The influence of the Gorsky effect on diffusion of the hydrogen and the formation of microcracks in vanadium films

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ABSTRACT

Diffusion of the hydrogen in the vanadium film in the presence of mechanical stresses produced by the inhomogeneous initial distribution of the hydrogen was investigated. Namely, the Gaussian distribution of hydrogen in the middle of the film was stated initially. Diffusion in the inhomogeneous field of mechanical stresses created by the hydrogen in the saturated places of the film was calculated. A strong dependence of the effective diffusion coefficient on the hydrogen concentration was revealed. We found critical concentrations of hydrogen, at which the accumulation of the hydrogen appeared in the part of the film with the highest concentration.. Since mechanical stresses increased strongly in places with large concentration of the hydrogen, it was assumed that microcracks were formed in these places of the sample. We compared results with our experimental data of diffusion of the hydrogen in the vanadium film.

The model

The influence of strains produced by the hydrogen on diffusion of the hydrogen were taken into account in the one-dimensional model of diffusion from an infinitely small layer in the middle of the infinite vanadium sample.

The diffusion flux of the hydrogen is equal to $\vec{j} = -Bc\vec{\nabla}\mu,\ B = \frac{D}{k_B T}$ is the mobility.

$$\text{If } \mu = \mu(c), \text{then } \vec{j} = -Bc\frac{\partial \mu}{\partial c}\vec{\nabla}c.$$

For small concentrations: $c \to 0\ \ \frac{\partial \mu}{\partial c} = \frac{k_B T}{c},\ \vec{j} = -D\vec{\nabla}c,$

$$\frac{\partial c}{\partial t} = D\Delta c. \quad (1)$$

If $\mu = \mu(c, \varepsilon_{ik})$, then $\mu(c, \varepsilon_{ik}) = \mu(c, 0) + \frac{\partial \mu(0, \varepsilon_{ik})}{\partial \varepsilon_{ik}},\ \ \vec{j} = -cB\left(\vec{\nabla}\mu(c, 0) + P\nabla\varepsilon_{ii}\right).\ P<0.$

$$P_{ik} = \frac{\partial \mu(0, \varepsilon_{ik})}{\partial \varepsilon_{ik}} = -c_{iklm}\frac{\partial \varepsilon_{im}}{\partial c}$$

$$\frac{\partial c}{\partial t} = D\Delta c - \frac{D \cdot P}{k_B T}\vec{\nabla}c\nabla\varepsilon_{ii} - \frac{D \cdot c \cdot P}{k_B T}\Delta\varepsilon_{ii}. \quad (2)$$

The Numerical solution of Eq. (2)

$$c_i^t = c_i^{t-1} + \eta\left(c_{i+1}^{t-1} - 2c_i^{t-1} + c_{i+1}^{t-1}\right) - \lambda\left(c_{i+1}^{t-1} - c_{i-1}^{t-1}\right) - v \cdot c_i^{t-1},\ i = 1, \ldots, n.$$

$$\eta = (D \cdot \Delta t)/(\Delta x)^2,\ \lambda = (D \cdot P \cdot \nabla\varepsilon_{ii} \cdot \Delta t)/(k_B \cdot T \cdot 2\Delta x),\ v = (D \cdot P \cdot \Delta\varepsilon_{ii} \cdot \Delta t)/(k_B \cdot T).$$

Calculated values

- $c(x,t)$ - the dependence of the concentration of the hydrogen on the coordinate and time.
- $X^2 = \frac{\int_0^L (x-\bar{x})^2 \cdot c(x,t)}{\int_0^L c(x,t)}$
- The dependence $X^2 \equiv \overline{(x-\bar{x})^2} = 2Dt$ was checked.

Parameters of calculations:

$D = D_0 e^{-\frac{U}{k_B T}},\ U$=0.045 eV, $D_0 = 3{,}1 \cdot 10^{-8}$ m²/s.

ε_{ii}=0,0633 per 1% (at.).

