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Observation of the β–δ phase transformation in deuterated iodide titanium films by electrical resistance measurements

F. Cuevas*, J.F. Fernández[1], C. Sánchez

Dpto. Física de Materiales C-IV. Universidad Autónoma de Madrid, Cantoblanco 28049, Madrid, Spain

Abstract

The β–δ phase transformation of titanium deuteride has been studied with the help of a newly developed experimental system by means of simultaneous recording of electrical resistance and volumetric measurements. The β–δ phase boundaries can be well defined from the relationship between the sample electrical resistance and the deuterium pressure in a closed reactor. It has also been observed that there is a reduction of the sample electrical resistance on passing from the delta phase to the beta phase which is associated to a partial elimination of hydrogenation induced defects and also to a possible higher resistivity value of the hydride phase (δ) in comparison with that of the solute phase (β).

Keywords: Titanium hydride; Phase transformations; Electrical resistivity; Hydrogen embrittlement

1. Introduction

One of the most relevant properties of the early transition metals is their high capability for hydrogen absorption. Among them, titanium metal is outstanding in that property and the corresponding titanium–hydrogen (deuterium) system has been widely studied by many techniques that have contributed to delineate the features of the Ti–H(D) phase diagram [1]. The Ti–H phase diagram is composed of four phases under usual thermodynamical conditions: two hydrogen solid solutions -α(cph) and β(bcc)- and two hydride phases -δ(fcc) and ϵ(fct)-. In some cases, the electrical resistivity technique was used to get the phase boundary lines, e.g., $\alpha-\alpha+\delta$ [2] and $\delta-\epsilon$ [3] boundaries, or to follow the evolution of the electrical properties of the material with its hydrogen content, e.g., the electrical resistivity of Ti–H across the β-phase [4]. However, no resistivity data are available up to now around the β–δ transition. This fact is connected with intrinsic experimental difficulties that should be overcome: mainly to avoid the fracture of the sample due to strong volume changes upon hydrogen absorption–desorption.

In this paper, we present a newly developed experimental set-up to monitor the β–δ phase transformation in titanium deuteride by means of electrical resistance and volumetric measurements accomplished at the same time. To carry out this study, the titanium sample was prepared in our laboratory by the iodide process, using a tungsten ribbon filament as the substrate [5,6]. The clamping of the titanium film to the substrate avoids drastic fracture of the film during hydride formation and allows more accurate electrical resistance measurements.

2. Experimental

A 150 μm thick titanium film was uniformly deposited over a tungsten substrate ($4\times0.2\times2.5\ 10^{-3}$ cm^3) electrically selfheated to 1450 K. This deposition temperature is low enough to prevent significant diffusion of the substrate into the titanium film which has been typically checked to be of high purity by EDX and AES analysis [7]. The mentioned substrate is located inside of a reaction chamber made of glass ($V_H=374\pm10$ ml) and is held by two electrodes that carry the necessary electrical current to maintain the deposition temperature. In addition, two thin tungsten wires are welded to the edges of the substrate to be used as voltage sensors, so that the well known four probe resistance method is accomplished. When the titanium deposition was ended, the reaction chamber was sealed off under vacuum conditions to protect the sample

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*Corresponding author. Present address: Max-Planck-Institute für Metallforschung, Institut für Physik, Heisenbergstr. 1, D-70569 Stuttgart, Germany.

[1] Present address: University of Salford, Physics Dept., Joule Laboratory, M5 4WT, Salford, UK.

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from superficial oxidation. Then, the chamber was attached to a deuterium reservoir (V_R=77.5±1.5 ml) constructed in SS-316 and equipped with vacuum and pressure (Kistler 4043A) gauges. The connection between both chambers is initially avoided by a brittle glass wall that is smashed with a magnetic striker device once the reservoir chamber is evacuated. The evacuation is carried out with a turbomolecular pump to reach a residual pressure of 10^{-5} torr.

