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DIFFUSION OF HYDROGEN IN HAFNIUM AND TITANIUM

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We measured the coefficients of diffusion of hydrogen in the hydride phases of hafnium and titanium at 1073-1273°K on the basis of the solutions of Fick's second law for diffusion in a finite cylinder and in a sector of it.

Hafnium is one of those scattered rare metals which have become important in industry during the past 25 years. In the interaction of hydrogen with hafnium, at least three phases are formed: if the hydrogen content is low, there is an α-solid solution; in addition, there are two other phases of variable composition — a nonstoichiometric dihydride and a β-solid solution. Data on hydrogen diffusion are necessary for the establishment of well-grounded conditions in the thermovacuum processing of metals, the production of hafnium hydrides, the manufacture of parts made from these, etc. [1, 2].

In the present study, we investigated the diffusion of hydrogen by the method of desorption into a vacuum with mass-spectrometric recording. The metal specimens consisted of disks of "iodide" hafnium 1 cm in diameter and 0.4 cm thick; after cutting, they were washed with ethyl alcohol and air-dried. The experiments were conducted on a vacuum main (Fig. 1) combined with the admittance system of an MI-1305 mass spectrometer.

To calculate the diffusion coefficients, we used Fick's second law, and our solution for the diffusion of a gas in a finite cylinder for zero boundary conditions at constant initial concentration C_0 has the form

$$C(r,\ \varphi,\ z,\ t) = \frac{16C_0}{\pi} \sum_{\substack{i=1\\ m=0}}^{\infty} \frac{J_0\left(\frac{\mu_0^i}{R} r\right)}{(2m+1)(\mu_0^i)^2} \sin\frac{\pi(2m+1)}{l} z \exp\left\{-\left[\left(\frac{\mu_0^i}{R}\right)^2 + \frac{\pi^2(2m+1)^2}{l^2}\right] Dt\right\}. \quad (1)$$

The zero boundary conditions were ensured by constant pumping of the gas from the volume V above the specimen. Taking account of the fact that the experimentally measured quantity was not the concentration of the gas inside the specimen but the pressure of the gas generated, we solved the differential equation for the "balance" of the gas [3]

$$dQ_{\mathrm{rel}}/dt = V \cdot dp/dt + pF \quad (2)$$

and obtained

$$p = \frac{1}{V} \exp\left(-\frac{F}{V} t\right) \int \frac{dQ_{\mathrm{rel}}}{dt} \exp\left(\frac{F}{V} t\right) dt. \quad (3)$$

Since $Q_{\mathrm{rel}} = Q_0 - Q(r,\ \varphi,\ z,\ t)$, it follows that $dQ_{\mathrm{rel}}/dt = -dQ(r,\ \varphi,\ z,\ t)/dt$. The quantity $Q(r,\ \varphi,\ z,\ t)$, in turn, is given by the formula

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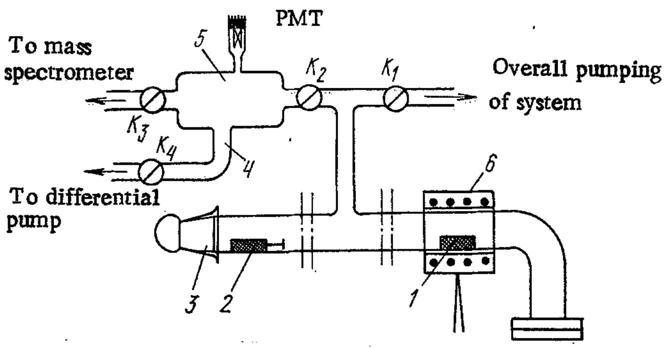

Fig. 1. Theoretical scheme of the vacuum apparatus: 1) specimen; 2) magnetic push-rod; 3) ground-glass plug; 4) channel with calculated pumping admittance; 5) calibrated intermediate space; 6) heater; K_1-K_4) vacuum valves.

