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INTERACTION OF TANTALUM WITH GASES

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Kinetics of tantalum degassing by vacuum extraction of gases of heated metal in temperature range 1675—2275 K is studied. Main component of the gases that separated from metal is nitrogen. The dependence for determination of the residual content of nitrogen in degassed tantalum is obtained. It was established that during heating in the temperature range 1825—1875 K tantalum maximally absorbs oxygen and nitrogen.
Keywords: tantalum, gas desorption, degassing, mass transfer, impurity.

ВЗАИМОДЕЙСТВИЕ ТАНТАЛА С ГАЗАМИ

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Вакуумной экстракцией газов нагретого металла в диапазоне температур 1675—2275 К изучена кинетика дегазации тантала. Основной составляющей выделившихся газов является азот. Получены закономерности, позволяющие определить остаточное содержание азота в дегазируемом тантале. Установлено, что при нагреве тантала в температурном интервале 1825 — 1875 К происходит максимальное поглощение танталом азота и кислорода.
Ключевые слова: тантал, газовыделение, дегазация, массоперенос, примесь.

ВЗАЄМОДІЯ ТАНТАЛУ З ГАЗАМИ

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Вакуумною екстракцією газів нагрітого металу в діапазоні температур 1675—2275 К вивчена кінетика дегазації танталу. Основною складовою газів, що виділилися, є азот. Отримані закономірності, що дозволяють визначити залишковий вміст азоту в танталі, що дегазується. Встановлено, що при нагріванні танталу в температурному інтервалі 1825—1875 К відбувається максимальне поглинання танталом азоту і кисню.
Ключові слова: тантал, газовиділення, дегазація, масоперенесення, домішка.

For some industrial sectors tantalum with low gas saturation is required. There are no methods of influence on the content of gases in products from tantalum in the process of their receipt. Therefore task of development of degassing methods of tantalum arises and so the study of the kinetics of tantalum degassing is of scientific and practical interest.

Absorption and desorption reactions of diatomic gases from metals can proceed by a mechanism shown schematically in Fig. 1. Thus it is possible to distinguish the following stages:

I. Transfer of gaseous molecule through gas phase to the metal surface followed by the physical adsorption of molecule.
II. Dissociation of gas molecule with simultaneous chemisorption of gas atoms.
III. Transition of atom through the surface of the metal.
IV. Diffusion of gas atom into the crystal lattice.

During degassing these stages are repeated in reverse order. In most cases degassing is carried out in a high vacuum where the pressure from the initial value p_0 corresponding to the initial concentration c_0 is reduced to the pressure p' which is determined by the desorption of gas from the metal, inleakage of the gas through apparatus leak, separating the gas from the walls and pumping speed of the pumps.

Concept of gas desorption as the characteristic function of the material can only be used in such regime vacuumization in which the adsorbed molecules impeding diffusion of dissolved gases from the volume of the material are absent.

This is achieved by long time vacuumization of system or its high speed pumping. Gas diffusion from solid body will begin after removal

process of gas molecules from the volume of the vacuum system and the desorption gases from layer adsorbed on the surface.

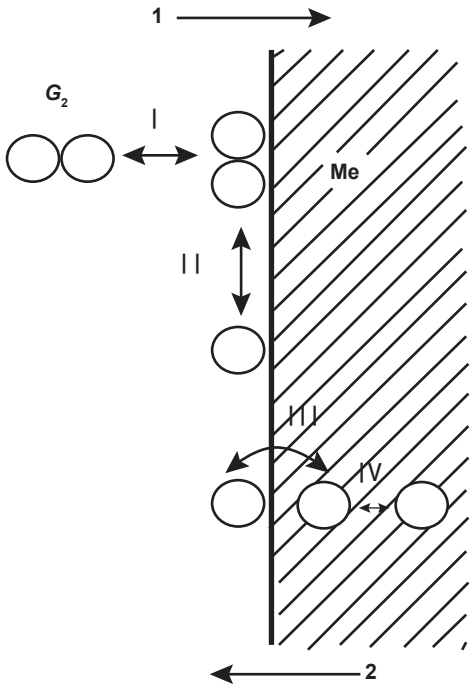

Fig. 1. The reversible absorption and desorption of a diatomic gas: 1 — dissolution; 2 — degassing

