

KINETICS AND THERMODYNAMICS OF THE ABSORPTION OF HYDROGEN IN β -TITANIUM ALLOYS

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Abstract

A thermogravimetric method was applied to study the hydrogen uptake in the near- β -titanium alloy Ti 10 2 3 and the metastable β -titanium alloy Ti 21S. The tests were performed in H_2 -He gas mixtures with various partial pressures of H_2 at temperatures between 600 and 800°C.

Basic findings such as the decreasing solubility of H_2 with increasing temperature could be verified, and first information on the effects of surface conditions was gained. Thus, it could be shown that, despite the low atomic mass of hydrogen, thermogravimetry is an appropriate tool for investigation of the H_2 /metal interactions of titanium alloys.

Keywords: absorption diffusion and solubility of hydrogen, β -Ti alloys, TG

Introduction

The main applications for this class of alloys are in aircraft and space technology, due to the combination of high strength, excellent corrosion resistance and low density. It is well known that the mechanical properties of titanium alloys are strongly influenced by their hydrogen content. The background of this article is to develop a quantitative prediction of the resistance of β -titanium alloys vs. H_2 on basis of experimental data. Therefore, as a first step, a detailed knowledge of the rate of H_2 uptake and the solubility of H_2 as functions of temperature and H_2 partial pressure is necessary in order to provide a sound basis for application of these alloys under conditions where H_2 is present or being formed.

Two alloys of the β -phase (near- β : Ti 10 2 3 and metastable β : Ti 21S) with different stabilities were investigated in this study. The primary method applied was gravimetry at elevated temperatures on specimens charged in He/ H_2 gas mixtures at various H_2 partial pressures.

Experimental

Material

The titanium alloys used for this study contain V, Mo, Fe and Nb, which exert a stabilizing effect on the β -phase, and also Al, which improves the stability of the α -phase (see also Table 1).

Table 1 Compositions of Ti 21S and Ti 10 2 3

| Alloy | Al equivalent /% (α -stabilizing) | Mo equivalent /% (β -stabilizing) | Classification |
|----------------------------------|--|---|---------------------|
| Ti 10 2 3 (10V 2Fe 3Al) | 3 | 12.5 | near- β |
| Ti 21S (15Mo 2.7Nb 3Al 0.2Si) | 3 | 15.8 | metastable- β |

Heat treatment

The microstructure of Ti 10 2 3 as delivered reveals globular primary α within a matrix composed of β -phase and lamellar α -phase. This condition provides optimal forging properties. With the background of hydrogen as a temporary alloying element, no further heat treatment was necessary.

Ti 21S was solution-annealed at 850°C for 2 h in an inert gas (Ar) or vacuum, followed by aging at 500°C for 8 h. Under these conditions, the alloy exhibits high strength in combination with sufficient ductility, so that this treatment is of relevance for practical application. The microstructure is composed of a β -phase matrix with needles of precipitated secondary α -phase.

Sample preparation

For thermogravimetric measurements, cylinders approximately 10 mm in thickness were cut from rods 10 mm in diameter. These cylinders were ground to grade 1200 and polished with different diamond pastes down to 3 μ m grain size, with subsequent ultrasonic cleaning in ethanol.

Depending on the temperature, H₂ charging was performed on samples with or without a palladium coating. At temperatures higher than 600°C, the influence of the surface oxide formed during gas charging on the H₂ absorption decreases [1, 2], whereas at temperatures lower than approximately 550°C, the oxide impedes H₂ uptake by inhibiting the dissociation of molecular H₂ [3, 4]. In order to promote H₂ absorption in the temperature range from 500 to 600°C, those samples which were used to establish equilibrium conditions were coated with a palladium layer, a common method of promoting H₂ charging.

The coating was produced by a method described by Driver [5], slightly modified according to the current requirements [6]. Palladium was deposited cathodically at a constant current density of -15 mA/cm^2 for 5 min.

Thermogravimetry

The thermogravimetric measurements were carried out in a gas-tight thermobalance, as shown schematically in Fig. 1. The self-compensating electromag-

netic precision microbalance system (Linseis) operates on the basis of an inductive system which allows for the detection and compensation of deviations from the balance condition. The current necessary to nullify the displacement of the balance is measured, and thus the change in mass can be calculated. This principle provides a resolution of the change in mass down to 10^{-5} g in the case of the type of microbalance used in this study (maximum mass of the sample 25 g).

