# The influence of internal strains induced by the hydrogen on the electrical resistivity of the nanocrystalline vanadium film


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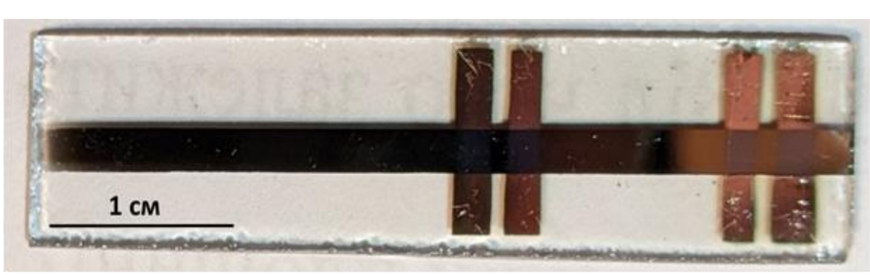
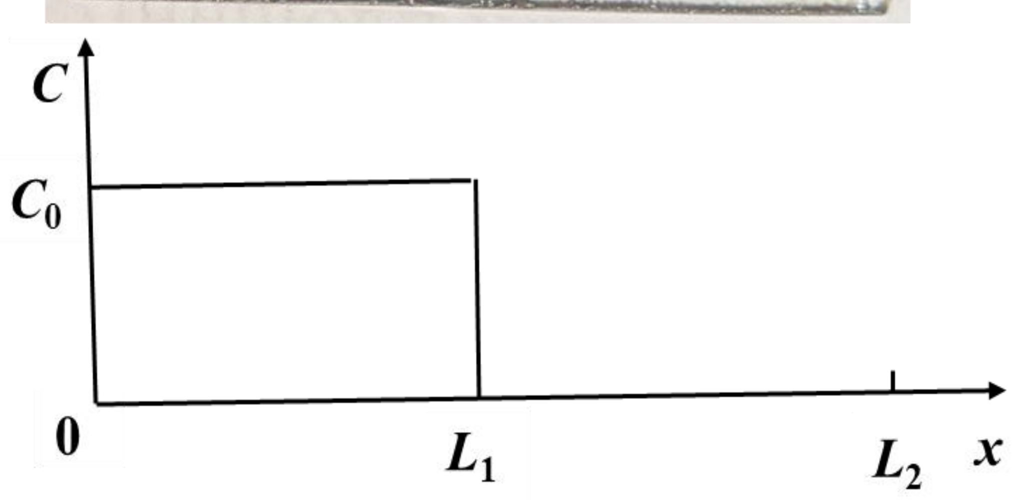
**ABSTRACT**

**Unusual changes of the electrical resistivity of a nanocrystalline vanadium film during diffusion of the hydrogen are found. A part of the film was saturated by hydrogen electrolytically. Changes in the electrical resistivity of another (non-saturated) part of the film due to diffusion of the hydrogen were measured as functions of time. The electrical resistivity of the non-saturated part of the film should increase during time of diffusion, but we found that the resistivity of the non-saturated part had a minimum, so the resistivity decreases to values smaller than those before the saturation. We supposed that the decrease of the resistivity was stipulated by strains produced by the hydrogen in the diffusion zone. These strains influence the diffusion process. We calculate distributions of concentrations along the quasi-one-dimensional vanadium sample taking into account mentioned strains and calculate changes of the electrical resistivity during time of diffusion. Results of this approximation are in good agreement with experimental data.**


