FIELD-ELECTRON-MICROSCOPY STUDIES OF POTASSIUM LAYERS ON RHENIUM: AVERAGE WORK FUNCTION CHANGE*

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Investigations of the adsorption of potassium on rhenium were carried out. Potassium was first adsorbed around the high work function planes. The variation of the average work function $\overline{\phi}$ with the atomic density of potassium was measured. The values of the work function at the minimum $\overline{\phi}_m = 1.72 \pm 0.05$ eV and at the saturation $\overline{\phi}_s^3 = 2.18 \pm 0.05$ eV of the $\overline{\phi}(\overline{N})$ relationship were obtained. The minimum and the saturation of the $\overline{\phi}(\overline{N})$ relationship occured at the atomic densities $\overline{N}_m = (3.50 \pm 0.34) \times 10^{14}$ atoms/cm^2 and $\overline{N}_s = (4.67 \pm 0.34) \times 10^{14}$ atoms/cm^2, respectively.

1. Introduction

Many works on the emission and adsorption proprieties of the potassium-refractory metal system were previously reported. These investigations were carried out in two directions: for micro single crystal (FEM [5, 15], flicker noise methods [1, 2]) and for large single crystals (LEED [11, 16], RHEED [4], CPD [3] methods). Information about the electronic and atomic structure of the potassium layers has been obtained. Surface diffusion, field and thermal desorption have been investigated. The field emission method is very useful for investigating the emission proprieties of the potassium-refractory metal system and for measuring the work function. Studies of potassium on the bcc structure substrates (tungsten [5, 6], molybdenum, tantalum [7]) have recently been carried out using this method. In recent years the theory of alkali adsorption on metals has been developed [19, 20]. The alkali-refractory metal systems are the most favourable for theoretical investigations. The experimental studies of alkali adsorption on the bcc structure substrates confirm these theoretical models. Studies of the K/Re system by the FEM method were made in this work. The $\overline{\phi}(\overline{N})$ relationship was measured. It may be used

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for calibration in the investigations on single crystal planes. The general purpose of this work was to compare the experimental results of the adsorption of potassium on rhenium (hcp structure) with the theoretical models and to find out if the adsorption of potassium depends on the crystallographic structure of the substrates.

2. *Experimental*

The experimental system (see Fig. 1) consisted of four field emission tubes [8, 10] connected in series. All the emitters (E), the magnetic value (V) and the potassium reservoir (R) were on one line. One microscope had a rhenium emitter and the others had tungsten

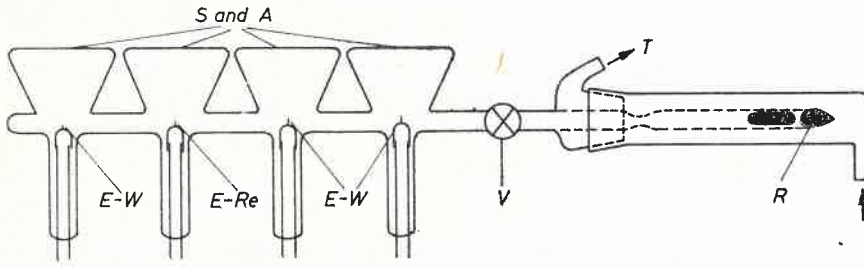

Fig. 1. The experimental system: E — emiters, S and A — phosphor screen and anode, V — valve, R — potassium reservoir, T — to thermostat

emitters. The tungsten emitters were used only for calibrating the potassium source and testing the vacuum. The K-source was heated by hot glycerine. The atomic flux was constant with respect to time. The residual gas pressure in the microscopes was lower than 10^{-10} torr.

The average work function was determined by using Fowler–Nordheim plots. The value of $\overline{\phi}$ for the clean rhenium emitter was taken as 4.85 eV [9]. Since potassium, in the presence of an electric field, shows considerable surface diffusion, the rhenium emitter was cooled to liquid nitrogen temperature before measurements. Potassium was deposited onto the cool emitter. Then the emitter was heated in such a way that the potassium spread uniformly and the entire surface of the emitter after each dose was thermally equilibrated. Then the emitter was cooled again in order to measure the current-voltage characteristics from which the average work function was determined. Thus, using the stable potassium flux and succesive dosing a continuously greater atom density of potassium on rhenium was obtained.

