DEPENDENCE OF THE TRITIUM ELECTROMIGRATION EFFECTIVE CHARGE ON CONCENTRATION OF HYDROGEN IN TITANIUM AND ZIRCONIUM

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The dependence of the tritium electromigration effective charge in titanium and zirconium on the concentration of hydrogen in these metals has been investigated. It has been found that the effective charge changes at the phase transition $\alpha+\gamma \rightarrow \gamma$.

For many years the electronic properties of titanium and zirconium hydrides were studied. Recently, it was discovered that studies of diffusion in an electric field (often called electromigration) can be used to trace purely electronic processes occuring in the investigated systems [1–4]. Nearly all existing electromigration theories emphasize the strong influence of the electronic structure (particularly the Fermi surface topology) on this phenomenon [1–3].

In the present work we have investigated the dependence of hydrogen electromigration in titanium and zirconium on the hydrogen concentration in the metal. The results obtained may throw additional light on the problem of hydrogen electronic state in these metals.

1. Method of measurement

Foil samples 0.005 cm thick, 1.6 cm wide and 3 cm long were used. They were doped with a hydrogen tritium mixture (spectrally pure) up to a given concentration and under a pressure up to 500 mm Hg at 300°C. Total doping time (including cooling off time) was 30 hours. The absorbed tritium mass was determined in vacuum using a quartz scale.

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After doping the samples were placed in a tank filled with Argon under normal pressure, and then for 150 hours an electric current was allowed to pass through the sample along the x direction. The temperature of the sample at that time was 35°C. When the electromigration process was over the sample was divided into two parts each $x/2$ long, and investigated for the presence of tritium. The detecting device for determining tritium β activity and the apparatus where the electromigration took place are described in detail in [5]. The solution of Fick's equation with boundary conditions imposed by this experiment can be found in [6]. For a given sample length and diffusion time, the ratio of hydrogen masses Q_1 and Q_2 from the range $(0, x/2)$, $(x/2, x)$, respectively, is a single-valued function of V/D, where V is the migration velocity, D — diffusion coefficient. The quantity V/D is easily determined from measurements of the hydrogen masses Q_1 and Q_2 found in each half of the sample (initially $Q_{1,0} = Q_{2,0}$). Next, using Einstein's formula

$$\frac{V}{D} = \frac{Z_{\text{eff}}E}{kT}, \tag{1}$$

value of the electric charge Z_{eff} is determined. E in Eq. (1) denotes the external electric field strength, k — Boltzman constant and T — temperature.

2. *Results of measurements*

The dependence of the tritium electromigration effective charge in titanium and zirconium on the concentration of hydrogen in the sample is presented in Fig. 1. It has been found that this dependence is nonlinear and that the effective charge changes its value

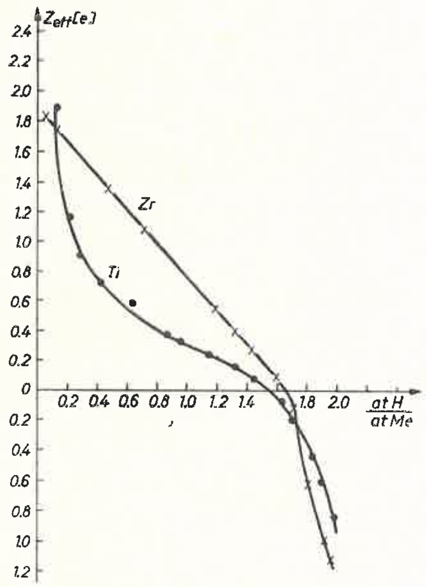

Fig. 1. Dependence of tritium electromigration effective charge on the concentration of hydrogen in Ti and Zr

from positive to negative for concentration 1.65 at H+T/at Me and 1.63 at H+T/at Me, respectively, for titanium and zirconium. As it is known [7, 8] for concentrations close to those values these metals undergo a phase transition from the $\alpha+\gamma$ phase into the γ phase. On the other hand, on the basis of the Fiks-Glinchuk model [1, 2] the electromigration effective charge Z_{eff} can be written as

$$Z_{\text{eff}} = (qe+en_d l_d A_d - en_e l_e A_e), \tag{2}$$

where q is the valency of a hydrogen ion in a metal, e — absolute value of an elementary charge, n_d and n_e — concentrations of holes and electrons, respectively, in the sample l_d and l_e — mean free path for doles and electrons, respectively, A_d and A_e — scattering cross sections for holes and electrons, respectively. Taking, after Norhheim and Mott [11, 12], the scattering cross section for holes and electrons to be

