

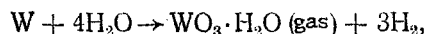
THE MECHANISM OF TUNGSTEN MASS TRANSPORT IN THE OXYGEN OF  
RAREFIED AIR AND IN WATER VAPOR

A. S. Evsikov, A. A. Makeev, L. L. Lyubimova,  
and V. V. Sinyavskii

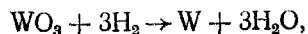
UDC 536.423.1

Experimental data are presented as a generalization of semiempirical relationships. The physical mechanism of tungsten mass transport in water vapor is clarified.

The processes of tungsten mass transfer are observed in electrovacuum devices and installations operating at high temperatures, and these assume particular urgency in the operation of heat-generating energy converters because of the specific nature of their operation in nuclear reactors. The interelectrode gap of a thermoemissive energy converter (TEC) is 0.1-0.2 mm. Disruption of the interelectrode gap may cause a short circuit between the emitter and the collector and cause the breakdown of the thermoemissive converter. The basic reason for these short circuits may be processes of nondesign transfer of mass from the emitter to the collector at operating temperatures of 1800-2500°C. It is usually assumed that in addition to the temperature factors the transfer of mass is intensified by the physico-chemical processes of metal oxidation by water vapor, leading to the so-called hydrogen cycle which promotes mass transfer [1]. The mechanism of the hydrogen cycle of tungsten mass transfer involves the fact that at temperatures above 700°C [2] the tungsten reacts with the water vapor:



and the products of tungsten interaction are atomized through the vacuum system; the higher tungsten oxide in this case is deposited on the cooled surface, while the free hydrogen reduces the tungsten from the oxide in accordance with the reaction



thus forming a tungsten layer with release of water vapor which may be retained in the vacuum system and may participate in the process of subsequent tungsten mass transfer from the heated surfaces to the cooled surfaces.

The vaporization transfer of material mass has been studied to a degree sufficient for purposes of estimation; the quantitative relationships have been generalized by a function that is structurally reminiscent of the Richardson law for the current density of electron emission. The literature contains tables on the rate of emitter material vaporization as well as calculation formulas [3].

The effect of oxidation processes on the transfer of mass from a tungsten emitter to a collector has been studied to a lesser degree; the literature does not fully reflect questions on the effect of residual oxygen and water vapor on mass transfer. There is no basis for excluding the existence of residual oxygen and water vapor in the evacuated circuit of a heat-generating converter. The loop channel has an extended pumping circuit which, even in the degasification regime, may result in the retention (because of residual gas release) of comparatively great partial pressure from the oxygen of the air and water vapor for a prolonged period of time; it is impossible, even with operational technology, completely to eliminate leakage through weld seams and because of the gas permeability of the walls. Bearing in mind the difficulties of achieving a high vacuum in high-temperature designs, it is important for us to clarify the extent to which the oxygen and water vapor affect the transfer of mass in startup regimes for TEC.

---

Kirov Polytechnic Institute, Tomsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 56, No. 2, pp. 242-246, February, 1989. Original article submitted October 27, 1987.

Studies have been conducted into the transfer of tungsten mass which involved estimates of the degree to which atmospheric oxygen and water vapor influence the quantitative characteristics of mass transfer.

The goal of this study, i.e., the establishment of the nature of mass transfer in the oxidizing processes involving tungsten in order to answer the question as to the meaning of the hydrogen cycle in mass transfer in the high-temperature interelectrode gap, is achieved by determination of the relationship between the vaporization rate and the partial pressure of the oxygen and water vapor in a series of experimental measurements involving the vaporization of a tungsten wire onto a substrate in a vacuum and in water vapor at the very same temperature. The experiments were conducted on a VUP-4K type commercial vacuum installation at a tungsten-wire temperature of  $2600 \pm 60^\circ\text{C}$ . The temperature was measured by means of a VIMP-0.15M type optical micropyrometer with a rated error of 2%; the micropyrometer was calibrated to the melting point of copper and niobium. The brightness temperature was converted to actual temperature on the basis of tables contained in the certification of the micropyrometer. In accordance with the data published in monograph [3], we note that at a temperature above  $2000^\circ\text{C}$  the rate of tungsten oxidation is determined exclusively by the pressure of the oxidizing medium; at the same time, the experimental accuracy of  $\pm 60^\circ\text{C}$  has no effect on the characteristics of mass transfer. The water-vapor pressure was calculated from readings of PMI-2 and PMT-2 sensors in terms of relative sensitivity in accordance with the formula

$$P_{\text{H}_2\text{O}} = \alpha_{\text{H}_2\text{O}} P_a,$$

$$\alpha_{\text{H}_2\text{O}} = 0.81 \frac{\chi - 1}{\chi + 1} \frac{M^{1/2}}{1 - \exp(-0,244M^{1/2})} \quad [4].$$

The partial pressure of the oxygen was calculated from the volumetric fraction in the air in accordance with the Dalton law of partial pressures.