A first, the average work function $\overline{\phi}$ as a function of deposition time t was measured for the K/Re system. The wellknown $\overline{N}_m$ and $\overline{N}_s$ value for the K/W system was used to calibrate the potassium source [9]. The theoretical $\overline{N} \sim 1/r^2$ relationship for the spot--source was used. The experimental system, shown in Fig. 1, was used to test experimentally this relationship for a nonspot-source. It appeared that the $\overline{N} \sim 1/r^2$ relationship held rather well. The error in calculating the square exponent of the source-emitter distance r did not exceed 2%.

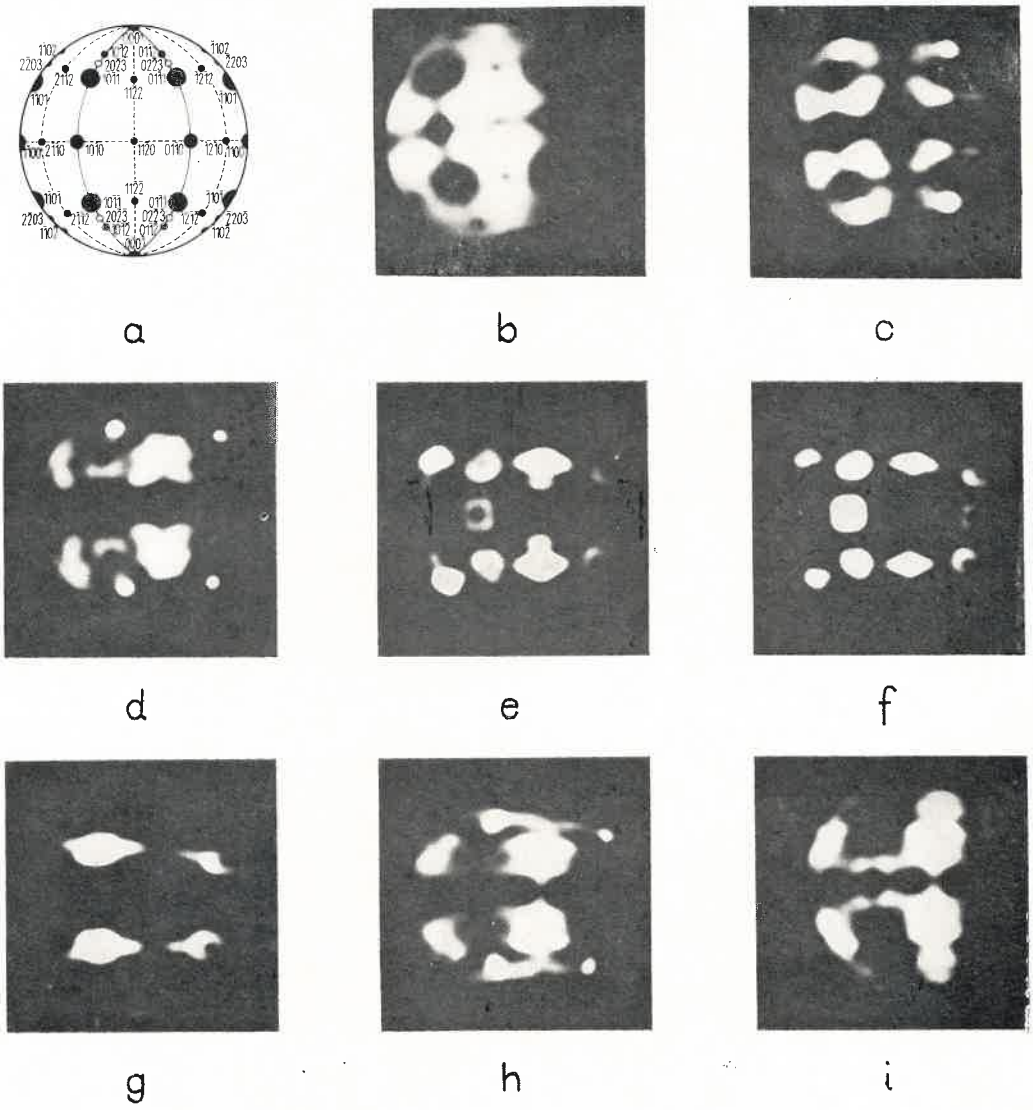

Fig. 2. Principal field-emission pattern changes for K adsorption on Re. The total current $I_t = 1 \times 10^{-7}$ A. a — the orthographic projection of hcp structure; b — clean rhenium; c — $\overline{\phi} = 3.58$ eV, $\overline{N} = 0.83 \times 10^{14}$ atoms/cm^2; d — $\overline{\phi} = 2.41$ eV, $\overline{N} = 1.87 \times 10^{14}$ atoms/cm^2; e — $\overline{\phi} = 2.05$ eV, $\overline{N} = 2.50 \times 10^{14}$ atoms/cm^2; f — $\overline{\phi} = 1.88$ eV, $\overline{N} = 2.83 \times 10^{14}$ atoms/cm^2; g — $\overline{\phi} = 1.72$ eV, $\overline{N} = 3.50 \times 10^{14}$ atoms/cm^2, h — $\overline{\phi} = 2.10$ eV, $\overline{N} = 4.33 \times 10^{14}$ atoms/cm^2; i — $\overline{\phi} = 2.18$ eV, $\overline{N} = 4.67 \times 10^{14}$ atoms/cm^2

