INFLUENCE OF INTERSTITIAL HYDROGEN ON HALL VOLTAGE AND ON ELECTRIC RESISTANCE OF THIN ZIRCONIUM FILMS

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Results on Hall voltage changes of thin zirconium films and electric resistance changes of zirconium films and filaments are reported upon hydrogen absorption over the atomic ratio region $0 < H/Zr < 1.8$. The Hall coefficient of thin films and the electric resistance of zirconium filaments reach the maximum values in the region of the atomic ratio $H/Zr \approx 1.6$, where the precipitation of the ε-phase of hydride occurs according to the phase diagram of the studied system. However, the character of variation of the electric resistance of the thin films during hydrogen sorption is qualitatively different from the character of variation of the resistance of the zirconium filaments. This difference is presumably due to the microcrystalline structure of thin films which affects the distribution of the particular phases of hydride in the film and due to the expansion of crystal lattice of the metal during hydrogen dissolving. The application of phase diagrams is discussed to thin hydride films as well as the utilization of the results of the electric resistance and the Hall voltage changes for obtaining information on phase composition.

Transition elements of the fourth and the fifth group of the periodic system are able to dissolve large amounts of hydrogen to form non-stoichiometric compounds of a metallic character. The electronic structure of these systems has not been fully elucidated despite numerous studies by various experimental methods.

According to several authors[1-3], hydrogen exists in the metal as the H^- anion and transition metal hydrides are thus analogous to alkali metal hydrides. A specific case of this model is the "lattice strain" model[4] as suggested recently.

However, it follows from theoretical considerations[5,6] that the presence of hydrogen atoms in metals leads to the formation of a localized state only if the density of conduction electrons is sufficiently low. As the density of the conduction electrons increases, such a state is absorbed by the conduction band. Usual densities of the conduction electrons in transition metals make the formation of a bound state of hydrogen below the conduction level not very probable. This result, together with some experimental data, led to the formulation of the protonic model[1,7,8]. According to it, the 1s electron of the hydrogen atom fills up the vacant states in the band of the electronic states of the metal. The charge of the proton formed must be, however, screened off by the conduction electrons of the metal and the distribution of the electron charge in the neighbourhood of this hydrogen "pseudoatom"[9] can differ only slightly from that one of the free hydrogen atom[10].

Each one of these two models is supported by some experimental data, but numerous data make an ambiguous explanation possible. Thus, the choise of an appropriate model is still rather arbitrarily dependent on the author.

It followed from the studies of the influence of interstitial hydrogen on the Hall voltage in thin layers of titanium and niobium[11] that the experimental data could be accounted for, in the first approximation, by the proton model. Therefore, it was interesting to verify the validity of this explanation on the system ZrH_x. Here, in view of a similar arrangement of the electronic structures[12] of zirconium and titanium, one could expect similar changes of the Hall voltage as in the earlier investigated system TiH_x. Data on changes of the Hall coefficient and of the electric conductivity in the system ZrH_x have been so far scarce and limited to the atomic ratio region $1·3 \leq x \leq 2$. Experimental methods reported in ref.[13,14] did not make it possible to fully remove from the samples the chemisorbed and incorporated oxygen whose presence in zirconium substantially influence the character of the interaction with hydrogen, in particular the kinetics of sorption and the phase diagram of the system.[15-18] Besides that, the measurement of electric transport coefficients are rather difficult with bulk samples, as the ZrH_x samples are very brittle and contain a large amount of microcracks. As it was shown earlier, some of these shortcomings can be partly eliminated by using a thin layer of the metal (a metal film) prepared by the vacuum sublimation.

The measurements, the results of which are reported in this paper were carried out at $273 \pm 0·3$ K over the atomic ratio region $0 < x < 1·8$. For comparison and also in order to estimate the size of a possible correction to the absorption by the non-evaporated residual filament of zirconium, changes of the electric resistance of a zirconium filament during the hydrogen sorption at 300 ± 1 K were measured, too.