Different gas mixtures composed of H_2 and He were used to achieve different H_2 partial pressures. The reasonable thermal conductivity and a negligible change in buoyancy caused by the change of the H_2 partial pressure favour He as carrier gas. The gas was either provided ready mixed by the gas supplier and delivered in gas cylinders, or it was mixed from pure and pre-mixed gases by means of a gas mixing system. The mixing system allows change of the H_2 partial pressure during experiments at one temperature. The total gas flow rate was 12 nl/h during all experiments.

A change in mass caused by oxidation is difficult to avoid. This was corrected by weighing the sample after H_2 degassing and assuming a linear mass gain with time due to oxide formation as a first rough assumption. The mass gain during H_2 charging corrected in this way was then used to calculate a mean hydrogen content of the sample as a function of time.

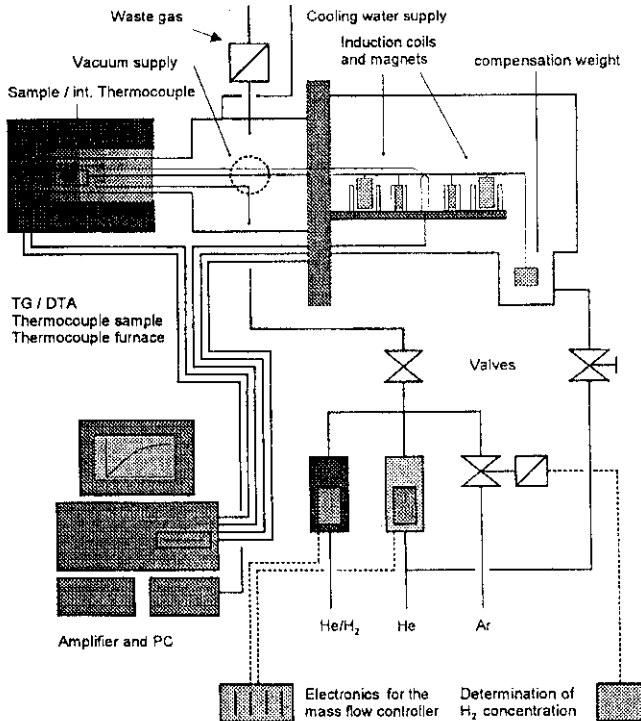


Fig. 1 Thermobalance with gas supply

In order to determine the diffusion coefficients of hydrogen in titanium alloys, the received data were compared with an analytical solution [7]. The analytical solution provides the relation between mass uptake and time for a cylinder of known geometry and diffusion-controlled H_2 uptake. By varying the diffusion coefficient in the analytical solution and comparing the resulting mass change vs. time curves with the results of the thermogravimetric experiments, a diffusion coefficient could be determined.

Results

The increases in the hydrogen contents of samples of Ti 10 2 3 and Ti 21S during H_2 charging can be recorded continuously by means of thermogravimetry (Fig. 2). The experimental conditions described above resulted in a mass gain in the range of some mg with a sample mass of approximately 3–4 g. Figure 2 also shows the reasonable signal-to-noise ratio and the high resolution of the measurement.

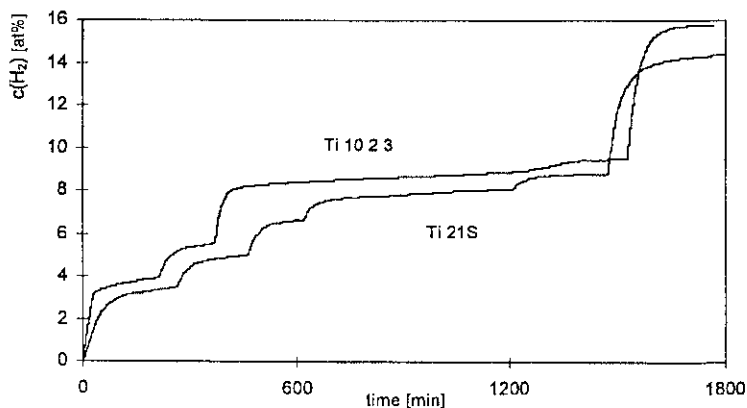


Fig. 2 H_2 uptakes of the alloys Ti 21S and Ti 10 2 3 at 800°C and stepwise increases of the H_2 partial pressure at 4.8/9.2/16.9/23.4 (only Ti 21S)/28.9/100 mbar

