PHASE COMPOSITION OF ELECTROSPARK TUNGSTEN CARBIDE-BASED COATINGS AFTER HEATING AND ISOTHERMAL SOAKING

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Abstract: A study of phase formation on electrospark coatings with WC –Co –Cu electrodes on R6M5 high-speed steel during isothermal heat treatment at the operating temperature of the coating. Copper tungstateCuWO4 has been found to form, with its crystal lattice coherently bound to the basic carbide phase of thecoating, tungsten monocarbide, through tungsten semicarbide as intermediary. The results complementthe data on phase formation during the application of WC-based coatings and during their subsequent use with sliding friction.

Research in electrospark alloying (ESA) shows that the secondary phase structures of surface layers form during the deposition of the electrospark coatings and function during their use. Such results about the features of phase formation in surface layers both during deposition of electrospark coatings and during use.

Must study the features of phase formation in the structure of ESA coatings under furnace heating and isothermal holding at the temperature at which the coating functions. This in turn, enables us to understand the processes that occur at coupled surfaces under sliding friction. Studying the behavior of hardened surfaces during use (fast processes) is very complicated, since it involves an examination of the structure and phase composition of thin surface layers which are periodically removed in the zone of tribotechnical contact at high temperatures (800-1000°C).

Compounds that are present in insignificant amounts in the surface layers cannot be identified by the x-ray method. In order to study the phase formation processes that occur in electrospark coatings during use and tribotechnical tests, therefore, the coatings were heated in air with isothermal holding in the interval of operating temperatures. The amount of phases formed by interaction of the electrospark coating and the substrate with oxygen could thus be increased and those phases could be identified by the x-ray method.

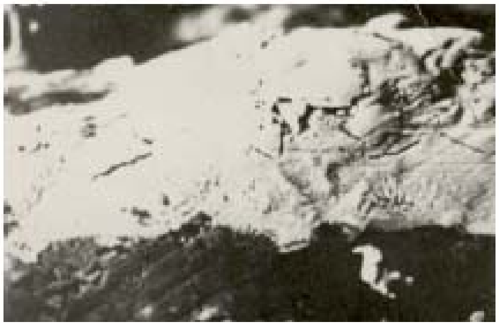


Fig. 1. Microstructure of electrospark coating of the alloy VK5D3.

Studies were conducted on electrospark coatings of commercial VK hard alloys and electrode materials based on copper-alloyed tungsten with a cobalt binder, which had been specially developed and recommended for ESA. Hard-alloy coatings were applied to specimens of heat-treated R6M5 steel by electrospark alloying on an “Élitron-22” unit at an operating current of 2 A and a specific alloying time of 1.5 Msec/m^2.

The ESA-hardened steel specimens were heated to 860°C in an electric furnace for 90 min. The isothermal holding time was 120 min. That temperature, according to data in the literature, is only slightly higher than the upper limit of operating temperatures at spots of actual contact during cutting (500-700°C) and corresponds to the lower limit of operating temperatures with dry sliding friction (800-1000°C). Moreover, that temperature lies in the interval of sublimation of tungsten oxides. An x-ray analysis was made on a DRON-3.0 diffractometer in cobalt and copper radiation.