A 55-mm heated length of tungsten wire, washed and annealed in a vacuum, weighed on VLR-200 analytical balance, was placed in the vacuum chamber of a VUP-4K installation on current leads and covered with shields, one of which functioned as the substrate. Oxygen-free copper, niobium, and stainless steel were used as the materials for the substrate. The substrate temperature in these experiments was  $800\text{--}1000^\circ\text{C}$ , depending on the dimensions and the material. The specimen was degasified at a temperature of  $1500^\circ\text{C}$  in a vacuum chamber at a pressure on the order of  $1 \cdot 10^{-5}$  mm Hg. After degasification and removal of the voltage, the working pressure of the air or water vapor was established in the overflow chamber. After establishment of the working pressure, the specimen was heated to a temperature of  $2600^\circ\text{C}$  which was maintained for 20 min. On conclusion of the experiment the specimen was weighed on the analytical balance and a determination was made of the quantity of vaporized tungsten, with the mass-transfer products subjected to x-ray structural analysis.

The experimental results (see Fig. 1) show similarity between the processes of tungsten vaporization in the atmosphere of rarified air and water vapor. We note that the transfer of tungsten mass in the presence of atmospheric oxygen and water vapor is significantly intensified, depending on the pressure, which, when increased by an order of magnitude, leads to an increase in the flow of vaporized mass by a factor of 3-5.

Comparison of the tabulated data from [3] dealing with the rate of tungsten oxidation and our experimental results, we note that the rate of oxidation and the rate of tungsten mass vaporization during oxidation are subject to quantitative relationships diverse in nature and different in terms of the physical mechanism. The great rate of tungsten mass vaporization, increasing as the air and water-vapor pressure rises, provides a basis for assuming that the action of the oxidizers (oxygen, water vapor) on the tungsten surface enhances scale formation of the surface structure. After the experiments have been completed, the surface of the tungsten is examined for traces of metal fragments, i.e., the oxidation of the tungsten on the surface is accompanied by the formation of tungsten dioxide, the scale formation of the surface structure of the metal, and by detachment of the surface layer. As an illustration, after being subjected to a vacuum on the order of  $1 \cdot 10^{-5}$  mm Hg the tungsten surface appears to be rough and homogeneous. In explaining this phenomenon we can take into consideration the data of [5] which puts forth the hypothesis that the oxygen penetrates beneath the outer layer of the tungsten surface, the atoms of the adsorbed oxygen and the

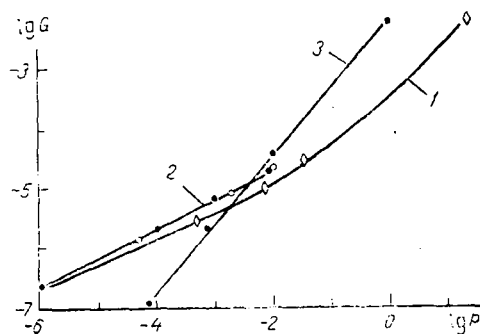


Fig. 1

Fig. 1. Rate of tungsten vaporization at a temperature of 2600 °C as a function of pressure: 1) H<sub>2</sub>O; 2) O<sub>2</sub>; 3) O<sub>2</sub> according to the data of [3].  $\log G$ , g/(cm<sup>2</sup>·sec);  $\log P$ , mm Hg.

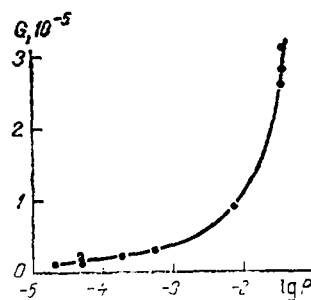


Fig. 2

Fig. 2. Rate of tungsten vaporization at a temperature of 2600 °C as a function of water-vapor pressure.  $G$ , g/(cm<sup>2</sup>·sec).

tungsten change places, to form a unique surface microstructure which enhances scale formation and an increase in the rate of metal vaporization. In this connection, the oxidation of the vaporizing tungsten in the space between the filament and the substrate has a secondary significance for the quantitative characteristic of mass transfer and determines only the final product of the interaction. As is demonstrated by data from x-ray structural analysis, the transfer of mass in an oxygen atmosphere is accompanied by the deposition of tungsten dioxide and tungsten on the substrate at low pressures, which confirms the hypothesis. At pressure of 10-30 mm Hg for atmospheric oxygen, the tungsten dioxide does not reach the substrate, oxidizing to the higher oxide WO<sub>3</sub>. The x-ray structural analysis shows the presence of intense peaks of reflection from the WO<sub>3</sub> lattice, while no reflections from the tungsten lattice are noted on the substrates. It is assumed that the lower oxide WO<sub>2</sub> is formed beneath the surface of the heated tungsten, which promotes scale formation on the surface of the metal. The tungsten dioxide is vaporized together with the metal and enters the gaseous medium where, in the process of motion, intermediate oxides such as W<sub>4</sub>O<sub>11</sub>, W<sub>18</sub>O<sub>49</sub>, and W<sub>20</sub>O<sub>59</sub> are formed, and these on subsequent binding with oxygen form the higher oxide WO<sub>3</sub>. With an atmospheric oxygen pressure of 10-30 mm Hg, the peeling tungsten particles are oxidized and do not reach the substrate; therefore, no traces of the tungsten are found on the x rays.