One basic finding is that the shape of the curve depends strongly on temperature. The reason for this is that the H_2 uptake in the case on an uncoated surface at lower temperatures is impeded by the surface oxide formed during charging. With increasing temperature, the impeding effect of the surface oxide diminishes and the shape of the curve changes. This can be seen in Fig. 3 as an increase in the slope of the curve at the beginning of charging with increasing temperature.

Furthermore, Fig. 3 documents that the H_2 equilibrium concentration decreases with increasing temperature. With increasing temperature, the time necessary to reach the equilibrium condition becomes shorter. Thus, for temperatures at or higher than 800°C , a H_2 saturation concentration can be reached within

about 5 h, whereas at 600°C the final concentration is reached after 60 h. Another interesting point is the fact that the less β -stabilized Ti 10 2 3 dissolves more H_2 than the stronger β -stabilized Ti 21S (Table 1 and Fig. 2).

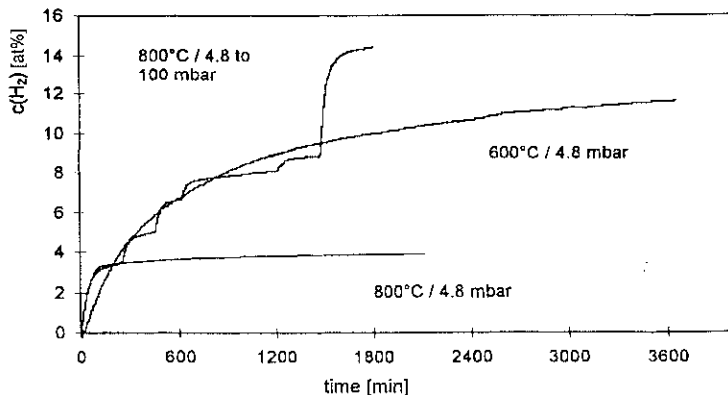


Fig. 3 Rate of H_2 uptake of Ti 21S at 600°C and a $p(H_2)$ of 4.8 mbar as compared to that at 800°C with a stepwise increase of $p(H_2)$ from 4.8 to 100 mbar, and a one-step experiment at 800°C and 4.8 mbar

In order to obtain more information about the reaction of H_2 with the alloy at the commonly used aging temperature of about 500°C (a temperature which still provides a sufficient hydrogen diffusivity), the surface was coated with palladium. Palladium layers are known to support H_2 absorption by catalyzing the dissociation of H_2 and have been used for permeation measurements [5]. The mass gain caused by H_2 at 500°C for a palladium-coated sample is significantly accelerated (Fig. 4) compared to the uncoated surface conditions at the same temperature.

The surface of the sample for 500°C coated with palladium permits rapid establishment of the saturation concentration. Therefore, this surface condition is suitable for study of the temperature dependence of H_2 solubility. Further experiments showed that the palladium-coated surfaces are not suitable for the determination of diffusion coefficients at lower temperatures. The rate of H_2 uptake is enhanced dramatically; the kinetics is still not diffusion-controlled (Fig. 4). The reason, therefore, is the incomplete surface covering with palladium.