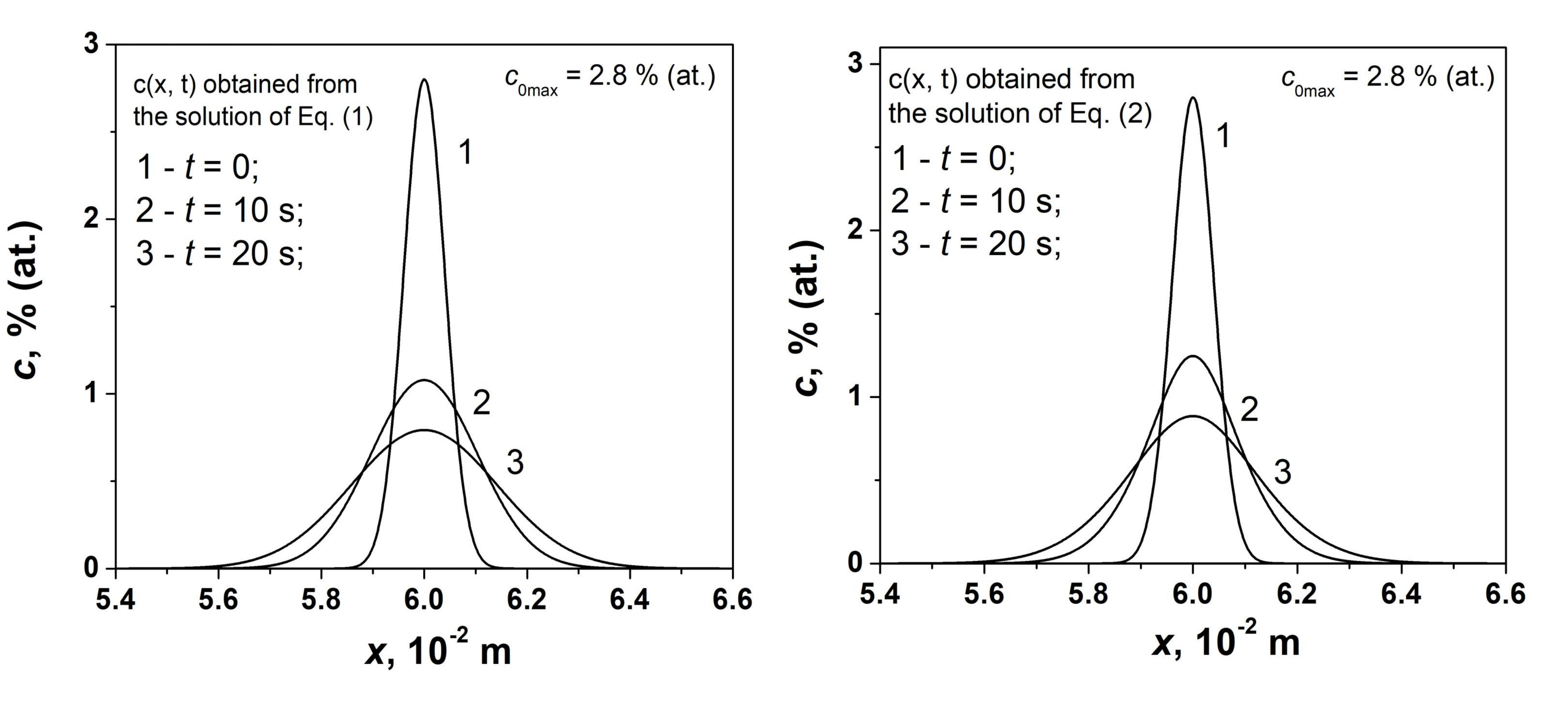
$P = 5.511 \cdot 10^{-19}$ J.

The length of the sample L = 12 cm.