$$Q(r, \varphi, z, t) = \int_0^R \int_0^{2\pi} \int_0^l rC(r, \varphi, z, t)\, dr d\varphi dz =$$

$$= \frac{32C_0R^2l}{\pi} \sum_{\substack{i=1\\m=0}}^{\infty} [(\mu_0^i)(2m+1)]^{-2} \exp\left\{-\left[\left(\frac{\mu_0^i}{R}\right)^2 + \frac{(2m+1)^2\pi^2}{l^2}\right] Dt\right\}. \tag{3'}$$

The last expression is a series which converges rapidly (by d'Alembert's principle). We shall use its first term; then Eq. (3) can be written in the form

$$p = \frac{32C_0DR^2l\,[(\mu_0^1)^2 l^2 + \pi^2R^2]}{\pi(\mu_0^1)^2\{FR^2l^2 - [(\mu_0^1)^2l^2 + \pi^2R^2]\,DV\}} \times$$

$$\times \left\{\exp\left[-\left(\left(\frac{\mu_0^1}{R}\right)^2 + \frac{\pi^2}{l^2}\right) Dt\right] - \exp\left[-\frac{F}{V}\, t\right]\right\}; \quad \mu_0^1 = 2.405. \tag{4}$$

The zero boundary conditions require that the pumping of the gas from the surface be carried out much faster than the diffusion of the gas within the specimen. In this case we must satisfy the inequality

$$\exp\left\{-\left[\left(\frac{\mu_0^1}{R}\right)^2 + \frac{\pi^2}{l^2}\right] Dt\right\} \gg \exp\left(-\frac{F}{V}\, t\right). \tag{5}$$

This is achieved for a given pumping rate and given dimensions of the vacuum system by an appropriate choice of the geometry of the specimens.

From (5) it follows that the second exponent in (4) can be disregarded. Then, taking the logarithm of (4), we obtain the equation of a straight line

$$\ln p = \text{const} - \left[\left(\frac{\mu_0^1}{R}\right)^2 + \frac{\pi^2}{l^2}\right] Dt, \tag{6}$$

and from the tangent of the angle of inclination of this line we can calculate the diffusion coefficient

TABLE 1. Coefficients and Parameters of the Diffusion of Hydrogen in Hafnium

T, °K	No. of meas.	$D_{av} \cdot 10^5$	$W=\sigma/D_{av}$	D_0	E	C_0, at. %
1073	5	2,29	6,1	$3,1 \cdot 10^{-3}$	43,8	1,51
1173	3	3,52	1,3			1,51
1273	4	5,00	3,6			1,51
1073	3	0,51	21,0	$3,5 \cdot 10^{-2}$	79,4	56,9
1173	4	1,03	8,0			56,9
1273	5	1,73	8,9			56,9

TABLE 2. Experimental Parameters of the Diffusion of Hydrogen in Hydrided Titanium

T, °K	$D_{av} \cdot 10^6$	$W=\sigma/D_{av}$	D_0	E
1073	2,46	13,5	$6{,}57 \cdot 10^{-4}$	49,4
1173	4,43	11,0		
1273	6,02	15,0		

$$D = \frac{R^2 l^2}{(\mu_0^1)^2 l^2 + \pi^2 R^2} \operatorname{tg} \eta. \tag{7}$$

In our experiments the pressure of the gas being generated was characterized by the value of the ion current corresponding to the second atomic unit of mass. Therefore tan η was determined from the relation $\ln I_{H_2} = f(t)$. The results of the measurements of the hydrogen diffusion in the initial and hydrided hafnium are shown in Table 1. The metal hydride was obtained by heating the specimens for 12 h in a hydrogen atmosphere at 1278°K and normal pressure.

According to the phase diagram of the hafnium–hydrogen system, the material of the primary specimens was an α-solid solution, from which, after primary diffusion measurements and subsequent saturation with hydrogen, we obtained the nonstoichiometric dihydride HfH_{2-x}. The resulting diffusion coefficients were in the initial and hydrided specimens; the corresponding values are shown in Table 1.