Experiments performed to determine diffusion coefficients at temperatures of 800°C and higher revealed satisfactory results for Ti 10 2 3 (Fig. 5). Obviously, at 800 and 900°C, the speed of H_2 uptake is still reduced by oxides formed on the surface. From a comparison of the results for 1000 and 1100°C with results from experiments carried out in the temperature range from 100 to 500°C with a different technique, analogous to the experiments of [8], it can be observed that no change is caused in the diffusivity of H_2 by the β transus analogous to pure titanium at 882°C. The experiments on Ti 21S showed that there is a strong influ-

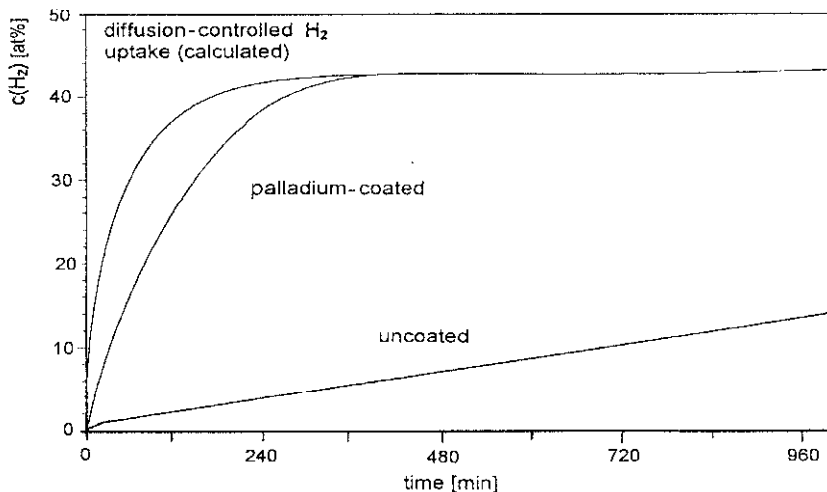


Fig. 4 Diffusion-controlled H₂ uptake of Ti 10 2 3 at 500°C (calculated) as compared with those for a palladium-coated and an uncoated sample

ence of the oxide layers up to 1000 and 1100°C, so that determination of the diffusion coefficient of this material is not possible within the temperature range of this thermobalance.

Since the onset of hydride formation is of interest as one of the origins of severe material degradation, the effect of the H₂ partial pressure was studied in multiple pressure step tests (Fig. 2). After the saturation concentration of one value of the partial pressure had been established, the partial pressure was increased. At a pressure of 100 mbar, an equilibrium condition could be reached within the duration of the test at 600°C. No steady enhancement of the hydrogen content with time (which is considered to be attributable to hydride formation) could be observed.

After transfer of the results from the multi-pressure step tests to Sieverts diagrams (concentration of H₂ vs. the square root of the H₂ partial pressure; Figs 6 and 7), it was found that the solubility of H₂ in the alloys is proportional to the square root of H₂ partial pressure up to concentrations of about 24–26 atomic percent for Ti 21S and Ti 10 2 3. Above these concentrations, the slopes of the plots incline and they can no longer be described with a linear approximation.

Discussion

The β -titanium alloys Ti 10 2 3 and Ti 21S exhibit considerable H₂ solubilities (Figs 6 and 7). From the point of view of a technical application, the observation is important that the onset of hydride formation occurs only under severe conditions that promote a high hydrogen concentration in the alloy. This was also shown for the stable β -Ti alloy Ti-30Mo and the $\alpha+\beta$ alloy TiAl6V4, where 66 and 46 at% hydrogen were necessary to produce hydrides, respectively [9, 10].

The effect is due to the bcc lattice of the β -phase, which displays an enhanced capability to dissolve H_2 [11, 12]. This is in contrast with the behavior of α -titanium alloys, where even a small hydrogen content is sufficient to cause hydride formation [13, 10].

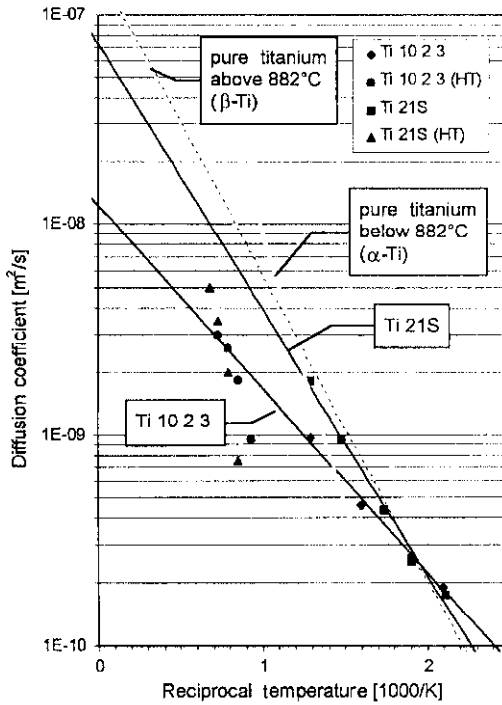


Fig. 5 Arrhenius plots for diffusions coefficients of Ti 21S, Ti 10 2 3 and pure titanium