Fig. 1 shows a schematic drawing of the experimental set-up at this stage. Two parts can be seen: one deals with electrical resistance measurements and the other is related to volumetric measurements. The first part comprises of a DC power supply (Kenwood PD35-20D) programmed by a Function Synthesizer (Keithley 3910) and the mentioned wire sensors welded at the sample edges. In particular, triangular intensity waves can be passed through the film in the range from 0 to 20A with time periods as long as 10^4 s. The second part comprises of a double chamber apparatus equipped with pressure sensors and a type-K (NiCr–NiAl) thermocouple which monitors the wall temperature of the reaction chamber.

In order to study β–δ phase transformation of the TiH(D) system, the titanium sample was initially deuterated to reach the δ-phase. To this aim, a 300 mb deuterium pressure (purity 99.999%) is imposed in the whole system. Then, the sample is selfheated to glowing temperature which is clearly achieved at an electrical current of 13 A. Finally, a decreasing electrical ramp is programmed through the sample to cool it slowly down to room temperature. Considering the reported isotherms of the P–X phase diagram of TiH(D) [1], the cooling of the sample from 1100 K to room temperature at a deuterium pressure of 300 mb implies the formation of the δ-phase at temperatures lower than 900 K. In agreement with this prediction, the deuterium concentration in the titanium film after this treatment was evaluated from the overall pressure drop in the system to be $TiD_{1.5\pm0.3}$. Later on, the titanium deuteride film is forced to undergo the $\delta\rightarrow\beta$ phase transformation (and vice-versa) by programming triangular intensity cycles through the film in the range of 6 to 13 A. This electrical current pattern produces long period heating oscillations in the film which absorbs and desorbs the deuterium gas mainly during the transformation. The average gas deuterium pressure in the system is also about 300 mb, so that the transformation is taking place at an approximate temperature of 900 K, according to the Ti–H(D) phase diagram. Following this scheme, it has been run a total of 16 electrical current cycles at 1250 s time period and other 16 cycles at a double speed. Meanwhile, the sample electrical resistance and the deuterium pressure in the chamber are monitored.

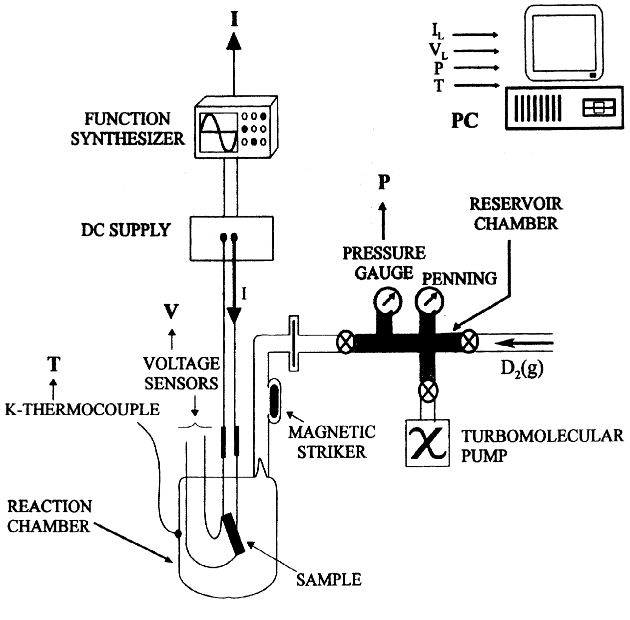

Fig. 1. Schematic drawing of the experimental system set-up.

3. Results and discussion

The time-evolution of the sample electrical resistance, R, and the deuterium pressure, P_{D2}, on the third cycle of the experiment are shown in Fig. 2. At the beginning of the cycle both parameters increase continuously as the electrical current does. R increases as a result of the joule heating effect while P_{D2} increases because of the induced temperature increase of the reaction chamber, as detected by the outer thermocouple. However, at a certain time there is a break at the resistance curve that is time-correlated with a sudden increase of the pressure, which denotes the deuterium desorption from the sample. Later on, there is another break in the resistance curve and then the trend of the pressure curve is recovered. Finally, when the electrical current starts to decrease both parameters follow a similar behaviour along the lower values.