Up to the present time, the diffusion of hydrogen in hafnium has been studied experimentally only by Khodosov et al. [4, 5]. They stated the results of investigations made by the NMR method for −160 and +240°C for HfH_x, where $x = 1.35$–1.98 and the diffusion activation energy values are 8.3-19.5 kcal/mole, which is close to our data for the corresponding compositions.

Hydride Phase of Titanium. The combination of valuable physical properties and good workability have led to the widespread use of titanium in the leading branches of today's industry [6].

Metallic titanium has two thermodynamically stable phases, α and β, the latter of which is stable above 1155.5°K. Hydrogen, like all penetrating impurities, has a significant effect on many properties of titanium. For example, it sharply reduces the impact ductility of titanium. Titanium absorbs hydrogen even at room temperature, with a maximum at 573°K. Hydrogen stabilizes the β phase, but it is incapable of fixing the tempering because the eutectoid reaction is extremely rapid. In addition to the α- and β-solid solutions, there is also a nonstoichiometric hydride TiH_{2-x}, which has a wide range of nonstoichiometricity, especially at high temperatures [7-11]. Obviously, the study of hydrogen diffusion requires taking account of the fairly complicated phase diagram of the metal–hydrogen system.

Method of Measurements. We measured the coefficients of diffusion of hydrogen in "iodide" titanium previously saturated with hydrogen at 1273°K for 11 h at 1 atm. The specimens, which had the shape of sectors of disks with a radius of 1 cm, a thickness of 0.3 cm, and an angle of π/2, were analyzed on a very simple vacuum apparatus with no mass spectrometer. Before the measurements, we determined that only hydrogen was released from the titanium when it was heated, and therefore its pressure was fixed directly by a manometer sensor.

To calculate the diffusion coefficients, we solved the Fick equation for a cylindrical sector

$$C(r,\ \varphi,\ z,\ t) = \frac{32C_0}{\pi} \sum_{\substack{m=0 \\ i=1}}^{\infty} \frac{\Gamma(n)\left(\frac{2}{\mu_n^i}\right)^n J_n\left(\frac{\mu_n^i}{R} r\right)}{(2m+1)\,\varphi_0\,(n+2)} \sin(n\varphi) \sin\frac{\pi(2m+1)}{l} z \exp\left\{-\left[\left(\frac{\mu_n^i}{R}\right)^2 + \frac{\pi^2(2m+1)^2}{l^2}\right] Dt\right\};$$
$$n = \frac{\pi(2k+1)}{\varphi_0};\quad k = 0,\ 1,\ \ldots,\ \infty. \tag{8}$$

Taking $\varphi_0 = \pi/2$ and making use of the first term of series (8), we obtain

TABLE 3. Parameters of the Diffusion of Hydrogen in Titanium according to Literature Data

T, °K	D_0	E	Literature source
1129—1488	$4{,}4\cdot10^{-4}$	48,0	[12]
723—1123	$5{,}2\cdot10^{-5}$	37,6	[13]
973—1173	$2{,}7\cdot10^{-3}$	59,4	[14]

$$C_1(r,\ \varphi,\ z,\ t)=\frac{8C_0}{\pi^2}\left(\frac{r}{R}\right)^2\sin 2\varphi\sin\frac{\pi z}{l}\exp\left\{-\left[\left(\frac{\mu_2^1}{R}\right)^2+\frac{\pi^2}{l^2}\right]Dt\right\};\quad \mu_2^1=5.136. \tag{9}$$

The gas "balance" equation was solved in an analogous manner for hafnium, and its solution has the form

$$p=\frac{4C_0DR^2l\,[(\mu_2^1)^2l^2+\pi^2R^2]}{\pi^3\,[FR^2l^2-\{(\mu_2^1)^2\,l^2+\pi^2R^2\}\,DV]}\exp\left\{-\left[\left(\frac{\mu_2^1}{R}\right)^2+\frac{\pi^2}{l^2}\right]Dt=\frac{4C_0R^2lV}{\pi^3F}\exp\left\{-\left[\left(\frac{\mu_2^1}{R}\right)^2+\frac{\pi^2}{l^2}\right]Dt\right\}\operatorname{tg}\eta. \tag{10}$$

