INVESTIGATION OF THE REACTION BETWEEN A FREE MOLECULAR FLOW AND THE SURFACE OF SILVER PICKUPS

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In [1-3] there was observed a change in the electrical resistance of thin films of silver on reaction with elemental particles and a change in total absorption of atoms of oxygen on the surface under conditions of the free molecular flow of a gas stream.

In the practical use of pickups made of thin films of silver, there have arisen difficulties connected with the absolute calibration of the pickups with respect to atomic oxygen [1-4]. Thus, calibration of the pickups in accordance with a method proposed in [3] permits determining O with an accuracy up to 25%. The present article gives the results of measurements of the degree of dissociation of a free molecular stream of molecular oxygen with flow around the pickups, using the method of electron paramagnetic resonance (EPR). It gives experimental data from electronographic and x-ray-structural analyses of the structure of the surface of the pickups.

The experiments were made in a unit described in [5, 6]. The free molecular flow of the gas stream in the working volume was set up using a gas accumulator with continuous evacuation of the vacuum system. Dissociation of the gases was effected using an electrodeless high-frequency discharge with a minimal power of the high-frequency generator [6].

The degree of dissociation α in O_2 was measured by the method of electron paramagnetic resonance, for which a Varian E-3 radiospectrometer was used. The scheme of the measurements is given in [1]. The method is based on measurement of the change in the intensity of the electron paramagnetic resonance spectrum of O_2 in the working volume due to dissociation of molecules of oxygen. Therefore, the principal error in determination of α depends on the accuracy of measurement of the intensity of the electron paramagnetic resonance spectrum in molecular and dissociated streams of gas. In accordance with the evaluations of the present authors, $\Delta\alpha/\alpha \sim 5\%$, and, in determination of the concentration of atoms of oxygens, $\Delta n/n \sim 7\text{-}10\%$.

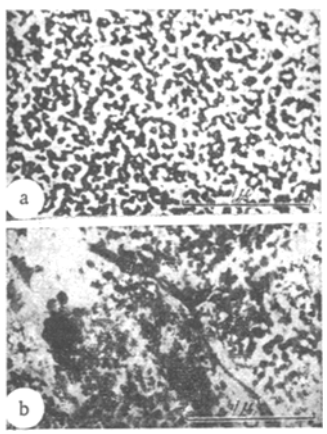

Fig. 1

The structure of the surface of the pickups was studied in a URS-60 x-ray unit, using a VRS camera. The source of illumination was an x-ray tube with a chromium anode. For recording the x-ray photographs, the sample was arranged at an angle of 15° to the x-ray beam. With a thickness of the deposited layer of silver $h \sim 1\mu$, the exposure was 3 h. The x-ray photographs were analyzed in accordance with a method described in [7, 8]. The error in determination of the interplane distances, d/n and θ, the Wulff–Bragg angle, did not exceed 2%.

The electron-microscope photographs and the microphotographs of the surface of the pickups were recorded in UÉMV-100 and TESLA BS 242 B electron microscopes. The electronograms were interpreted in accordance with the generally accepted method. The error in determination of the lattice parameters from 2-4 photos did not exceed 1-2%.

The measured values of α in the working volume for different pressures P_0, in the flow of gas are given below. With an increase in the pressure of the gas in the flow, within the measured narrow range of

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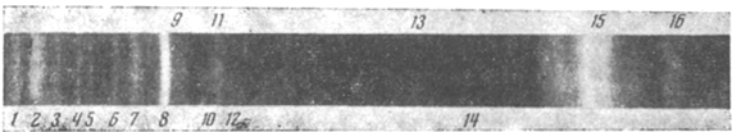

Fig. 2

TABLE 1

Lines	θ	d/n, Å: experimental data: x-ray analysis	d/n, Å: experimental data: electronographic analysis	d/n, Å: theoretical data	Substance	hkl silver
1	14.3°	4.63				
2	15.9°	4.18	4.16			
3	17.9°	3.72				
4	19.9°	3.36		3.35	Ag_2O	
5	21.1°	3.18				
6	23.8°	2.83		2.80	Ag O	
7	25.8°	2.63		2.63	Ag O	
8	27.8°	2.45	2.42	2.42	Ag O	
9	29.6°	2.31	2.36	2.36	Ag, AgO, Ag_2O	111
10	31.0°	2.22				
11	32.8°	2.11				
12	34.8°	2.04	2.04	2.04	Ag	200
13	52.0°	1.45	1.44	1.44	Ag, AgO, Ag_2O	220
14	57.0°	1.36		1.36	Ag_2O	
15	67.0°	1.24	1.23	1.23	Ag	311
16	75.5°	1.18	1.18	1.18	Ag	222
17			0.94	0.94	Ag	331
18			0.91	0.91	Ag	420
19			0.83	0.83	Ag	422
20			0.78	0.78	Ag	511

initial pressures, a tendency toward an increase in the degree of dissociation is observed α. The data on α correspond to the measurements made in this region in [9], using another method.

p_0, mm Hg	α
0.001	0.02
0.003	0.04
0.006	0.08
0.009	0.11

Figure 1 gives microphotographs of the surface of pickups, unexposed (Fig. 1a) and exposed (Fig. 1b) in the flow. The difference in the microstructure of the surface of the pickups can be seen on the photographs. For the exposed pickup, there is a breakdown of the microstructure of the thin surface layer. The results of analyses of the electronograms taken from these surfaces, in comparison with the data of other measurements, are given in Table 1. Interpretation showed that for the unexposed pickup only the lines of silver 9, 12, 13, 15-20 (Table 1) are present, while, for the exposed pickup, in addition to the lines of silver there appear the new lines 2, 8 (Table 1).

Figure 2 shows an x-ray photograph taken from the surface of a pickup exposed in a stream of O at a pressure of 10^{-3} mm Hg of O_2, $\alpha \approx 2\%$. On the x-ray photographs, along with the lines of Ag (9, 12, 13, 15, 16 on Fig. 2), lines of AgO (6, 8, 13 on Fig. 2) and Ag_2O (4, 9, 13, 14 on Fig. 2) are observed. Lines which do not relate to the above-listed substances (1, 2, 3, 5, 10, 11 on Fig. 2) are also observed.

The results of calculations of the lattice parameters of substances from the x-ray photographs are given in Table 1 in comparison with calculations taken from [7, 8]. The same table gives data from electronograms.

It follows from the data obtained that, under the conditions of the experiments described, the main reaction on the surface of the pickups is oxidation. This is brought out graphically by the data of x-ray-structural and electronographic analyses. On the x-ray photographs there are the lines of Ag, AgO, and Ag_2O, which points to the presence of these components in the crystalline phase on the surface of the pickups. The existence of three different phases on the surface of the pickups is confirmed also by the data of an electronographic analysis. This is confirmed by a comparison of the microstructures of the surfaces of the pickups (Fig. 1a, b) and by the results given in Table 1, obtained by analyses of electronograms. The

absence on the electronograms of a number of the lines of AgO and Ag_2O, which are observed on the x-ray photographs, is explained by the special characteristics of the method of investigation. The lines on the x-ray photographs (1, 2, 3, 5, 10, 11 on Fig. 2) are obviously either the lines of $AgNO_3$ or of $AgCO_3$ [8].

It follows from the results obtained that the changes in the electrical resistance of the pickups [1, 3] and the total decomposition of atoms of oxygen [2] are connected with the oxidation of the silver on the surface.

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