To study the kinetics of degassing the vacuum extraction method of gases from the heated metal was used with the measurement of the partial pressure of the desorbed gases and analysis of their composition by mass spectrometric meter of partial pressures IPDO- 2. Experiments were carried out in the temperature range 1675—2275 K. Samples of industrial tantalum of 0.05 mm thickness were used. Samples were placed in a chamber with an oil-free pumping system allowing to obtain the ultimate vacuum $6.6 \cdot 10^{-7}$ Pa. Heating of the sample was carried out by passing current through it.

At certain intervals pressure of desorbed gases was fixed to a constant pressure in the system which conditionally taken as equilibrium pressure. Changing the partial pressures of the main gases separating from tantalum at high temperatures is shown in Fig. 2. Analysis of composition of gases separated from tantalum revealed that one of the main components of the gas phase is nitrogen. Fig. 3 shows the results of measurement of the partial pressure of nitrogen with time.

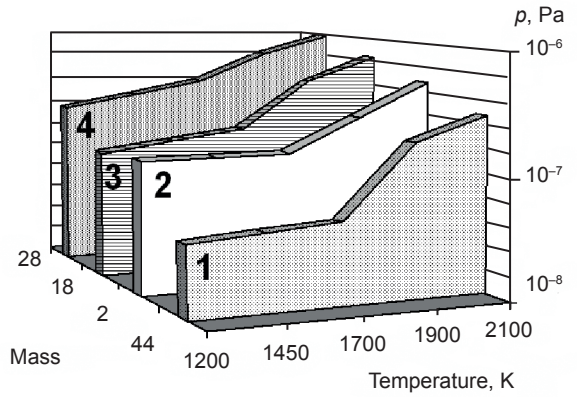

Fig. 2. Changing the partial pressures of gases when heated tantalum: 1 — CO_2; 2 — H_2; 3 — H_2O; 4 — $CO + N_2$

It is known [1—3] that the kinetics of gas desorption from metals satisfactorily described by the equation of Fick's law in the form

$$\ln \frac{p - p'}{p - p_0} = k \frac{F}{V} \tau , \qquad (1)$$

where p_0, p', p — initial, current and equilibrium pressure, mm Hg; F — area, cm^2; V — volume, cm^3; k — mass transfer coefficient, cm/s; τ — process duration, s.

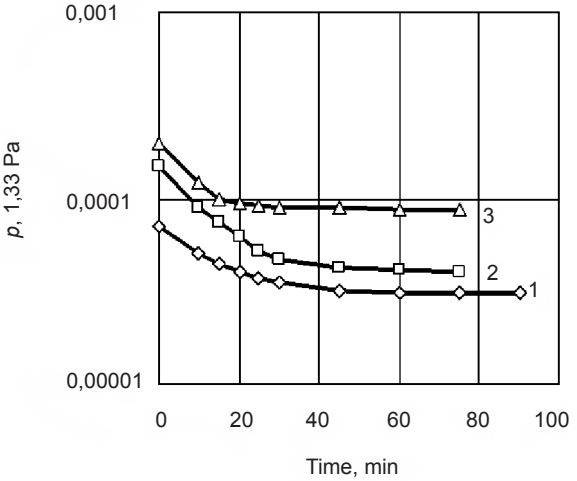

Fig. 3. Changing the partial pressure of nitrogen with time at different temperatures: 1 — 1675 K; 2 — 1825 K; 3 — 2075 K

To determine the mass transfer coefficient of nitrogen in tantalum the data shown in Fig. 3 were used in accordance with equation (1). To do this dependence [2] was used:

$$\ln \left(1 - \frac{p'}{P_p} \right) = -A\tau . \qquad (2)$$

Value of the coefficient A in equation (2) was determined by the method of least squares and then the mass transfer coefficients were calculated $k = AV/F$. Results of calculation are shown in Table [4, 5].