EXPERIMENTAL

The measurements were carried out using the apparatus described earlier[11,19]. Thin polycrystalline films of zirconium, $60-200$ Å thick, were prepared by evaporating zirconium of spectral purity (Johnson Matthey Metals Ltd., England), degassed under vacuum of 10^{-8} Torr, and by condensing the vapours onto a substrate of borosilicate glass, kept at 200 K during the deposition. Zirconium was evaporated from a tungsten support resistively heated to about 2100 K. The over-all pressure of residual gases during the evaporation did not exceed $7 . 10^{-8}$ Torr. To stabilize their electric properties at the temperature of the measurements, the evaporated films were kept for 40 minutes at 370 K. The zirconium filament used in the measurements of electric resistance changes was degassed under the vacuum of 10^{-8} Torr and a temperature of about 1800 K for approximately 30 hours. The hydride was prepared *in vacuo* by the reaction between the metal and gaseous hydrogen at the temperature of the measurements. Hydrogen was purified by diffusing through a palladium thimble and by passing through three liquid-nitrogen-cooled traps. Hydrogen prepared in this way can be regarded as a gas of spectral purity, according to the published data[20].

The electric current used in measuring the Hall voltage was $5-8 . 10^{-3}$ A and was measured with the accuracy of $1 . 10^{-5}$ A. The Hall voltage (of the order of 10^{-6} V) was measured with the accuracy of $1 . 10^{-7}$ V. Direct current and magnetic fields of a maximum induction of $0·325$ Wb/m^2 were used in the measurements. The electric resistance of the films and its changes were measured by the potentiometric method, the resistance changes of the filament by the bridge method. The relative error of the Hall voltage measurements was approximately 8%, that one of

the electric resistance measurements 0·5%. The experimental error was always by an order of magnitude smaller than the changes of the measured quantities caused by hydrogen sorption. The way of evaluating the experimental data and the theoretical relations used were given in the previous communications[11,21].

RESULTS AND DISCUSSION

The measurements were carried out on three different zirconium films whose thickness, calculated from the measured values of the Hall voltage and of the electric resistance in the way described earlier[22,23], varied between 60 and 200 Å (66, 85, and 196 Å, respectively). However, in view of the method used in obtaining the values of the film thickness, they should be regarded rather as orientation values only. The studied zirconium films behaved as p-type conductors ($R_{HF} > 0$), *i.e.* in the same way as the bulk metal[24]. The value of the Hall coefficient R_{HF} did not depend in the region of the magnetic fields used neither on the intensity of the magnetic field, nor on the magnitude of the longitudal electric field. This finding, together with the observation of a positive temperature coefficient of the electric resitance, showed that the films had an electrically continuous structure.

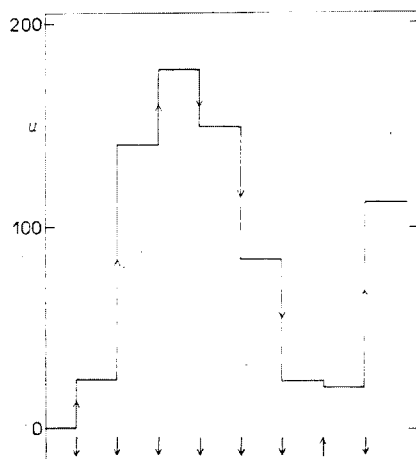Fig. 1 shows schematically the observed stationary values of the Hall voltage changes

FIG. 1

Changes of Stationary Values of the Hall Voltage u (%) of the Zirconium Film $\approx$ 66 Å Thick upon Hydrogen Sorption

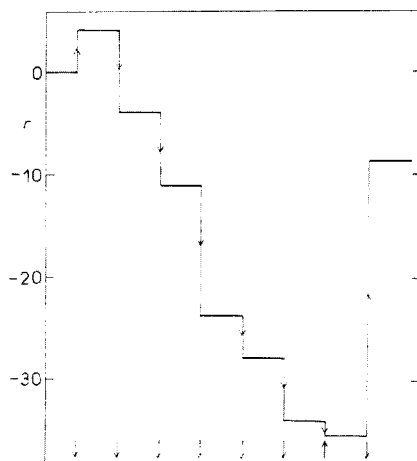↓ Hydrogen dose; ↑ gaseous phase pumped off, the last dose is oxygen.

FIG. 2

Changes of Stationary Values of the Electric Resistance r (%) of the Zirconium Film $\approx$ 66 Å Thick upon Hydrogen Sorption Designation of doses the same as in Fig. 1.

of a zirconium film during its saturation by hydrogen, introduced in separate doses into the measuring cell. A course of the same character was found for the other zirconium films, too.