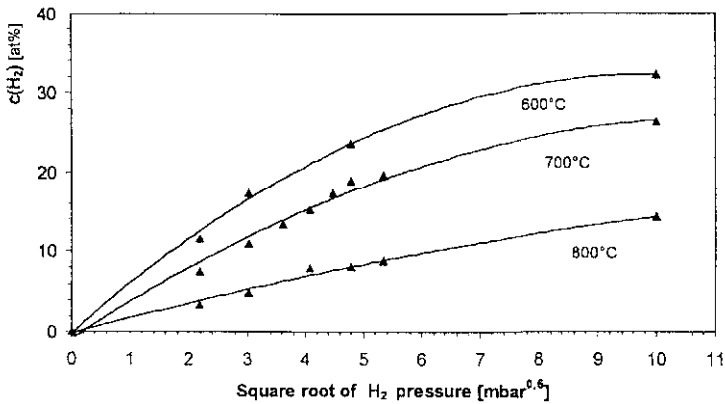


Fig. 6 Sieverts plot for Ti 21S

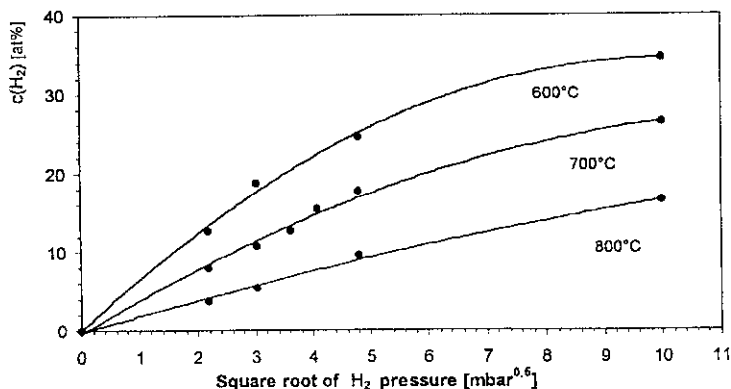


Fig. 7 Sieverts plot for Ti 10 2 3

Figures 6 and 7 show the hydrogen saturation concentrations as a function of temperature for different values of the H_2 partial pressure. Sievert's law is best obeyed at low pressures, in agreement with the findings of other authors [14, 15]. Deviations were observed at increased H_2 concentrations, i.e. at low temperatures and high H_2 partial pressures. This effect may be attributed to a limited ability, especially at low temperatures, to compensate the lattice distortions caused by the high content of protons.

The surface condition is of significant importance for the H_2 absorption process. As already mentioned above, the surface oxide can inhibit H_2 absorption [16]. Especially the measurement of the diffusion coefficients showed that, even at temperatures up to 900°C (Ti 10 2 3) or 1200°C (Ti 21S), surface layers are still present, reducing the rate of H_2 uptake. The difference between the investigated alloys might originate from the different alloying elements V, Fe (Ti 10 2 3) and Mo, Nb (Ti 21S) (Table 1), which could possibly form different stable surface layers.

Conclusions

Thermogravimetry is an appropriate method for the study of the H_2 uptake of titanium alloys from the gas phase at elevated temperatures. Basic findings could be confirmed, such as:

- The H_2 solubility decreases with increasing temperature.
- At temperatures below 550°C , the surface oxide impedes the uptake of H_2 .
- Hydride formation is restricted to severe hydrogenizing conditions, i.e. partial pressures higher than 100 mbar and temperatures below 600°C .
- Higher β -stabilization is no guarantee for a higher H_2 solubility.
- Thermogravimetric determination of the diffusion coefficients is possible, but restricted to titanium alloys forming not too stable oxides on the surface.

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