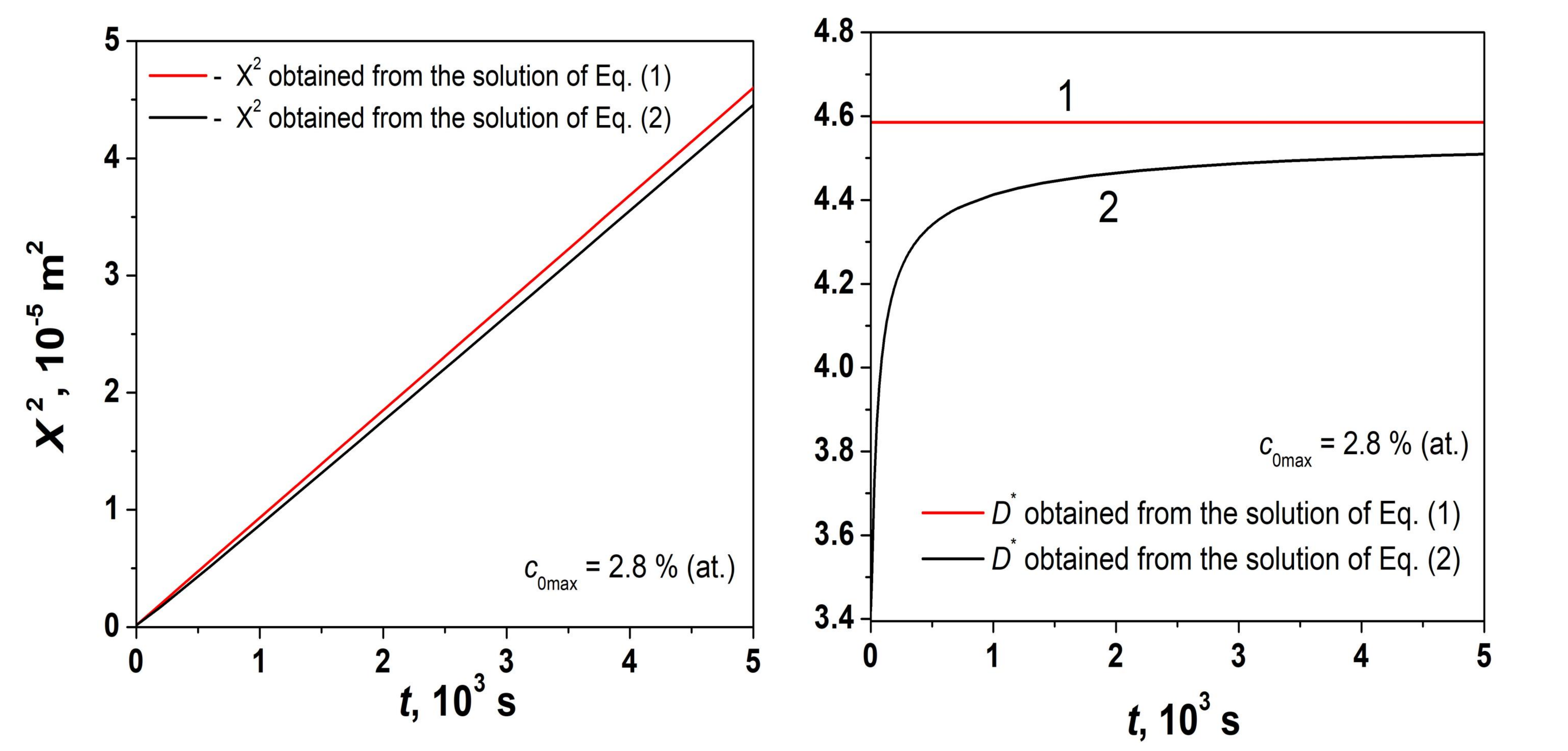
T = 273 K.

$D = 4.59 \cdot 10^{-9}$ m²/s $\Delta x = 10^{-5}$ m.