As not only that part of the film which served as the sample participated in the hydrogen sorption, but also the entire amount of zirconium evaporated onto the internal walls of the measuring cell and the evaporation mask, it was not possible to determine from the volumetric measurements the value of the atomic ratio H/Zr achieved in the separate doses. Information on the approximate composition of the sample had to be obtained indirectly. Sometimes for this purpose results of a simultaneous measurement of another physical quantity have been used (*e.g.*, of the electric resistance) whose dependence on the composition was known. However, no such dependence is known for the system H_2–Zr (film). Therefore, it was necessary to determine the approximate composition of the film by the method described in reference[11], *i.e.* from the amount of hydrogen added and with respect to the published data[25] using the observation that the maximum value of the atomic ratio under the conditions of the experiment is $x \approx 1{\cdot}8$. In this way the value of x cannot be estimated with a better accuracy than about $\pm 0{\cdot}2$. However, the reported conclusions, being mostly of a qualitative character, are not influenced by this inaccuracy, as it will be shown later.

It can be seen from Fig. 1 that the dependence of the Hall voltage of the film on the amount of absorbed hydrogen goes through a maximum occuring at about $x \approx 1{\cdot}6$, in agreement with the value of the atomic ratio reported for the region of the maximum value of the Hall coefficient of bulk zirconium hydrides[13,14].

The electric resistance of thin zirconium film increases in the region of very low amounts of absorbed hydrogen $(x \approx 10^{-2})$; however, with continuing sorption it shows only a decrease (Fig. 2). In contrast with the Hall voltage changes, the electric resistance changes of thin films differ qualitatively from those of bulk zirconium, as reported in the literature[13,14]. The same results, within the range of experimental accuracy, were found for the other studied films, too.

The initial increase of the electric resistance can be explained by hydrogen chemisorption. Similarly as in the systems H_2–Ta (film)[26], H_2–Ti (film)[27], and H_2–Pd (film)[28], in the system H_2–Zr (film) first of all a coverage of at least a part of the metal surface by adsorbed hydrogen presumably occurs. It follows then from the comparison of the data in Fig. 1 and Fig. 2 that the adsorbed hydrogen and the hydrogen dissolved in the metal influence in a different way the electric resistance of the film, but influence in the same way the value of the Hall voltage. The Hall voltage changes, as observed in the assumed chemisorption, are in agreement with the rule[21,29] that with the metals behaving as *p*-type conductors, hydrogen chemisorption leads to an increase of the Hall coefficient value.

It is interesting that the stationary values of the Hall voltage were reached after $5-15$ minutes after the particular doses of hydrogen were admitted (the variation of

the time being dependent on the amount of dissolved hydrogen), while the stationary values of the electric resistance of the films were reached only after $30-60$ minutes. A possible reason of this difference is the migration of hydrogen in the metal associated with the formation of clusters in the vicinity of lattice defects[30,31]. (The stationary values here mean the values which did not change, within the limits of accuracy of the maesurements, during the next 30 minutes). Detailed kinetic measurements were not carried out. However, it follows from the above mentioned difference in the times necessary to reach the stationary values of the Hall voltage and of the electric resistance that in contrast with the electric resistance, the value of the Hall voltage is probably very sensitive namely to the thin film composition, but less sensitive to the spatial distribution of hydrogen in the film.

After the zirconium film was saturated with hydrogen at a pressure of about 10^{-1} Torr, the gaseous phase was pumped out and a single dose of oxygen ($\approx 10^{-2}$ Torr) was admitted into the measuring cell. It can be seen from Fig. 1 and Fig. 2 that chemisorption of oxygen accompanied presumably by its partial incorporation[32], leads to an increase of the values of both the Hall voltage and the electric resistance of the film. Comparison of the magnitude of these changes with those observed during chemisorption on clean zirconium films[30,32] showed that the changes during the chemisorption on the films saturated with hydrogen as described above were significantly smaller.