## The experiment

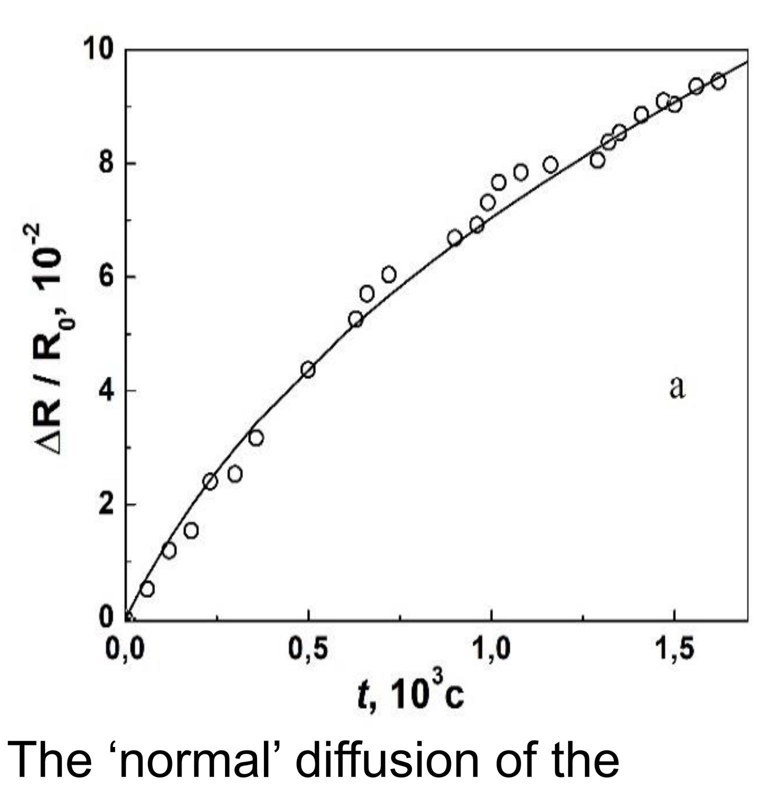




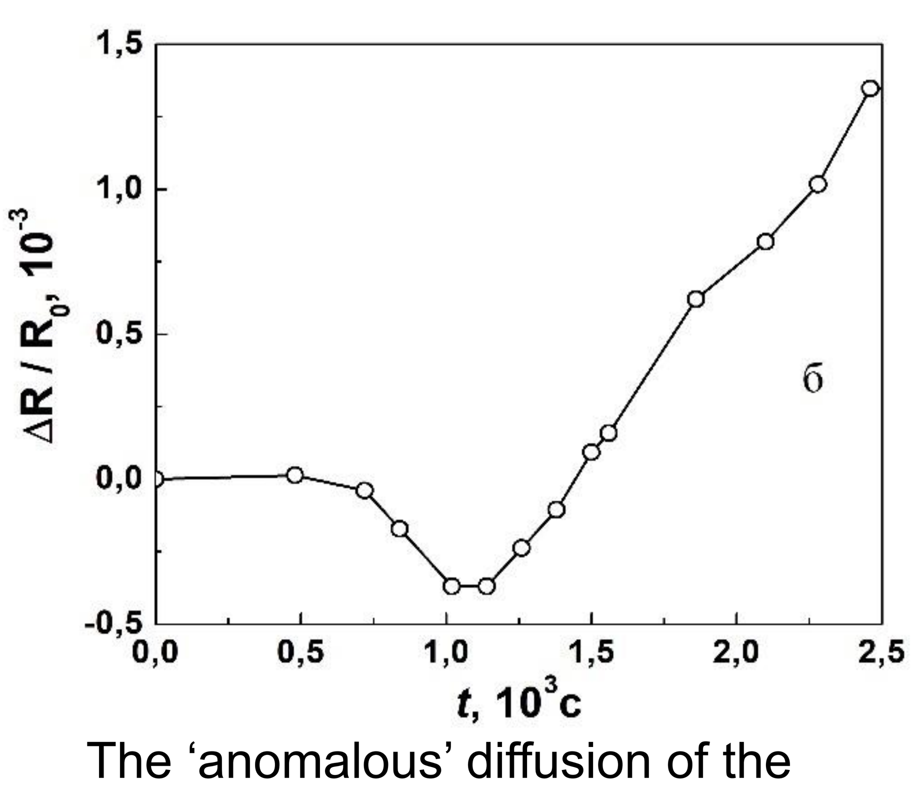

Tails of vanadium films were saturated by the hydrogen electrolytically. Normalized changes of the electrical resistivity $\Delta R/R_0$ of non-saturated parts of films were measured as functions of time.

$$\frac{\Delta R(t)}{R_0} = B\sum_{n=1}^{\infty}\left\{\frac{1}{n^2}\sin\left(\frac{\pi n L_1}{L_2}\right)\left(1-e^{-\frac{\pi^2 n^2 D t}{L_2^2}}\right)\right\} \quad (1)$$

Together with the 'normal' diffusion of the hydrogen there is 'anomalous' diffusion.