The studies of tungsten mass transfer in water vapor were primarily intended to confirm the hypothesis of the existence of a hydrogen cycle in the high-temperature interelectrode gap of the TEC, and to provide quantitative estimates.

The results of the experimental studies into the transfer of tungsten mass at a temperature of 2600°C for water-vapor pressures in the range from 0 to 10<sup>-2</sup> mm Hg were approximated in the form of the relationship

$$\frac{G}{G_t} = \left[ \frac{P_{H_2O}}{P_0} \right]^{0.57}$$

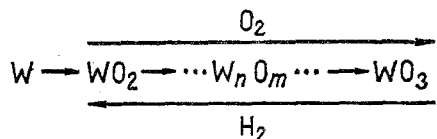
where  $P_0 = 1 \cdot 10^{-6}$  mm Hg is the pressure at which the tungsten-vaporization rate data presented in the table of [2] were obtained. These results are shown in Fig. 2.

The comparatively close values of the rates of tungsten-mass loss in water vapor and in an air atmosphere, obtained in these experiments, provide a basis for the assumption that, in terms of the nature of the action on the surface of heated tungsten, water vapor does not differ from atmospheric oxygen. This difference is noted in the final products of the interaction. Vaporization of tungsten in atmospheric oxygen revealed no intermediate metal oxides on the substrates, tungsten dioxide was recorded, as was tungsten, and the higher oxide WO<sub>3</sub> at greater pressures. The vaporization of tungsten in water vapor is accompanied by the formation on the substrates of intermediate oxides W<sub>4</sub>O<sub>11</sub>, W<sub>18</sub>O<sub>49</sub>, W<sub>20</sub>O<sub>59</sub>, tungsten dioxide, and traces of tungsten; we were unable to find any higher tungsten oxide. The x rays of the tungsten mass transfer product at water vapor pressures below 10<sup>-2</sup> mm Hg show images characteristic of the oxide WO<sub>2</sub>, accompanied by traces of tungsten and intermediate oxides. With

an increase in the water-vapor pressure the x rays show a predominance of intermediate oxides, and traces of tungsten dioxide are recorded.

It has thus been established that the presence of water vapor intensifies mass transfer; however, in this case the mechanism of the process differs from that of the hydrogen cycle, since metallic tungsten is formed on the cooled surface in the hydrogen cycle, while under the conditions of the performed experiments no indications of oxidation-reduction processes were found in which metallic tungsten was formed, nor were any traces of the higher tungsten oxide  $WO_3$  observed.

This circumstance can be explained by the fact that in the presence of water vapor in the interelectrode gap we encounter the simultaneous occurrence of oxidation-reduction reactions such as



Dynamic equilibrium is established between these reactions, as a result of which intermediate oxides of the  $W_n O_m$  type are formed, and this is in agreement with the experimental results and the data from the x-ray structural analysis of the mass transfer products.

#### NOTATION

$P$ , gas pressure;  $\alpha$ , relative sensitivity of the sensor;  $M$ , molecular mass;  $\chi$ , ratio of specific gas heat capacities at constant pressure and constant volume;  $G$ , tungsten vaporization rate;  $G_t$ , tabulated values of the tungsten vaporization rate at temperature  $t$ ;  $P_a$ , pressure of the air taken from the calibration curve of the sensor.

#### LITERATURE CITED

1. V. V. Sinyavskii, V. I. Berzhatyi, V. I. Maevskii, and V. G. Petrovskii, Design and Testing of Heat-Generating Elements [in Russian], Moscow (1981).
2. S. V. Ryabikov (ed.), The Technology of Heat-Generating Converters. Handbook [in Russian], Moscow (1974).
3. B. A. Ushakov, Fundamentals of Heat-Generating Energy Conversion [in Russian], Moscow (1979).
4. A. I. Pipko, V. Ya. Pliskovskii, and E. A. Penchko, Construction and Calculation of Vacuum Systems [in Russian], Moscow (1979).
5. F. Dumont and J. Morris, Construction and Design of Vacuum Systems, D. V. Karetnikov, R. Ya. Kucherov, and I. S. Mosevitskii (eds.) [Russian translation], Moscow (1971), pp. 84-90.