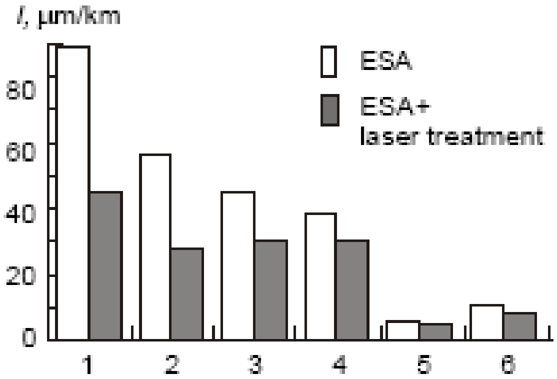
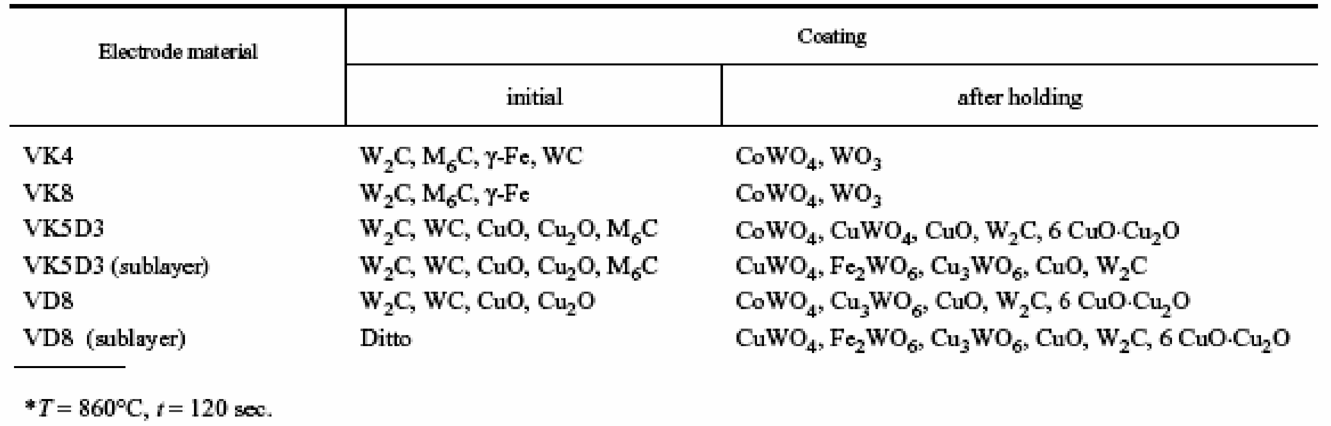


Fig. 2. Relative wear resistance of R6M5 steel (1), hardened by laser treatment of ESA coatings of thealloys VK8 (2), VK7D1 (3), VK6D2 (4), VK5D3 (5), and VK4D4 (6).

Copper additives were introduced into the WC - Co alloys to ensure that the surface layers of the cutting tool, hardened by electrospark alloying, had superior operating (tribotechnical) properties. Partial replacement of cobalt by copper in the binder of the electrode materials results in more liquid phase during ESA, producing coatings that are thicker and have improved tribotechnical characteristics.

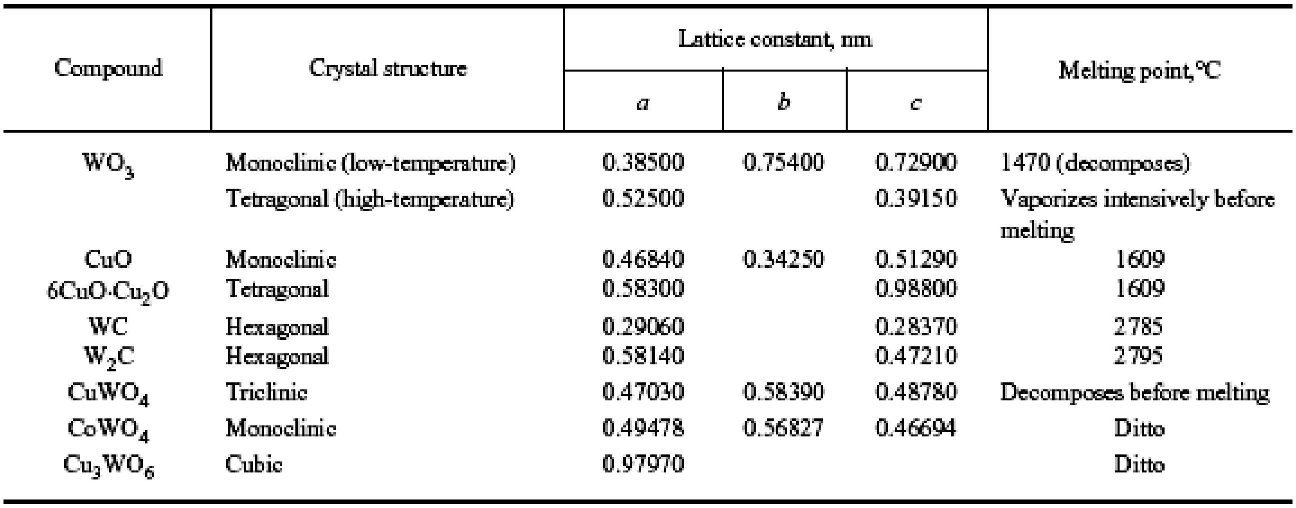
The erosion products during ESA with VK8 alloy have a size of 0.04-0.15 mm. The products of brittle fracture, constituting 20% of the volume, consist of larger particles (0.1-0.15 mm). A large fraction of the fused erosion products are particles measuring 0.04-0.1 mm. When alloys with a cobalt-copper binder are used in ESA the erosion products are mainly round. Partial replacement of cobalt with the more readily melted copper in VK8 alloy increases the volume of the binder fusion zone on the anode, causing the volume fraction of fused erosion products to increase to 90% and their size to decrease slightly (to 0.01-0.1 mm). X-ray phase analysis of coatings of hard alloys of the VK type showed that the main components of the layer are phases present in the electrode material or are products of their thermal dissociation in air and chemical reaction with the substrate material. For instance, when alloys of the VK group are used in the hardening the main coating is the semicarbide W_2C. The coatings were also found to contain a small amount of the carbides WC and M_6C, and austenite γ-Fe (Table 1).