Possible explanations of this phenomenon are the following: *1)* The presence of dissolved hydrogen limits the extent of oxygen incorporation. *2)* During the oxidation of the surface layer of the metal, the hydrogen present there is pushed into the layer, where its concentration increases; as the dissolved hydrogen influences in this con-
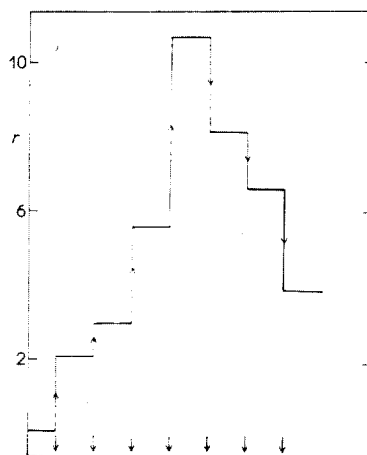

FIG. 3

Changes of Stationary Values of the Electric Resistance r (%) of the Zirconium Filament of 0·25 mm Diameter upon Hydrogen Sorption
   Designation of doses the same as in Fig. 1.

centration region values of both the Hall voltage and the electric resistance in the opposite direction than the adsorbed oxygen, the increase of hydrogen concentration inside the film may partly compensate the influence of chemisorbed oxygen. *3*) Hydrogen used contains traces of oxygen, water or carbon monoxide.

Fig. 3 shows the observed changes of the electric resistance of the zirconium filament during absorption of hydrogen. The maximum change was achieved at the atomic ratio $x \approx 1.6$, in agreement with the published data[13,14]. Reaching of the stationary value of the electric resistance of the zirconium filament took several $(3-5)$ hours from the moment of introducing hydrogen into the measuring cell. This was probably due to a low specific surface area of the filament. Regardless of other possible reasons, it follows from these experiments that in the measurements with thin films the correction on the sorption of the non-evaporated residue of the zirconium filament can be regarded as negligibly small.

The fundamental finding of this study is the fact that the character of the course of electric resistance changes of thin zirconium films during saturation with hydrogen is qualitatively different from the course of electric resistance changes of bulk samples (as, *e.g.*, of filaments), while the character of the course of Hall voltage changes is identical in both cases.

Possible reasons of changes of the electric transport coefficients of metals during hydrogen absorption are the following: *1*) Scattering of the conduction electrons on interstitial hydrogen atoms; at higher concentrations of dissolved hydrogen, scattering on vacancies. *2*) In the region of coexistence of two phases, scattering on the phase boundaries. *3*) Changes in the density of the conduction electrons. *4*) Changes of the electronic band structure.

In view of the fact that during dissolving of hydrogen in the transition metals of the fourth and the fifth group of the periodic system a change of the values of the metal lattice parameters occurs as well as the formation of new crystallographic phases[17], it is useful to look, in the first approximation, for a correlation between the observed changes of the transport coefficient values and the formation of the new phases[33-35]. The phase diagram of the system ZrH_x at 273 K, constructed with the use of the published data[13,14,17,36-38] is shown schematically in Fig. 4. Accurate values of the atomic ratios H/Zr which determine the boundaries of the particular phases cannot be given, as the data of various authors differ from each other. The

FIG. 4

Phase Diagram of the System ZrH_x at 273 K

α-phase (hcp) represents the metal with dissolved hydrogen. According to the published data[17], this phase is not found at 273 K at all; however, the measurements at 273 K so far carried out are not very accurate in the region of small amounts of dissolved hydrogen. In any case, the amount of hydrogen in the α-phase at 273 K will be comparable to the amount that can be adsorbed, and thus these two processes cannot be distinguished on the ground of the measurements performed. The formation of the δ-phase (fcc) in which hydrogen atoms occupy a part of tetrahedral interstitial sites is completed upon reaching the atomic ratio H/Zr 1·5. At H/Zr 1·63 − 1·66 the nucleation of the ε-phase (fct) occurs whose formation is completed at H/Zr 1·71. The comparison of the results obtained in this study with the phase diagram in Fig. 4 gives the following qualitative conclusions on the values of the measured transport coefficients: $R_{HF}^{(\delta)} > R_{HF}^{(Zr)}$; $R_{HF}^{(\varepsilon)} < R_{HF}^{(\delta)}$; $\varrho_B^{(\delta)} > \varrho_B^{(Zr)}$; $\varrho_B^{(\varepsilon)} < \varrho_B^{(\delta)}$; $\varrho_F^{(Zr)} > \varrho_F^{(\delta)} > \varrho_F^{(\varepsilon)}$; the upper indices denote the phase, ϱ_B and ϱ_F is the resistivity of the filament and the film, respectively. The observed changes of the Hall voltage during hydrogen adsorption can be thus easily explained as a result of a superposition of contributions of various phases. However, this explanation holds only if the phase diagram of thin-film hydrides can be regarded as congruent with the phase diagram constructed from the bulk hydride data. This condition does not have to be necessarily fulfilled, as, e.g., demonstrate the results obtained in the system H_2–Ta (film), where the existence of separate phases was not found[39], in contrast with the bulk hydride. Moreover, it can be expected that the phase composition of the hydride surface layer will be different from that one of the inside of the film in the region of the coexistence of two phases, and that the surface will be enriched by the phase with a lower surface energy. This again lowers the accuracy of the correlations between the hydride phase diagrams and the observed changes of the electric transport coefficients of the hydride films, particularly very thin ones where the contributions of the surface layer cannot be neglected.

