Thermionic Electron Emission of Tungsten Bronzes. $K_{0.30}WO_3$ and $Rb_{0.30}WO_3$

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The work functions and thermionic constants of the hexagonal tungsten bronzes $K_{0.30}WO_3$ ($\varphi = 1.76$ eV, $A = 3$ A/cm^2 K^2) and $Rb_{0.30}WO_3$ ($\varphi = 1.88$ eV, $A = 10$ A/cm^2 K^2) are determined and compared with those of the corresponding alkaline metals and hexagonal $Cs_{0.305}WO_3$.

Key words: Work function – Tungsten bronzes.

Tungsten bronzes, M_xWO_3, where M is a metal and $x < 1$, are non-stoichiometric compounds [1] which have a remarkable importance in several fields such as electrochemistry, catalysis, crystallography, etc. In a previous paper [2] the thermionic electron emission of the hexagonal bronze $Cs_{0.305}WO_3$ was studied. Also bronzes K_xWO_3 and Rb_xWO_3 can crystallize in the hexagonal system [3]. Hexagonal alkaline tungsten bronzes have similar structures based on a framework of corner sharing WO_3 octahedra forming hexagonal tunnels where alkaline atoms are located. Hussain [4] has shown that hexagonal M_xWO_3, where M is K, Rb or Cs, has the same composition range ($0.19 \leqq x \leqq 0.33$) in the phase diagram. Therefore it seemed interesting to measure the thermionic electron emission of $K_{0.30}WO_3$ and $Rb_{0.30}WO_3$ and to compare the data with those [2] of the hexagonal cesium bronze.

$K_{0.30}WO_3$ and $Rb_{0.30}WO_3$were prepared according to the method of Conroy and Podolsky [5] by heating a mixture of alkaline halide (in excess), WO_2 and WO_3 in a sealed quartz tube under a vacuum at 900 °C for 3 h. 99.998% KCl (Koch and Light), 99.99% RbCl (Aldrich), 99.9% WO_2 (Noah), and 99.99% WO_3 (Atomergic Chemetals) were used as reactants. The methods of purification and analysis of the products and also the experimental apparatus and procedure have already been described [2].

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The thermionic electron emission of $K_{0.30}WO_3$ was studied in the temperature range 459–625 °C. The study of the electron emission of $Rb_{0.30}WO_3$ was carried out in the 440–603 °C range.

Figure 1 shows the experimental data. $J_{0\,\mathrm{sat}}$ is the zero field saturation current density and T the absolute temperature. From the slopes of the straight lines of Fig. 1 we obtain the values of the work function of $K_{0.30}WO_3$ and $Rb_{0.30}WO_3$. Extrapolation of the straight lines for $1/T$ approaching zero gives the values of the thermionic constant for these bronzes.

Table 1 shows the work function and thermionic constant of $K_{0.30}WO_3$ and $Rb_{0.30}WO_3$ and also the corresponding data for $Cs_{0.305}WO_3$ and alkaline metals. Surprisingly, while the work functions of the alkaline metals are in the order $\varphi_{Cs} < \varphi_{Rb} < \varphi_K$, the work functions of the hexagonal alkaline tungsten bronzes follow the reverse order. We can advance the hypothesis that, under the operating conditions, the surface of a hexagonal alkaline bronze is covered with

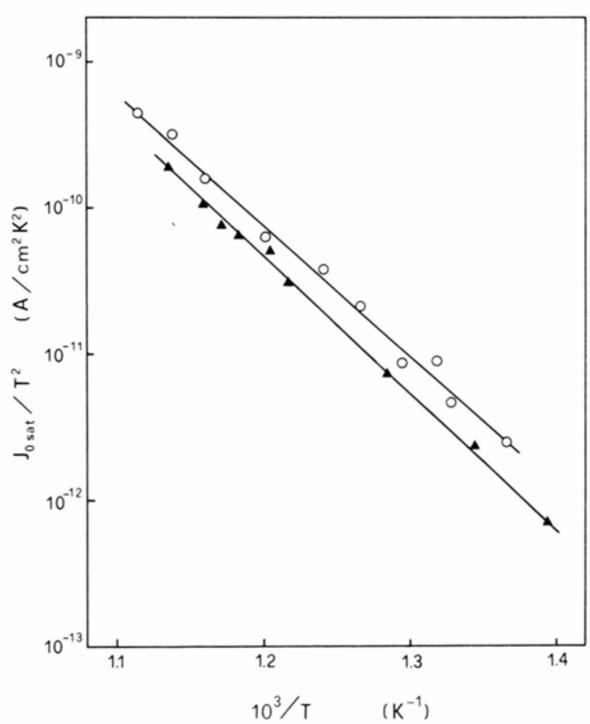

Fig. 1. $J_{0\,\mathrm{sat}}/T^2$ for $K_{0.30}WO_3$ (circles) and $Rb_{0.30}WO_3$ (black triangles) as a function of the reciprocal of the absolute temperature.

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Table 1. Work function and thermionic constant of hexagonal alkaline tungsten bronzes and corresponding alkaline metals.

Substance	Work function (eV)	Thermionic constant ($A/cm^2 K^2$)	Reference
$K_{0.30}WO_3$	1.76	3	this work
$Rb_{0.30}WO_3$	1.88	10	this work
$Cs_{0.305}WO_3$	2.12	115	[2]
K	2.39		[6]
Rb	2.21		[6]
Cs	2.14		[6]

a film of alkaline metal [7]. Moreover, even if the interpretation is not simple, we should admit that the interaction of the alkaline metal film with the WO_3 octahedra of the substrate is the greater, the smaller the alkaline metal. Actually, the interaction of the cesium film with the substrate should be small; in fact, as it can be seen in Table 1, the work function of $Cs_{0.30}WO_3$ is practically equal to that of metallic cesium. The thermionic constant of $Cs_{0.305}WO_3$ is close to the universal constant 120 $A/cm^2 K^2$, therefore indicating that the whole surface participates to the electron emission. $K_{0.30}WO_3$ and $Rb_{0.30}WO_3$, instead, show rather low values of the thermionic constant, so indicating a patch emission. With the aim of explaining these anomalies, a theoretical work will be undertaken. It will take into account both the energy of the dipole alkaline metal-oxygen in WO_3 (that could explain the observed reverse order of the work function) and the aggregation energy of an alkaline metal film onto WO_3, which could explain the patch emission of potassium and rubidium hexagonal bronzes.

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