3. Results and conclusions

Field-emission patterns of adsorbed potassium on rhenium are shown in Fig. 2. Fig. 2a shows the orthographic projection of hcp structure [13]. The central plane is the $(1\bar{1}20)$ plane. The field-emission pattern of clean rhenium is shown in Fig. 2b. The pattern is not symmetrical. The shift was caused by the bend of the emitter axis during mounting. As is shown in the pattern of clean rhenium, the $\{10\bar{1}1\}$ and $\{10\bar{1}0\}$ planes are very well formed. These planes have a high work function (higher than 5 eV [14]). Potassium adsorbs on the terraces around the $\{10\bar{1}1\}$ planes at low atom density (Fig. 2c). Bright spots appear on these terraces when the atom density increases (Fig. 2d). They correspond to the $\{20\bar{2}3\}$ planes. The atom density $\bar{N} = (2.50 \pm 0.34) \times 10^{14}$ atoms/cm^2 corresponds to the minimum of the work function of the $\{\bar{2}1\bar{1}2\}$ planes (Fig. 2e). Then the emission from the $\{10\bar{1}1\}$ and $\{10\bar{1}0\}$ planes increases. The field-emission pattern of the $\{10\bar{1}1\}$, $\{\bar{2}1\bar{1}2\}$ and $\{10\bar{1}0\}$ planes is shown in Fig. 2f. The minimum of the average work function occurs for $\bar{N} = (3.50 \pm 0.34) \times 10^{14}$ atoms/cm^2 (Fig. 2g). The field-emission pattern does not change for atom densities higher than $\bar{N} = (4.10 \pm 0.34) \times 10^{14}$ atoms/cm^2 (Fig. 2i).