The 'normal' diffusion of the hydrogen at $T$=293 K. Solid line is the approximation by Eq. (1). $D = (1{,}1\pm0{,}2)\cdot10^{-10}$ m²/s.




The 'anomalous' diffusion of the hydrogen at $T$=293 K.

## The model

We supposed that the decrease of the electrical resistivity was stipulated by strains produced by the hydrogen in the diffusion zone. These strains influences the diffusion process.

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

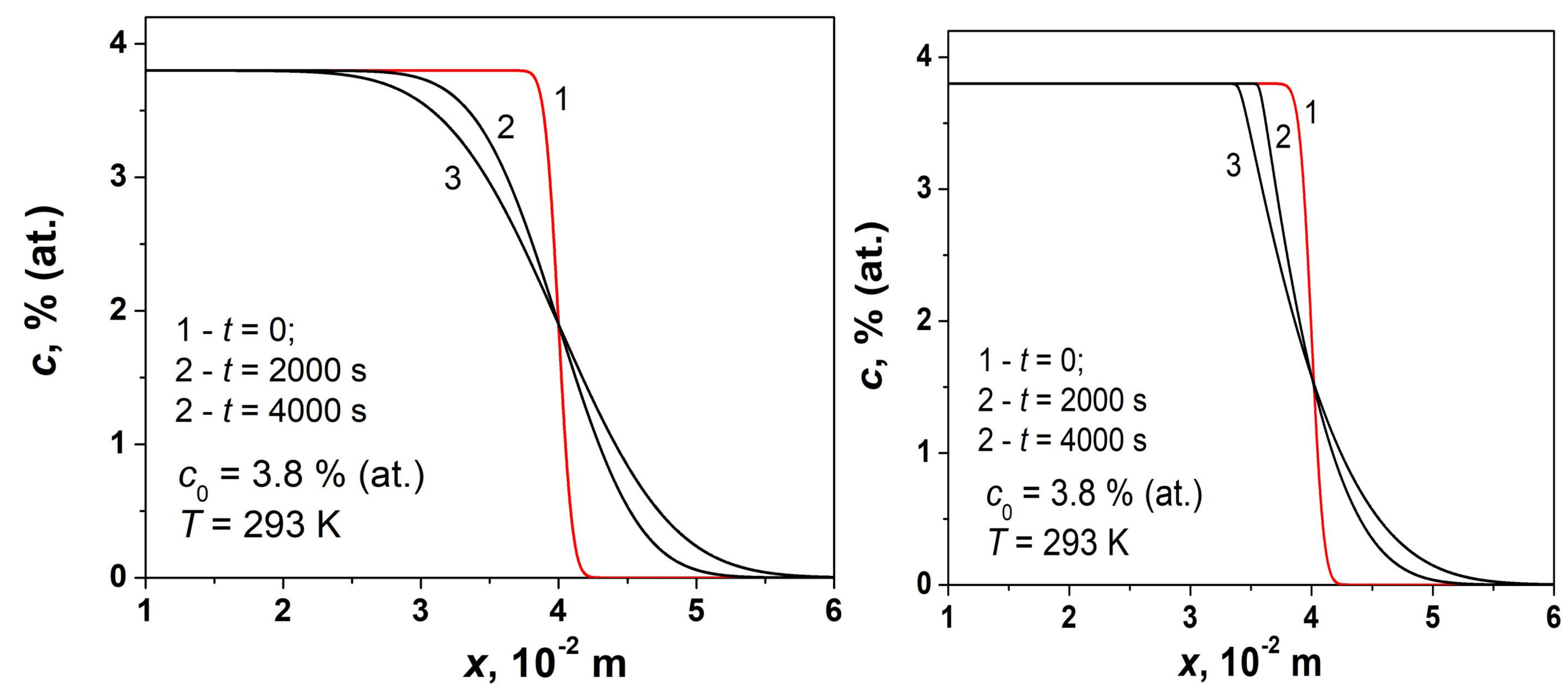
$$P_{ik} = -\frac{\partial\sigma_{ik}}{\partial c} = -c_{iklm}\frac{\partial\varepsilon_{im}}{\partial c}$$