Electrode material	Coating	
	initial	after holding
VK4	W_2C, M_6C, γ-Fe, WC	$CoWO_4$, WO_3
VK8	W_2C, M_6C, γ-Fe	$CoWO_4$, WO_3
VK5D3	W_2C, WC, CuO, Cu_2O, M_6C	$CoWO_4$, $CuWO_4$, CuO, W_2C, 6 $CuO{\cdot}Cu_2O$
VK5D3 (sublayer)	W_2C, WC, CuO, Cu_2O, M_6C	$CuWO_4$, Fe_2WO_6, Cu_3WO_6, CuO, W_2C
VD8	W_2C, WC, CuO, Cu_2O	$CoWO_4$, Cu_3WO_6, CuO, W_2C, 6 $CuO{\cdot}Cu_2O$
VD8 (sublayer)	Ditto	$CuWO_4$, Fe_2WO_6, Cu_3WO_6, CuO, W_2C, 6 $CuO{\cdot}Cu_2O$

*T = 860°C, t = 120 sec.

TABLE 1. Phase Composition of Electrospark Coatings on R6M5 Steel before and after Isothermal



Compound	Crystal structure	Lattice constant, nm			Melting point,°C
		a	*b*	*c*	
WO_3	Monoclinic (low-temperature)	0.38500	0.75400	0.72900	1470 (decomposes)
	Tetragonal (high-temperature)	0.52500		0.39150	Vaporizes intensively before melting
CuO	Monoclinic	0.46840	0.34250	0.51290	1609
$6CuO{\cdot}Cu_2O$	Tetragonal	0.58300		0.98800	1609
WC	Hexagonal	0.29060		0.28370	2785
W_2C	Hexagonal	0.58140		0.47210	2795
$CuWO_4$	Triclinic	0.47030	0.58390	0.48780	Decomposes before melting
$CoWO_4$	Monoclinic	0.49478	0.56827	0.46694	Ditto
Cu_3WO_6	Cubic	0.97970			Ditto

TABLE 2. Crystal Structure and Properties of Tungsten Carbide and Products of Its Reaction with Elements of the Binder, Substrate, and Ambient Medium during High-Temperature Heating.

Coatings of low-cobalt hard alloys (VK2, VK4) were found to contain a slight amount of carbide WC, while no carbide was detected by the x-ray method in coatings deposited with a higher cobalt content (VK8, VK15). The explanation for this is that in electrospark alloying with VK2 and VK4 the fraction of hard phase (undissolved WC surrounded by liquid cobalt binder) in the anode erosion products is higher than in alloying with VK8 and VK15. In the first case the carbide WC is subject to less thermochemical action since there is less contact with the liquid phase. The carbide WC is also detected in coatings of alloys with cobalt-copper and copper binders, VK5D3 and VD8 (Table 1).

