promise. Short electric pulses at high current strengths are used in that method [2]. The ZrN hetero-phase materials are of good prospects as ESA electrodes in preparation of wear-resistant coatings [3-5]. There are no works dealing with study of transfer mechanisms in the course of ESA with ZrN-based electrodes. The purpose of this work is to study the erosion characteristics of ZrN-(Cr, Ni, Al₂O₃) electrode material prepared using powder metallurgy techniques and to establish the correlation between the structure, phase composition of the coating, its mechanical properties and the material transfer intensity from the anode to the cathode.

The alloying materials were prepared by compacting and sintering in a SShV furnace under argon atmosphere at $1400-1700\,^{\circ}\mathrm{C}$. The spark alloying of steel-45 was carried out in an EFI-46A unit ($I_p=1.25$ A, C=300 $\mu\mathrm{F}$, $U_{x.x}=15$ V). For metallographic

examination a MIM-9 microscope was used, for durometry a PMT-3 device, for X-ray phase analysis (XPA), a DRON-3 and copper emission were applied. The tribotechnical characteristics of the compositions were measured using a M-22M unit [5] that made it possible to determine the friction coefficient (f) and the sample wear intensity (I, μ m/km) in the bush/shaft geometry. The tribotechnical parameters were determined in air without lubricating medium introduction into the contact area, in combination with the CrVMn steel at V=5 m/s, 10 m/s under pressure P=0.5 and 1.0 MPa.

The structure and properties of ESA-made coatings are known to be influenced substantially by the granulometry and phase composition of the electro-erosion products as well as by the electrode erosion [6]. The formation of alloyed layer and its properties are influenced, in first turn, by the phase composition of electrode material. According to XPA data, the ZrN-(Cr, Ni, Al₂O₃) electrodes comprise mainly ZrN, ZrNi, ZrCr₂ and, also Ni and Zr solid solutions [4]. We have studied the effect of the anode phase composition on the main parameters of steel-45 ESA process, namely, the specific erosion of anode Δa , the specific mass gain

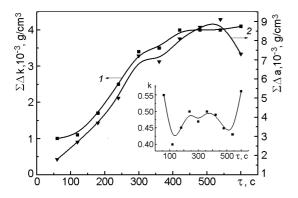


Fig. 1. Kinetic dependences of total cathode mass gain $\Sigma\Delta k$ (1) and total anode erosion $\Sigma\Delta a$ at the specific alloying duration $\tau=600~\text{s/cm}^2$ for steel-45 using ESA material ZrN-(Cr, Ni, Al₂O₃). Inset: transfer coefficient K at $\tau=600~\text{s/cm}^2$.

of cathode, Δk , measured for each minute of treatment per 1 cm² area, the total anode erosion, $\Sigma \Delta a$, and the total cathode mass gain, $\Sigma \Delta k$, measured for the alloying duration $\tau = 10 \text{ min/cm}^2$, and average mass transfer coefficient $K = \Sigma \Delta k / \Sigma \Delta a$ at $\tau =$ 10 min/cm². Fig. 1 shows the kinetic curves of the total anode erosion, $(\Sigma \Delta a)$ and the total cathode mass gain $(\Sigma \Delta k)$ for 10 min. The anode erosion is seen to attain its maximum value at the 9th minute of alloying (Fig. 1, curve 2). This seems to be due to the presence of brittle oxides ZrO2 that favor the anode destruction (Table), thus increasing the solid phase amount in the erosion products. The cathode mass gain increases gradually with the alloying duration (Fig. 1, curve 1). The average mass transfer coefficient of ZrN-(Cr, Ni, Al₂O₃) material at $\tau = 10$ min is 0.5 (inset in Fig. 1).

In the course of steel-45 ESA, the electric erosion products in solid, liquid, and gaseous phases interact within the melt micro-bath at the working surface with the substrate material and the air components (oxygen and nitrogen) [7]. As a result, a surface coating is formed having the phase composition distinct from that of electrodes. Under ultrafast cooling of the liquid and the gaseous phase condensation, metastable compounds may arise [7]. A layer is formed at the surface consisting of ZrN_zO_v , Cr(Ni) solid solution, ZrNi₃, ZrCr₂ intermetallic compounds, ZrO₂, ZrO_{0.35}, Fe₂O₃, Cr₂O₃ oxides (Table), the main phase in the alloyed layer being ZrO₂. In the course of spark coating, secondary phase structures

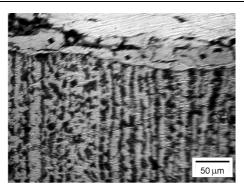


Fig. 2. Microstructure of ESA-made ZrN-(Cr, Ni, Al_2O_3) coating on steel-45. $\times 230$.