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

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

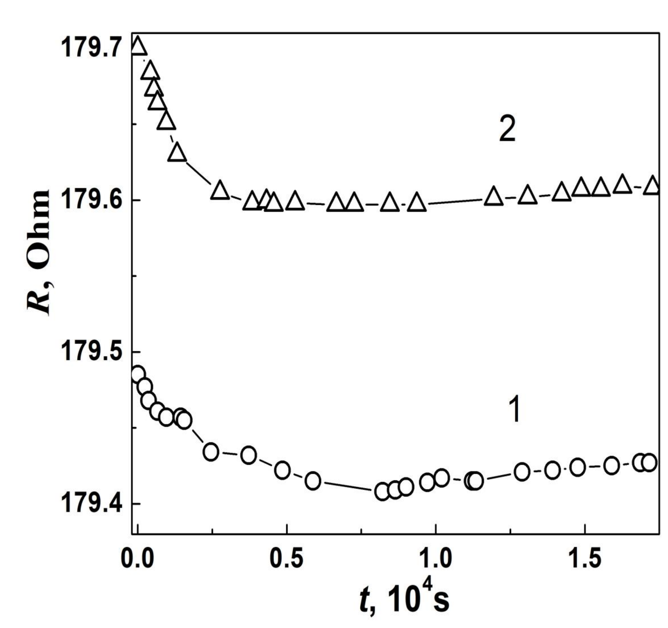
$$\frac{1}{R_0}\frac{dR}{d\varepsilon} = (1+2\mu) + \frac{1}{\rho_0}\frac{d\rho}{d\varepsilon}$$