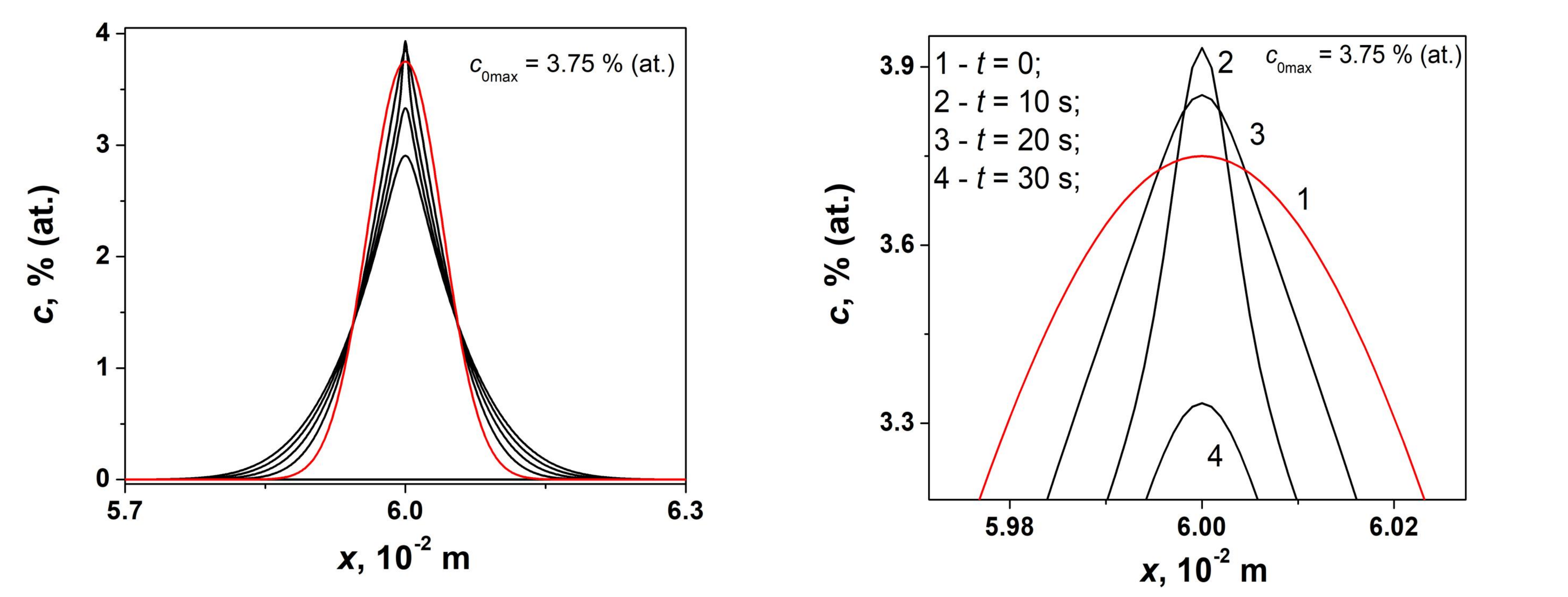
Spatial distributions of concentrations



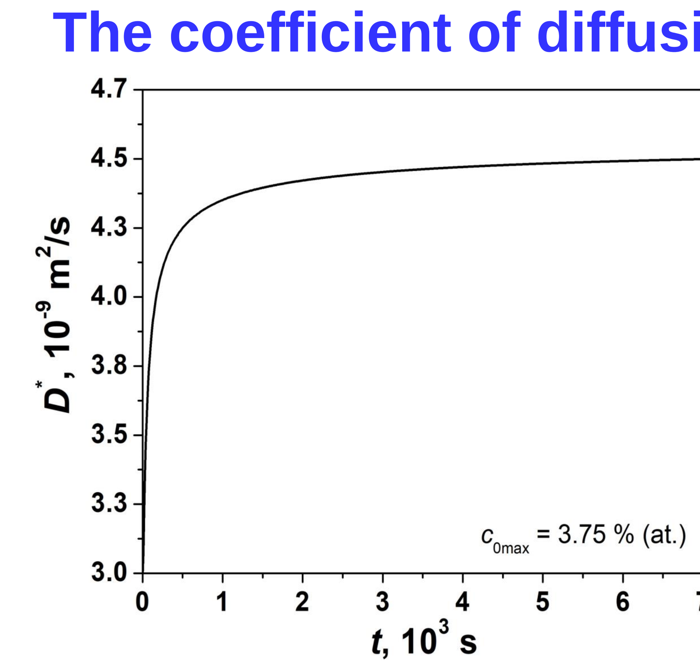
The coefficient of diffusion



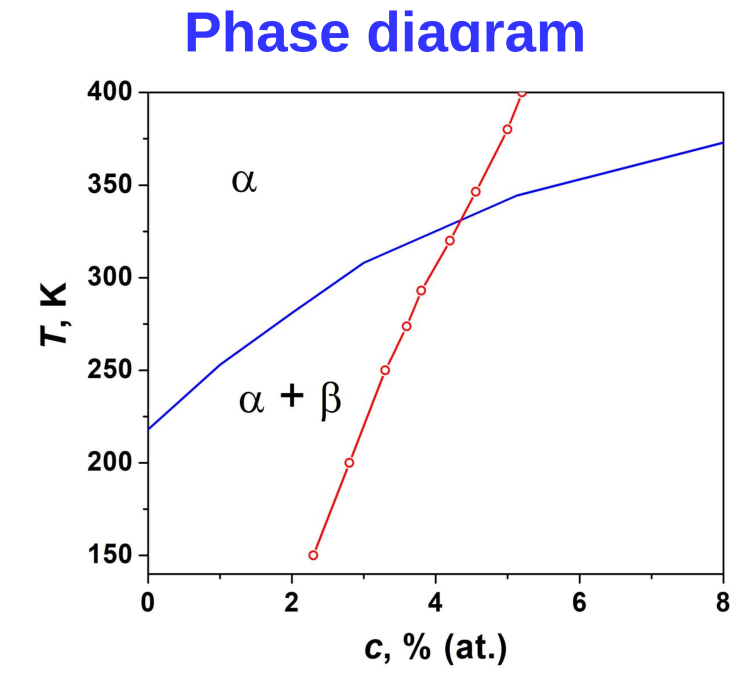
Diffusion near the concentration of the saturation