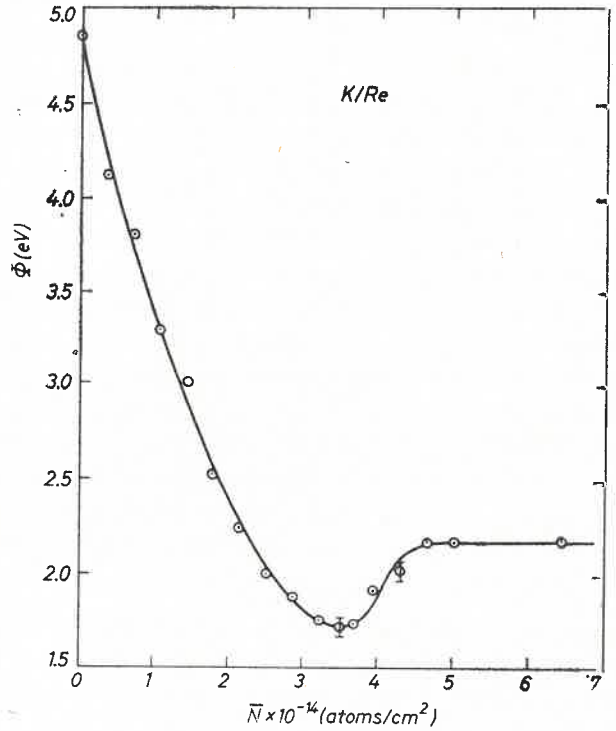

Fig. 3. The curve shows the average work function $\bar{\phi}$ vs average atom density of potassium $\bar{N}$ on rhenium

The average work function $\bar{\phi}$ versus the average atom density of potassium $\bar{N}$ on rhenium is shown in Fig. 3. The values of $\bar{\phi}$ are equal to 1.72 ± 0.05 eV at the minimum and 2.18 ± 0.05 eV at the saturation of the $\bar{\phi}(\bar{N})$ relationship.

As shown in the table, $\overline{\phi}_m$ and $\overline{\phi}_s$ for the various substrates do not differ from each other. It suggests that the electron structure substrates have no influence on the adlayer for atom densities higher than $\overline{N}_m$, in spite of the great differences in the electron density for the various substrates (41×10^3 a.u. for Ta $\div$ 71×10^3 a.u. for Re). It is caused by the large dimensions of the potassium atoms $r_K = 2.7$ Å, which shield the smaller substrate atoms ($r_{Re} = 1.38$ Å $\div$ $r_{Ta} = 1.67$ Å). This was suggested earlier in the papers [7, 17].

TABLE I

Summary of work function and atom density values at the minimum $\overline{\phi}_m$, $\overline{N}_m$ and at the saturation $\overline{\phi}_s$, $\overline{N}_s$ of the $\overline{\phi}(\overline{N})$ relationship for Re, W, Ta and Mo

Substrate	$\overline{\phi}_m$ [eV]	$\overline{\phi}_s$ [eV]	$\overline{N}_m \times 10^{-14}$ [atoms/cm^2]	$\overline{N}_s \times 10^{-14}$ [atoms/cm^2]	References
Re	1.72±0.05	2.18±0.05	3.50±0.34	4.67±0.34	This paper
W	1.70±0.05	2.20±0.05	3.10±0.15	4.77±0.15	[12]
Ta	1.73±0.05	2.26±0.05	2.87±0.15	4.50±0.15	[18]
Mo	1.76±0.05	2.14±0.05	—	—	[18]

The values shown in the table refer to the total emitter. However, mainly the {110} planes for bcc structure and the $\{10\bar{1}1\}$ planes for hcp structure (Fig. 2g) emit electrons at the minimum of the $\overline{\phi}(\overline{N})$ relationship. We can neglect the field emission from the other planes. One can treat the work function values at the minimum of the $\overline{\phi}(\overline{N})$ relationship as the work function of the {110} and $\{10\bar{1}1\}$ planes. It is possible to compare these values with those obtained theoretically by Lang [19] and Wojciechowski [20]. The work function at the minimum and at saturation are in good agreement with Lang's calculations. Wojciechowski explains the properties of adsorbed alkali layers within the framework of a jellium model similarly as Lang. It follows from his paper that the work function of an alkali monolayer on a metal is very close to the work function of the bulk alkali metal. The work function values at saturation shown in the table do not differ from the value 2.2 eV for clean potassium. The concept of metallization of the alkali submonolayers for the high atom densities was suggested by many authors [22–24, 19, 17].

Investigations of the total system do not represent all real phenomena of K/Re adsorption. Studies of single crystal planes are desired.

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