the process slows down, its rate from that point being limited by carbon diffusion in the layer of reaction products and oxygen diffusion in the oxide phase.

Evidence in support of the conclusion that the process of formation of molybdenum coatings by the method described in [1] takes place under diffusion conditions is provided by the magnitude of the energy of activation of the process: Calculations based on the variation of the logarithms of the rates of change of the diamond weight gain and metallizing agent weight loss with the reciprocal of temperature gave values of 328 and 261 kJ/mole. According to [7], the energy of activation of carbon diffusion in molybdenum and its carbide is 348, and that of oxygen diffusion in molybdenum trioxide [5] 256 kJ/mole.

LITERATURE CITED


EMISSIVE ELECTRIC-SPARK COATINGS BASED ON LANTHANUM HEXABORIDE


From an engineering point of view, emission-active materials are best employed in the form of coatings, since this enables electrodes of complex shapes and large surface areas to be produced. In this connection, in recent years there has been an increasing interest in the emission properties of lanthanum hexaboride coatings, applied both by conventional (covering with a paste [1], sintering [2], and evaporation [3]) and by radically new methods, such as plasma pulse acceleration [4], which give high quality of deposited layers. One of these methods is electric-spark alloying (ESA), which is characterized by low power consumption, a high coefficient of material transfer, simplicity of operation, and good adhesion of coatings to basis materials [5]. Our earlier investigation into the ESA of molybdenum with nitrides of Group IV transition metals [6] has demonstrated the feasibility of application of emission-active electric-spark coatings.

In the work described below, in continuation of earlier investigations [6, 7], a study was made of the effective work functions ($\phi_e$) of coatings forming during the ESA of constructional materials (tungsten, commercial-purity molybdenum, and U8 and St3 steels*) with zone-melted lanthanum hexaboride with and without Co, Ni, and Mo additions. The choice of LaB$_6$-base alloys as alloying electrode materials was prompted by the preferential erosion of lanthanum hexaboride in the solid phase [7]. It was therefore considered necessary to add to it a ductile binder with the aim of improving the conditions of formation of alloyed layers and at the

*0.8% C and mild steels, respectively. - Translator.

Fig. 1. Kinetic curves of total anode erosion (1'-4') and total cathode weight gain (1-4) in ESA of molybdenum with zone-melted LaB$_6$ (1 and 1') and LaB$_6$-15% Ni (2 and 2'). LaB$_6$-15% Ni (3 and 3'), and LaB$_6$-30% Ni (4 and 4') alloys. Efficiency of ESA: 1.5·$10^{-4}$ (1), 4.5·$10^{-5}$ (2), 2·$10^{-4}$ (3), and 3.2·$10^{-6}$ cm$^3$ (4).

Fig. 2. Time dependence of $\varphi_{1400\cdot K}$ of coating produced by ESA of St3 steel with zone-melted lanthanum hexaboride.

same time find out how such additions affect the thermionic emission of coatings.

Alloy specimens were produced by hot pressing. Sintering was performed for 30 min in a vacuum at 1673 K. To prevent strong evaporation of the metallic component, the residual pressure was maintained at a level of ~1.3 Pa. Metallographic examinations established that alloy structure formation involved the recrystallization of lanthanum hexaboride through a liquid phase based on the metallic addition. The LaB$_6$ grains had a regular shape characteristic of cubic system crystals. The binder was evenly distributed throughout the specimens. In the sintered condition the alloys were three-phase mixtures composed of LaB$_6$, Me$_2$B (Me is the metallic component of an alloy), and a boride of the La-Me-B system.

Coatings were applied in air, using a mechanized high-frequency alloying apparatus. The treatment parameters* were such that the processes corresponded, according to the classification adopted in [8], to "thermomechanical" ESA (R = I/E = 53.2 A/J), i.e., alloying in which electrode material erosion is affected not only by thermal action but also by cyclic mechanical loads generated by spark discharges. After the alloying of each square centimeter of the surface, the anode erosion ($\Delta A$) and cathode weight gain ($\Delta C$), obtained by averaging the results of not fewer than five measurements, were recorded.

Thermionic emission measurements were made in a working vacuum corresponding to not more than 1.3·$10^{-6}$ Pa, in the range 1300-1625 K on disk-shaped coated specimens with indirect electronic heating by the "full current" method; the measurements were accurate to within ±0.05 eV. The experimental procedure employed, which enabled eight specimens to be investigated under identical conditions, and design of the tube are described in [9]. X-ray diffraction phase analyses of alloyed surfaces were carried out, using Cu K$_\alpha$ radiation, in an RKD camera. Figure 1 shows typical kinetic curves of total anode erosion and cathode weight gain, obtained for the ESA of molybdenum with the zone-melted LaB$_6$ and alloys of the LaB$_6$-Ni system. As can be seen from these plots, the concentration of the addition in the alloy strongly affected the weight gain $\Delta C$, the brittle rupture threshold of the cathode $t_b$ (time corresponding to the maximum total weight gain of the cathode), and the coefficient of transfer $K = \Delta C/\Delta A$. The efficiency of the ESA process, assessed by the quantity

$$\gamma = \Sigma \Delta c K$$  [8], proved to be an optimum for the composition LaB$_6$-15% Ni (Fig. 1).

Thus, the introduction of metallic additions into lanthanum hexaboride changed the efficiency of the coat-

* Frequency 1 kHz, short-circuit current $I = 0.45$ A, pulse energy $E = 8.45$ mJ, and discharge circuit capacitance $C = 4.0 \mu$F.