Clearer evidence of the correlation between both parameters and their relation with the β–δ phase transformation can be obtained from the R vs. P_{D2} plot shown in Fig. 3. The circulated electrical current is denoted in the figure by the depicted arrows and some data labels. Now, R increases monotonically with the pressure till a break in the curve appears, leading to a plateau-like appearance that extends over the whole transition. During such plateau, the sample electrical resistance keeps nearly constant in spite of the expected increase of the sample temperature, while the deuterium pressure rises considerably. This plot unambiguously indicates the presence of the β–δ phase transformation and the phase boundary lines can be well depicted. It should be remarked that there is an apparent hysteresis behaviour during the cycle, which far from being a real property has to be assigned to the finite thermal convection value of the deuterium gas.

Besides the clear identification of the β–δ transformation, the most significant result from the experiment is the

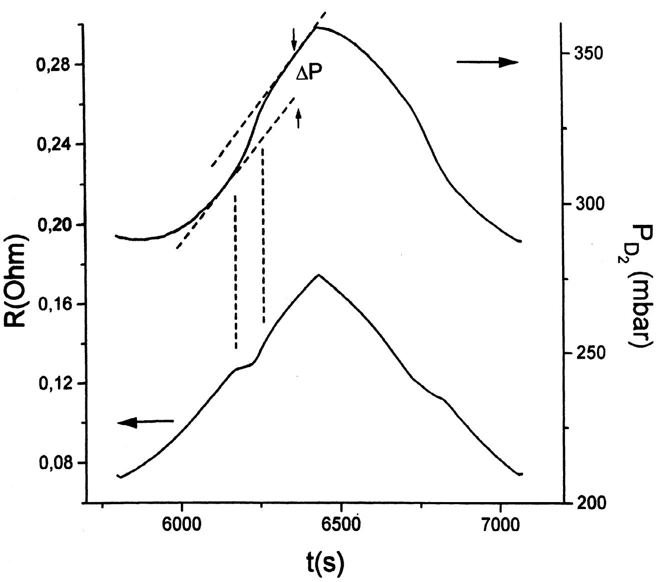

Fig. 2. Time-evolution of the sample electrical resistance (down) and system deuterium pressure (up) during the third electrical current cycle of the experiment. Dotted lines indicate the time correlation between sudden variations of both parameters during the ascent part of the electrical current cycle.

reduction of the sample electrical resistance with the deuterium desorption, i.e., during the $\delta \rightarrow \beta$ transition. This phenomenon can be due to either of both of the following effects: a higher electrical resistivity value of the δ-phase in comparison with that of the β-phase and a reduction in the size of the cracks, which are somehow closed when the desorption takes place. Both mechanisms are discussed now.

The reduction of the resistivity during the transformation from a hydride phase to a solute phase is usually unexpected. The hydride phase should be connected with a less-disordered arrangement of hydrogen atoms in the metal lattice, whereas the solute phase involves the random distribution of the interstitial hydrogen atoms in the matrix [8–10]. However, some intrinsic characteristics of the Ti–H(D) system could favour the opposite resistivity behaviour. Thus, the δ-hydride phase of this system is a nonstoichiometric or defect structure [1] while the β-solute phase presents a reported evidence of H–H attractions [11,12]. Therefore, a big difference in the hydrogen arrangement does not exist between both phases, where the hydrogen atoms are distributed over the tetrahedral sites. On the other hand, Ames and McQuillan [4] have reported that the electrical resistivity of the β-phase suffers a strong reduction with its hydrogen content, to reach values even lower than that of pure β-titanium. This fact was explained by changes in the electronic structure in the d-band of titanium metal. To summarize, it is reasonable to suggest that the δ to β phase transformation could lead to variations in the conduction band of the system which would affect to the resistivity in a higher degree than the arrangement of the H-atoms. In conclusion, the electrical resistivity of the δ-phase could be higher than that of the less-ordered β-phase.