## Spatial distributions of concentrations



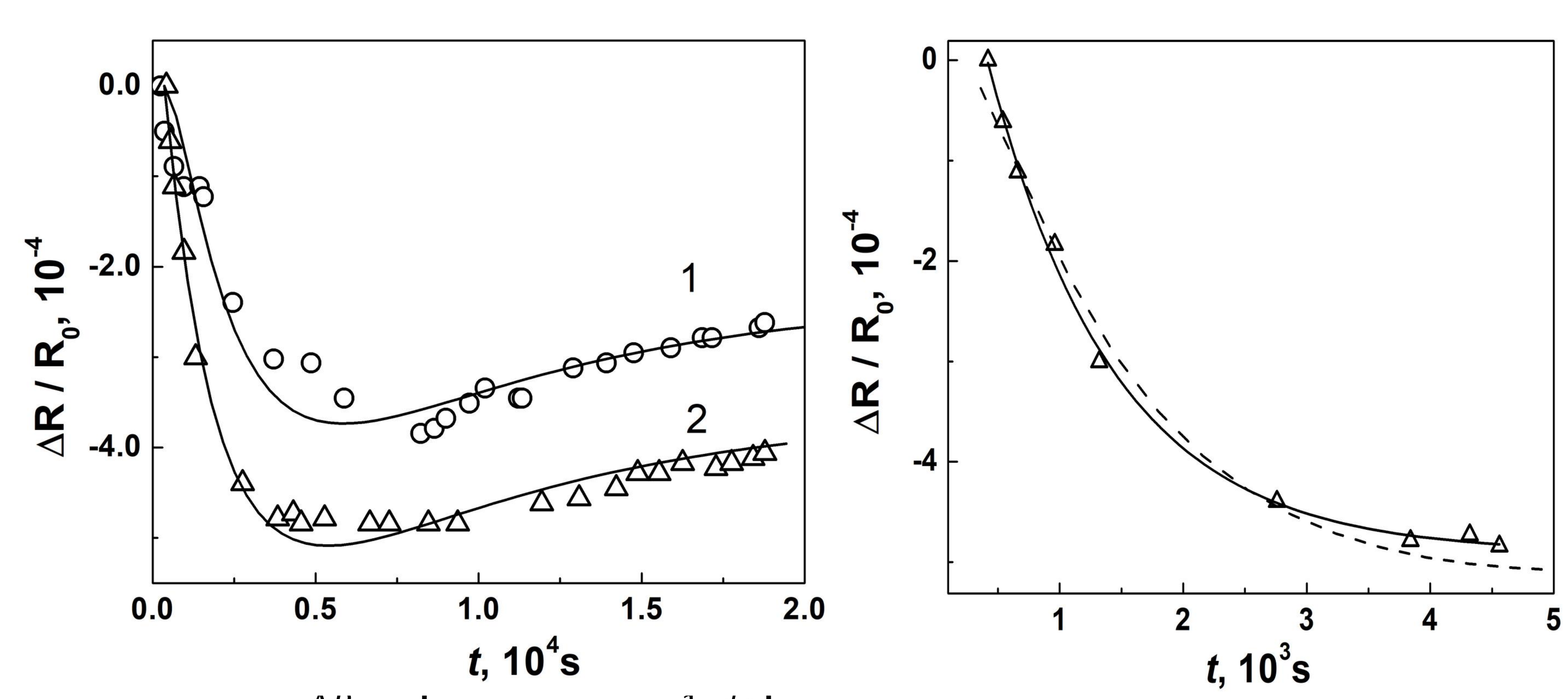

Dependences $c(x,t)$ calculated for $D = 4.59\cdot10^{-9}$ m²/s and with the same initial conditions for $P$ =0, $\varepsilon_{ii} = 0$ (left plot) and $P = 5.511\cdot10^{-19}$ J, $dV/\Omega = 0.19$ per 1% (at.) (right plot).

## Results of the experiment




- The tail of the film with thickness 60 nm was saturated by the hydrogen twice by the current 15 mA during 15 s. The interval between saturations was 4 days. The estimate concentration of H after each of the saturations is 1% (at.).
- The measurement of $R(t)$ was at T=293 K.
- Curves 1, 2 – dependences $R(t)$ of the non-saturated part of the film after the first and the second saturations, correspondingly. The minimum $R(t)$ is at $7.5\cdot10^3$ s for the curve 1 and at $5\cdot10^3$ s for the curve 2.
- The value $R(t)$ at the minimum is smaller than that before the saturation.

## The approximation of experimental data




$$\frac{\Delta R}{R_0} \cong \left[(1+2\mu) + \frac{1}{\rho_0}\frac{d\rho}{d\varepsilon}\right]\Delta\varepsilon + \frac{1}{\rho_0}\frac{d\rho}{dc}c \quad (3)$$

The approximation of experimental data was made with the use of Eqs. (2), (3).

## Parameters of calculations:

$T$ = 293 K. $D = D_0 e^{-\frac{U}{k_B T}}$, $D_0 = 3.1\cdot10^{-8}$ m²/s, U = 0.045 eV, $D=4.59\cdot10^{-9}$ m²/s, $P= 5.511\cdot10^{-19}$ J, $dV/\Omega = 0.19$ per 1% (at.), $\mu$ = 0.3, $\rho_0 = 3.4\cdot10^{-6}$ Ohm·m, $\frac{1}{\rho_0}\frac{d\rho}{dc} = 7.42\cdot10^{-5}$ for the curve 1 and $5.83\cdot10^{-5}$ for the curve 2, $\tau = 1023 \pm 65$ s.

## CONCLUSONS

1. **We found the unusual changes of the electrical resistivity of a non-saturated part of a nanocrystalline vanadium film during diffusion of the hydrogen to this part of the film from the saturated part. The resistivity has a minimum at small times of diffusion. The value of resistivity at the minimum is smaller than that for the non-saturated sample.**
2. **It was supposed that described changes of the resistivity were stipulated by strains produced by the migrating hydrogen. We developed the quasi-one-dimensional model of diffusion in the field of deformations.**
3. **Experimentally measured dependences of the electrical resistivity on time of diffusion were approximated with the use of the developed model. Results of the approximation are in good agreement with experimental data at reasonable values of parameters.**