The coefficient of diffusion

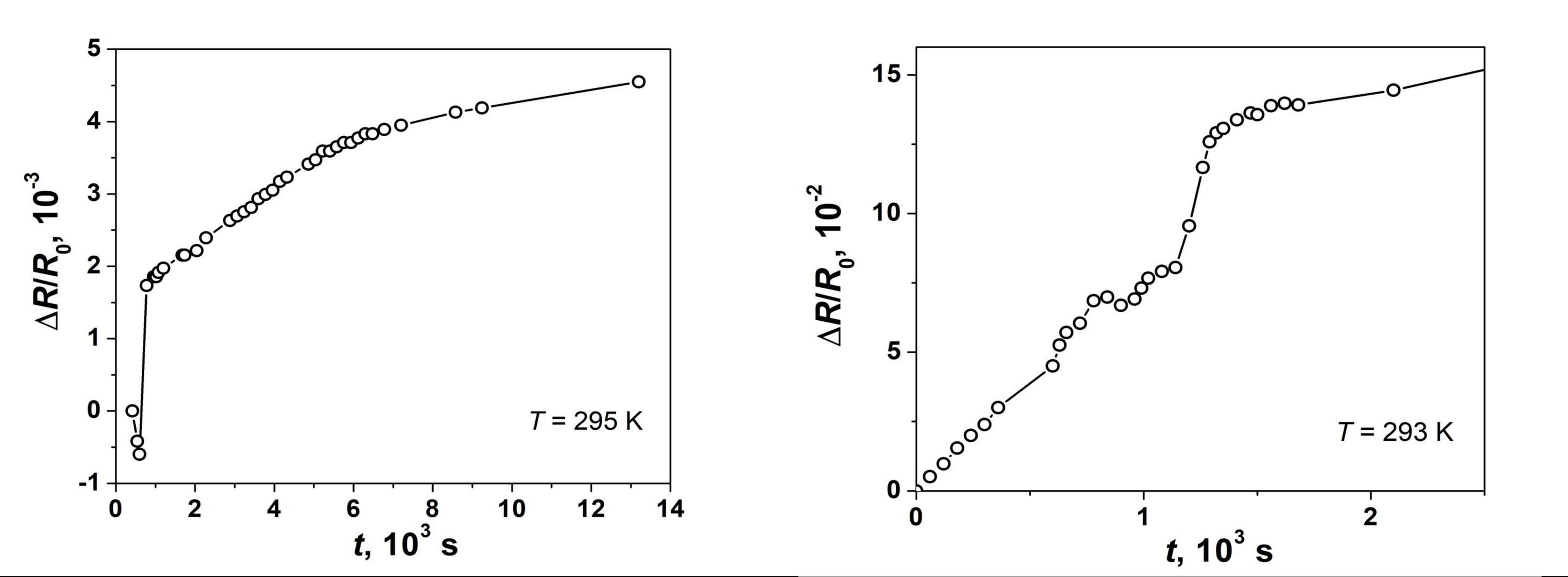


Phase diagram



The formation of microcracks during diffusion of the hydrogen

In the experiment about one half of the vanadium film was saturated by the hydrogen electrolytically. The normalized change of the electrical resistance $\Delta R/R_0$ of the non-saturated part of the film was measured as a function of time. Strong concentration stresses in the diffusion zone led to microcracks in the film.



CONCLUSONS

1. **We modeled one-dimensional diffusion of the hydrogen from an infinitely small layer in the middle of the infinite vanadium sample. The influence of strains produced by the hydrogen on diffusion were taken into account.**
2. **We found the strong dependence of the effective diffusion coefficient on time of diffusion. This means the concentration dependence of the diffusion coefficient. This dependence is explained by the influence of the Gorsky effect.**
3. **If the concentration of the hydrogen reaches some critical value, then the diffusion coefficient becomes so small that the concentration of the hydrogen begins in this place. However, this concentration is unreachable because the β- phase is formed at smaller concentrations of the hydrogen. Nevertheless, mechanical strains become strong and can lead to microcracks.**