The second mechanism that can contribute to the sample resistance reduction during the $\delta \rightarrow \beta$ transformation is the closing of previously formed cracks during the deuteration of the sample. It is well known that the processes of hydrogen absorption that are associated with phase transitions produce strong stresses in the metal lattice [13,14]. These stresses are commonly relieved by plastic accommodation, i.e., the formation of dislocations and even cracks in the material. In this respect, Fig. 4 shows the time-evolution of the R parameter all over the experiment. It can be observed that there is a linear drift of the resistance with the number of cycles performed. This result can be

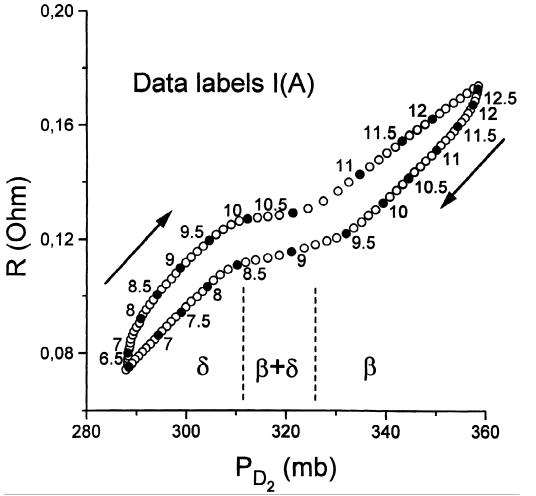

Fig. 3. Identification of the β–δ phase boundary lines. Sample electrical resistance vs. system deuterium pressure relationship obtained from Fig. 2. Some data labels corresponding to different electrical current values are given and also the time evolution of the cycle is indicated by arrows. The phase boundaries are depicted by dotted lines.

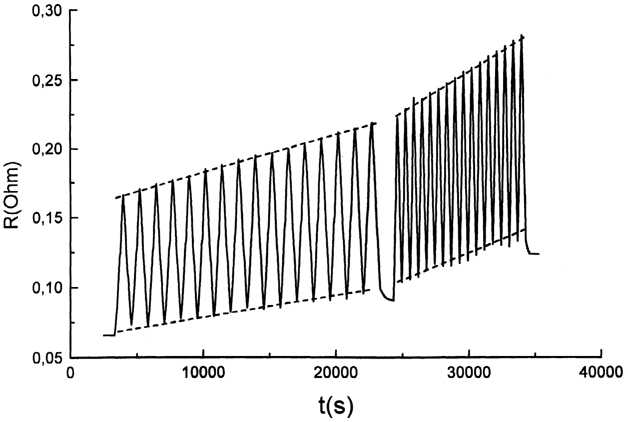

Fig. 4. Time-evolution of the sample electrical resistance during the whole experiment. The drift of the sample resistance at maximum and minimum values is indicated by dotted lines.

assigned to the growth of an equal density of defects in every cycle. It is worthy to note that the drift is increased by a factor of ~2.6 when the cycle frequency was doubled. This value indicates that the defect generation depends slightly on the transformation rate, as we pointed out in a previous publication [15]. In conclusion, the overall cycling of the sample around the β–δ transition produces an increment of the sample electrical resistance due to crack formation, however during the $\delta \rightarrow \beta$ transition the R parameter can follow a slight decrease due to partial closing of the previously formed cracks. This mechanism of electrical resistance reduction associated with hydrogen desorption has been previously reported by Ishikawa et al. [9] in relation with the $LaNi_5$–H and $LaCo_5$–H systems.

In summary, we present here a new type of experimental system which allows to obtain valuable information about the β–δ phase transformation in Ti–H(D). The identification of the phase transition is obtained from simultaneous measurement of the sample electrical resistance and the system deuterium pressure. It has been observed a reduction of the R parameter during the $\delta \rightarrow \beta$ transformation that can be assigned to a partial closing of cracks and may also to a higher electrical resistivity value of the δ-phase in comparison with that of the β-phase.

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