Table

Mass transfer coefficients of nitrogen in tantalum

T, K	$k \cdot 10^4$, cm/s
1675	0.028 — 0.032
1875	0.047 — 0.057
2075	0.065 — 0.072
2275	0.091 — 0.097

Temperature dependence of mass transfer coefficient of nitrogen for industrial samples of tantalum is described by equation:

$$\ln k = -8.35 - 7270.5/T .$$

The activation energy for the process of removing nitrogen from tantalum is 60490.6 J/mol which is consistent with the data of [3].

Small values of mass transfer coefficient and insignificant their dependence on temperature give reason to assume that limiting stage in the process of nitrogen removal under these conditions is the recombination of nitrogen atoms on the metal surface in N_2 and subsequent desorption of N_2 in gas phase.

Knowing the value of mass transfer coefficient of nitrogen, the geometric dimensions of the samples and the initial nitrogen content we can calculate the residual content of this impurity at the vacuum degassing by formula describing the kinetics of gas desorption:

$$\ln \frac{c - c'}{c - c_0} = k \frac{F}{V} \tau , \qquad (3)$$

where c, c', c_0 — equilibrium, current and initial concentrations of impurities in the metal.

The obtained experimental results are of great practical importance because they allow to determine the residual content of nitrogen at vacuum degassing tantalum for any period of time.

Character of interaction tantalum with residual gases in the vacuum chamber at heating temperatures up to 2400 K was investigated by measuring residual electrical resistivity [6, 7]. Dependence of relative residual electrical resistivity RRR = R (300 K) / R (4.5 K) on annealing temperature of tantalum is shown in Fig. 4. Annealing at 1875 K causes a decrease in the value of RRR that indicates about maximum absorption of gases by tantalum in said temperature regime. Degassing occurs at temperatures above 1875 K: adsorption becomes very small resulting in the boundary concentration of atoms becomes less than the concentration of the gas atoms in the metal, whereby the diffusion flow is directed toward surfaces [4].

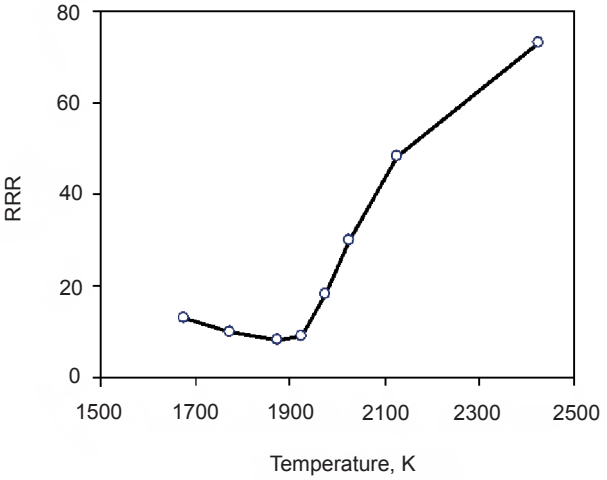

Fig. 4. Dependence of RRR on annealing temperature

In order to determine temperatures of maximum absorption of nitrogen and oxygen by tantalum the investigated sample of technical purity tantalum (RRR = 16, Hμ = 1700 MPa) was heated in a vacuum $6.6 \cdot 10^{-4}$ Pa to a certain temperature and then the chamber was filled with nitrogen or oxygen. Character of interaction of tantalum with these gases was investigated by methods of measuring relative residual resistivity RRR and microhardness. Fig. 5 shows the relative change RRR on annealing temperature of tantalum samples in

vacuum at a partial pressure of nitrogen $1.5 \cdot 10^{-3}$ Pa which shows that at the temperature 1825 K the maximum absorption of nitrogen by tantalum occurs. Above the temperature 1825 K adsorption is reduced and degassing is increased. Degassing rate obeys the equation of the second order [3]. Significant degassing in the case of nitrogen removal occurs at an annealing temperature of 1875 K and above.