$$A_d = A_d^0 \frac{1}{c(1-c)}, \quad A_e = A_e^0 \frac{1}{c(1-c)}, \tag{3}$$

where c is the percentage of the diffusing component, A_d^0 and A_e^0 are constants, and assuming for the investigated metals in the first approximation that

$$A_d^0 = A_e^0 = A^0 \quad \text{and} \quad l_d = l_e = l \tag{4}$$

we get

$$(n_d - n_e)A^0 el = (Z-q)(1-c)c. \tag{5}$$

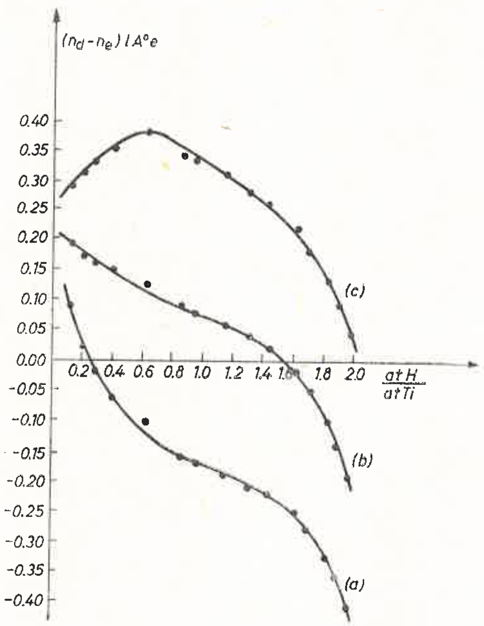

Fig. 2

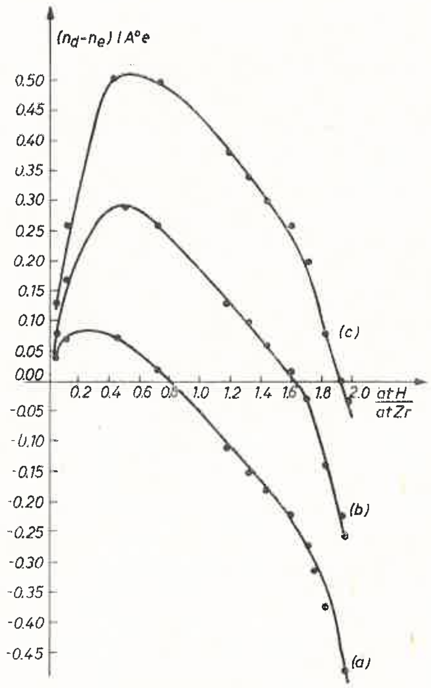

Fig. 3

Fig. 2. Dependence of $(n_d-n_e)\,el\,A^0$ on the hydrogen concentration in titanium

Fig. 3. Dependence of $(n_d-n_e)\,el\,A^0$ on the hydrogen concentration in zirconium

The quantities appearing on the right hand side of Eq. (5), apart from q are known from experiment. Therefore, for a given constant value of q one can determine the dependence of $(n_d - n_e)e/A^0$ on the hydrogen concentration. This relation for the investigated metal--hydrogen system is presented in Figs 2 and 3 for $q = 1(a)$, $q = 0(b)$ and $q = -1(c)$, respectively. For the Zr–H system the curve (b) has a character resembling the Hall constant dependence on hydrogen concentration, as obtained by Bickell and Berlincourt [9]. They found the normal Hall effect for concentrations in the range from 0 up to 1.63 at H/at Zr. Above this concentration the Hall constant change its sign from positive to negative. A similar correlation between the electromigration effective charge and the Hall constant has been observed for $CuAl_3$ alloy in β and γ phases [10].

Interpretation of the results obtained, based on Fiks-Glinchuk model [1, 2], leads to the conclusion that the observed decrease in effective charge with decreasing concentration, as described by Eq. (2) and under the assumptions (3), can be only caused by an increase in electron concentration (or decrease in the number of holes). One can conclude, therefore, that in the investigated metals, at concentrations not exceeding 2 at H/at Me, hydrogen turns electrons over to free electron gas. The character of the dependence of $(n_d - n_e)e/A^0$ suggests also a strong screening of hydrogen by electrons.

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