The working formula for finding the diffusion coefficient has the form

$$D=\frac{R^2l^2}{(\mu_2^1)^2\,l^2+\pi^2R^2}\operatorname{tg}\eta. \tag{11}$$

Table 2 shows the results of the measurements of the coefficients of diffusion of hydrogen in hydrided titanium at 1073-1273°K, each result being the average of three measurements. The diffusion coefficients obtained were used for calculating the initial concentration of hydrogen in the specimens investigated. In the present case the value of C_0 was 52.5 at.% of hydrogen in the titanium. According to the phase diagram of the titanium—hydrogen system [7], this corresponds to nonstoichiometric TiH_{2-x}. The good agreement of our results with the data of [12-14] (Table 3) enabled us to assume that the authors of [12-14] also worked with hydrided titanium in which the hydrogen concentration was ≈50 at.%.

It should be noted that we verified the correctness of the method by using the example of nickel, concerning which there are objective diffusion data available today [15]. The maximum discrepancy between our measured coefficients and the objective coefficients of the diffusion of hydrogen in nickel was only 25%.

In conclusion, it should be noted that the values obtained for the diffusion characteristics are entirely consistent with the existing system of temperature relations for ten transition metals [16].

NOTATION

C_0, initial concentration of gas in the metal, $\mathrm{ncm^3/cm^3_{Me}}$; $C(r, \varphi, z, t)$, instantaneous gas concentration in the finite cylinder; i, k, m, n, ordinal numbers (indices); $J_n(\mu_n^i r/R)$, Bessel function of order n; μ_n^i, i-th root of the Bessel function of order n; R, l, radius and thickness of the specimen, cm; D, diffusion coefficient, $\mathrm{cm^2/sec}$; t, time, sec; V, calibrated volume above specimen, $\mathrm{cm^3}$; F, admittance of gas pumping channels, $\mathrm{ncm^3/sec}$; dQ_{rel}/dt, rate of gas release, $\mathrm{ncm^3/sec}$; p, pressure of released gas, torr; dp/dt, change in released-gas pressure per unit time, torr/sec; tan η, tangent of the angle of inclination of the straight line in equation (6), 1/sec; I_{H_2}, ion current of hydrogen; $\Gamma(n)$, gamma function; W, coefficient of variation, %; σ, mean-square deviation; D_0, preexponent, $\mathrm{cm^2/sec}$; E, activation energy, kJ/mole; T, absolute temperature of specimens; B, universal gas constant, kJ/deg•mole.

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EXPERIMENTAL INVESTIGATION OF THE ELECTRICAL CONDUCTIVITY OF A TWO-PHASE STREAM

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We consider the question of the effective electrical conductivity of a bubbling stream, for which a computation relation is proposed. We give the results of the experiment.

Two-phase streams of an electrically conductive liquid with bubbles of a gas which is not electrically conductive (bubbling streams) appear to have come into widespread use in the liquid-metal MHD generators of self-contained power installations [1-3].

To perform the calculations for an MHD channel with a bubbling stream of working substance, we must know the variation of the electrical conductivity as a function of the amount of the gaseous phase per unit volume. Literature [4-6] contains some well-developed methods for calculating the coefficients of generalized conductivity of heterogeneous structures in which the concentrations of the components present are expressed by functions $C_i = f_i(x, y, z)$.

The distinguishing feature of bubbling streams is the interaction of the interface between the phases with turbulent pulsations of the carrying phase. The problem of determining the conductivities in a bubbling stream is complicated further by the fact that the gas bubbles may be in chaotic motion in the stream, may have arbitrary shape, and may be deformed, pulsate, break up, and coagulate. The result is that the stream parameters become nonstationary; e.g., the concentration of bubbles is expressed by the function $C = C(x, y, z, t)$, and we must obtain a space—time average. Furthermore, bubbling streams

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