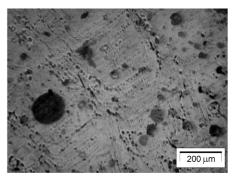


Fig. 3. Morphology of erosion product particles after ESA with ZrN-(Cr, Ni, Al_2O_3) electrode. $\times 75$.

are formed [7], what is confirmed by formation of Fe_2O_3 in the coating. According to XPA data, the erosion products comprise ZrO_2 and Cr as the main phases. In addition, $ZrNi_3$, $ZrCr_2$ intermetallic compounds, $\gamma-Ni_2O_3$, $\alpha-Al_2O_3$, Fe_2O_3 , $\gamma-Cr_2O_3$ oxides are present.

The metallographic studies have shown that the micro-structure of ESA-made ZrN-(Cr, Ni, Al₂O₃) coating is a non-etchable "white" layer of about 35 µm thickness. The layer microhardness attains 1.4 GPa. The alloyed "white" layer includes rather numerous areas of "gray" layer with 1.8 GPa microhardness. That seems to consist of ZrO₂ that is evidenced by XPA data and confirmed by the ZrO₂ microhardness values reported in [9]. The steel-45 microstructure is a ferrite-perlite one having 0.22 GPa microhardness (Fig. 2). Under the hardened layer, there is a 1 to 2 µm thick fine-grain thermal zone (Fig. 2). The morphology of the electric erosion product particles is presented in Fig. 3. According to XPA data, these particles contain mainly intermetallic (ZrNi3, ZrCr2) phase as well as oxide (ZrO₂) one. The erosion products are irregularly shaped particles and globules of

2θ	D_{exp}	Phase composition						
	owp	ZrO ₂	ZrO _{0.35}	Cr	α -Al ₂ O ₃	α -Fe ₂ O ₃	ZrNi ₃	ZrCr ₂
18.25	4.86		4.86 ₁₀					4.14_{20}
30.72	2.91	2.92_{100}						
31.71	2.82		2.82 ₅₀					
32.67	2.74					2.69		2.79_{20}
34.67	2.59		2.60 ₅₀		2.55_{100}			
35.75	2.51	$2.53_{(60)}$				2.51_{75}		2.54_{80}
36.42	2.47		2.48_{100}				$2.45_{(40)}$	
40.7	2.217							2.1780
43.8	2.07			2.05_{100}	2.09_{100}		2.08_{100}	
45.57	1.99						1.99_{30}	
47.33	1.92		1.91_{50}	1.8780				1.94_{20}
51.33	1.78	1.80 ₁₀₀				1.84 ₆₃		1.82_{40}
53.25	1.72				1.74_{50}	1.69 ₆₃		
60.9	1.52	1.53_{100}						1.54_{50}
63.75	1.46	1.46_{30}	1.475_{50}	1.441_{50}	1.45_{50}	1.48 ₅₀	1.41	
70.5	1.336		1.359_{50}		1.375_{50}		1.33_{50}	
72.67	1.30			1.327_{30}				
75.17	1.264	1.267_{30}		1.274_{40}			1.22	
83	1.163	1.164_{30}		1.145_{35}				
96.42	1.034	1.035_{30}		1.022_{40}				
104.83	0.973	0.976_{30}						

20 to $80~\mu m$ size (Fig. 2), the globules amounting about 40~%. Dendrites are observed within the globules, thus evidencing the presence of a metallic phase therein.