In that case the conservation of WC in the coating is promoted by the formation of more thermally stable copper tungstates, coherently bound via a W2C interlayer with the main carbide phase of the electrode material, tungsten monocarbide (Table 2).

Coherent binding of the lattices of the copper tungstate and the tungsten semicarbide is indicated by their similar lattice parameters (the lattice constants differ by 2-4%). Figure 1 shows the microstructure of the initial electrode material VK5D3 and of an electrospark coating of it. The structure of the coating exhibits WC particles from the initial material that did not dissolve during the ESA.

Particles with a regular geometric shape (triangle) are encountered. Such a microstructure was not observed in other ESA coatings of alloys based on tungsten carbide. Bearing in mind that the temperature of the spark discharge in the interelectrode gap is the same, we can assume that during sintering of the electrode material as well as during erosion in the course of the ESA, tungsten carbide particles are covered with a dense film of chemical compound, which protects them from interaction with the ambient medium and the substrate.

That assumption is supported by the fact that partial replacement of the cobalt by copper in the binder of the hard alloy VK8 substantially weakens the material (σbend ≅300 MPa for the alloy VK5D3 in comparison with σbend ≅1980 MPa for the alloy VK8). Moreover, the erosion products of the alloys WC – Co – Cu, which are of smaller size than the erosion products of the alloys WC – Co, should be more oxidized and interact with the material of the binder and the steel substrate.

The formation of copper tungstateon the surface of the tungsten monocarbide particles reduces the probability of oxidation and dissociation of the monocarbide WC. This is so because copper tungstate is more thermally stable than is cobalt tungstate, and its lattice is coherently bound via tungsten semicarbide with the main carbide phase of the electrode material. Thus the coating formed has superior operating properties as indicated by the results of tribotechnical tests (Fig. 2).

The most wear-resistant under the conditions studied were specimens hardened by alloys based on VK with copper additives, i.e., VK5D3 and VK4D4. This can be explained by the good tribotechnical properties (low friction coefficients) of the copper-containing compounds of the system W – Cu – O.

The copper oxides formed in the decomposition of copper tungstates act as a solid lubricant in the hard-alloy coating. Copper, which has a higher thermal expansion factor ($\alpha = 18 \cdot 10^{-6}$ K^{-1}) than does the alloy VK8 ($\alpha = 5.1 \cdot 10^{-6}$ K^{-1}) and is plastic, forms thermostable copper tungstates and oxide film on the rubbing surfaces, which substantially decrease the wear of the friction pair. In summary, it is desirable to use a copper additive to enhance the operating properties of WC – Co coatings which form volatile tungsten and carbon oxides under the effect of spark discharge and tribochemical processes in air.

During the heating the copper forms a thermally stable copper tungstate $CuWO_4$, whose lattice is coherently bound to the main carbide phase of the electrode material, tungsten monocarbide, through tungsten semicarbide. The phase formation processes, which occur in the thin surface layers of composite hard-alloy ESA coatings during use and in tribotechnical tests, are most expediently studied by means of furnace heating to the operating temperatures with isothermal holding for several hours, followed by cooling in the furnace. Under such conditions more of the products required for reliable x-ray phase analysis are formed in the interaction of elements of the composite material with the ambient medium.

Bibliography

[1]. A. I. Yuga, S. S. Zatulovskii, A. S. Zatulovskii, et al., “Influence of temperature in the contact zone on the tribotechnical characteristics of a macroheterogeneous composite,” *Poroshk. Metall.,* Nos. 3-4, 30-32 (1997).

[2]. A. D. Verkhoturov, I. A. Podchernyaeva, L. F. Pryadko, and F. F. Egorov, *Electrode Materials for Spark Alloying* [in Russian], Nauka, Moscow (1988).