To explain the Hall voltage changes the earlier suggested[11] phenomenological two-band model can be used, too. It follows from it that hydrogen occurs in the metal in the form of screened protons. The situation with the system H_2–Zr and with the system H_2–Ti is thus similar. This is not surprising, if we consider the similarity of electronic band structures of both metals[12].

However, the observed difference in the behaviour of the electric resistance in the systems H_2–Zr (film) and H_2–Zr (filament) cannot be explained solely as a result of the surface effects, as then it would have to be assumed that in the surface region of the film a conduction channel is formed which is electrically continuous and has a low specific resistance. This seems to be rather improbable. Therefore, probable reasons have to be looked for in the microcrystalline granular structure of thin metal films[40,41]. One of the consequences of the microcrystalline granular structure of thin films is their higher resistivity in comparison with bulk metals which results from the scattering of conduction electrons both on the external surfaces of the film and on the grain boundaries[41,42].

The decrease of the electric resistance of zirconium films upon hydrogen absorption can be then explained as a result of lowering the contribution of the electron scattering on the grain boundaries due, on the one hand, to the improved contact between the grains caused by an expansion of the crystal lattice upon hydrogen dissolving[17], on the other hand, to a decrease of the potential barrier height on the grain boundaries caused by a preferential formation of the δ-phase in these regions[17]. This explanation is supported by the fact that a similar behaviour of the electric resistance was observed in the system H_2–Ti (film), where a pronounced expansion of the metal crystal lattice occurs[11,17,27,30]. In the system H_2–Nb (film) the expansion of the crystal lattice during hydrogen dissolving is substantially smaller and the qualitative difference in the electric resistance changes of films and filaments[11,19,34] was not observed.

It follows from what has been said above that in general no conclusions can be made from data on the electric resistance changes of films concerning the phase diagrams, namely in the case of hydride films with microcrystals of small lateral size. This holds in particular for metals, where hydrogen dissolving is accompanied by a larger expansion of the crystal lattice and sometimes also by a preferential formation of certain phases on the grain boundaries and in the vicinity of defects.

These conclusions might be verified by a direct investigation of the phase distribution of hydride in films, *e.g.*, by the secondary electron method. Also, a study of the dependence of the electric resistance changes on the film thickness over a wider range of thicknesses during hydrogen dissolving would be useful. However, even in this case, the dependence of the mean value of metal microcrystals size on the film thickness would have to be known to make quantitative conclusions.

As long as the phase diagrams derived from bulk hydride data can be applied to thin films, it appears more convenient to exploit measurements of the Hall voltage changes to obtain information on the phase composition; this, of course, assumes that values of the Hall coefficient of various phases are significantly different. This is because the scattering on the grain boundaries has a substantially smaller influence on the value of the Hall coefficient than on the value of the electric resistance of the film[43]. *E.g.*, changes of the Hall coefficient during the film sintering are significantly smaller than changes of the electric resistance[19].

In a detailed interpretation of the experimental data obtained in the range of coexistence of two phases with a different electric conductivity, it would be necessary to start from relations valid for non-homogenous materials. At the present time existing theories of electric transport effect in inhomogeneous materials[44–46] are based on considerably simplified models and cannot be applied to the systems discussed in this communication.

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