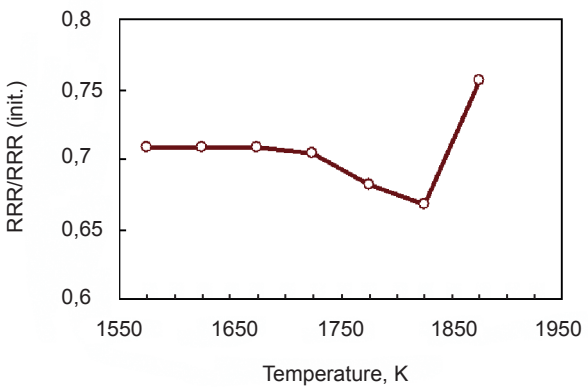

Fig. 5. Dependence of the relative change RRR tantalum on the annealing temperature at a partial pressure of nitrogen in the chamber $1.5 \cdot 10^{-3}$ Pa

Increasing the oxygen partial pressure in the chamber at the same temperature and holding time increases the dissolution of oxygen in tantalum. At 1875 K and the oxygen partial pressure $7.3 \cdot 10^{-4}$ and $15 \cdot 10^{-3}$ Pa relative residual resistivity of samples is 13 and 9, respectively.

Microhardness of tantalum samples after annealing at 1875 K and $1.5 \cdot 10^{-3}$ Pa of oxygen within 5 and 10 minutes is 2700 and 3900 MPa. Further increase of the annealing time does not lead to significant increase microhardness due to filling the metal surface by oxygen atoms. Degassing of tantalum samples at 1875 K and $1.5 \cdot 10^{-3}$ Pa of nitrogen within 5 and 10 minutes leads to a reduction of microhardness up to 1600 and 1500 MPa, respectively. Simultaneously with the nitrogen removal the oxygen absorption occurs and after 15 minutes the absorption process dominates over degassing that is expressed in the value of microhardness of 1700 MPa.

Microhardness data are well correlated with the data on the measurement of RRR (RRR decreases in 1.43 and 1.22 times compared with RRR of initial samples at annealing within 5 and 10 minutes and in 1.24 times at annealing within 15 minutes) [7].

Thus during heating of tantalum in vacuum there are two competing phenomena. On the one hand it is the increasing solubility of gases in the metal caused by expansion of crystal lattice with increasing temperature; on the other hand the decrease of adsorption reduces the solubility. Below the temperature of 1875 K the first factor affects more, at higher — the second factor. Minimum value of the relative resistivity and the maximum value of microhardness at a heating temperature of 1875 K can be explained by the presence in tantalum the maximum amount of dissolved gases.

The maximum absorption of nitrogen and oxygen by tantalum occurs in the temperature range 1825—1875 K. The beginning of this interval corresponds to the maximum absorption of nitrogen, and its ending characterized by the fact that at this temperature the maximum oxygen absorption and significant nitrogen removal occurs. At temperatures above 1875 K degassing mainly occurs: adsorption becomes very small resulting in the boundary concentration of atoms becomes less than the concentration of the gas atoms in the metal, whereby the diffusion flow is directed toward surface.

CONCLUSIONS

At research the temperature dependence of the mass transfer coefficient of nitrogen in tantalum was installed and the equation for calculating the residual nitrogen at the vacuum degassing of tantalum was determined. Process of interaction of tantalum with residual gases in vacuum was studied. It was established that in the temperature range 1825—1875 K tantalum maximally absorbs nitrogen and oxygen. Above 1875 K degassing of tantalum occurs mainly.

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