The tribotechnical tests were carried out at the sliding speed of 5 and 10 m/s and load P = 0.5 and 1 MPa. The wear intensity I for the coating under study is about $5 \mu m/km$ at the sliding speed of 5 m/s. As the sliding speed is increased to 10 m/s, the wear intensity is 2.6 times higher $(I = 13 \mu m/km \text{ at } P = 0.5 \text{ MPa})$. The further load increase up to 1 MPa at sliding speed of 10 m/s results in a sharp increased wear intensity $(I = 23 \mu m/km, Fig. 4a)$. That is, as the sliding speed increases from 5 to 10 m/s, the wear intensity of ESAmade $ZrN-(Cr, Ni, Al_2O_3)$ coating rises in about 4.7 times. As the load increases from 0.5 MPa to 1 MPa, the wear intensity rises by a factor 1.8 at sliding speed of 10 m/s. The friction coefficient for ESA-made ZrN-(Cr, Ni, Al₂O₃) coating is essentially independent of sliding speed and load and amounts about 0.32 (Fig. 4b). The presence of ZrO_2 , Al_2O_3 oxides as well as of $ZrCr_2$ intermetallic in the alloyed layer has been shown to effect favorably the coating wear resistance. The formation of $ZrO_{0.35}$ oxide having layered structure in the alloyed layer increases the coating wear resistance.

Thus, the electric spark alloying process of steel-45 using ZrN-(Cr, Ni, Al₂O₃) electrode prepared by powder metallurgy is characterized by stable values of the cathode mass gain, anode erosion and by the transfer coefficient exceeding 0.5. In the ESA-made ZrN-(Cr, Ni, Al₂O₃) coating, the major phases are ZrO₂ oxide and ZrNi₃, ZrCr₂ intermetallic compounds. The presence of ZrCr₂ intermetallic and ZrO₂ oxide increases the hardened layer wear resistance. The highest wear resistance ($I=4.9~\mu m/km$) is attained in the ESA-made ZrN-(Cr, Ni, Al₂O₃) coating at sliding speed of 5 m/s and load of 0.5 MPa.

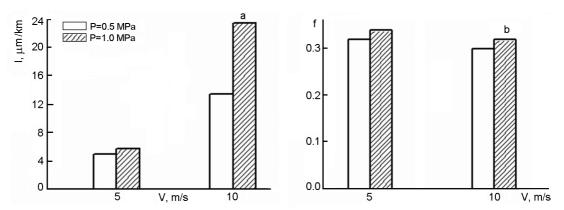


Fig. 4. Dependence of wear resistance I (a) and friction coefficient f (b) for ZrN-(Cr, Ni, Al_2O_3) coating on rotation speed under load P.

References

- 1. A.D Verkhoturov, I.M.Mukha, Technology of Electric Spark Coating of Metal Surfaces, Tekhnika, Kiev (1982) [in Russian].
- 2. A.D. Verkhoturov, I.A. Podchernyaeva, F.F. Egorov, Electrode Materials for Electric Spark Alloying, Nauka, Moscow (1988) [in Russian].
- 3. G.V.Samsonov, Nitrides, Naukova Dumka, Kiev (1968) [in Russian].
- F.F.Egorov, O.V.Pshenichnaya, V.P.Popov, V.E.Matsera, Poroshkovaya Metallurgia, No.1-2, 89 (2002).

- 5. F.F.Egorov, V.E.Matsera, Poroshkovaya Metallurgia, No.11/12, 35 (2004).
- 6. L.F.Kolesnichenko, V.V.Polotay, V.V.Zabolotny, Poroshkovaya Metallurgia, No.3, 61 (1970).
- 7. V.A.Kim, D.N.Korotaev, A.V.Golik, *Fiz. Khim. Obrab. Mater.*, No.1, 78 (2001).
- 8. V.S.Kovalenko, A.D Verkhoturov, N.F.Golovko, I.A.Podchernyaeva, Laser and Electro-Erosion Hardening, Nauka, Moscow (1986) [in Russian].
- 9. R.F.Voytovich, Oxidation of Carbides and Nitrides, Naukova Dumka, Kiev (1981) [in Russian].

Електроіскрове легування електродним матеріалом на основі ZrN

О.В.Паустовський, В.Н.Новікова, Н.М.Мордовець

Досліджено залежності ерозійних характеристик електродного матеріалу ZrN-(Сr, Ni, Al₂O₃) та встановлено зв'язки між фазовим складом, структурою та триботехнічними властивостями електроіскрового покриття, одержаного методом ЕІЛ.