

THE THERMODESORPTION SPECTROMETRY METHOD FOR CONSTRUCTING T-c DIAGRAMS WITH THE Ti-D SYSTEM AS AN EXAMPLE

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Introduction

For metal-hydrogen systems, there should be recognized two types of equilibrium specified by the presence or absence of the exchange of hydrogen contained in both the metal matrix and the gaseous environment. The first type of equilibrium is realized in the presence of external hydrogen pressure. By varying values of external hydrogen pressure and temperature, it appears possible to construct the projections of maximum solubility lines on the temperature-composition plane. The handbooks give, as a rule, just these diagrams. However, strictly speaking, these diagrams cannot be used in all cases for determining the composition of phases existing in equilibrium. The second type of equilibrium is realized at low partial pressures of hydrogen or in its absence. In this case the phase-state stability of the metal-hydrogen system is governed by the metal matrix, and the phase states of the system are described by the T-c diagrams. The present paper offers the method of constructing T-c diagrams through the use of thermodesorption spectrometry with the Ti-D system as an example.

Results and discussion

The thermodesorption spectrometry (TDS) and electron diffraction methods were used to investigate the state of the Ti-D system versus the dose (concentration) of the implanted deuterium [1-3]. The initial (nonirradiated) titanium films had the hcp structure with the parameters $a=0.296$ nm and $c=0.469$ nm characteristic of α -Ti. As the radiation dose increases, there occurs a gradual change in the crystalline structure of the specimen. The structural transition is determined by the formation of titanium hydride TiD_2 (hcp lattice of α -Ti is transformed into the fcc lattice of TiD_2). The appearance of hydride nuclei is observed as early as at a dose of $\sim 3 \times 10^{16} \text{ cm}^{-2}$ (first marks of diffraction lines of the fcc lattice). As the dose (implanted deuterium concentration) increases, a rise in diffraction line intensity of the fcc lattice (TiD_2 hydride) takes place, while the diffraction line intensity of the hcp lattice (α -Ti) decreases.

At a dose of $\sim 1.3 \times 10^{18} \text{ cm}^{-2}$, the structural transition $\alpha\text{-Ti} \rightarrow \text{TiD}_2$ is fully completed. The estimation of deuterium concentration implanted into titanium has demonstrated the fulfillment of the stoichiometric ratio $\text{Ti/D} = 1/2$ characteristic of the TiD_2 hydride. The smooth nature of the transition of the α -Ti hcp structure to the TiD_2 fcc phase with an increasing dose of implanted deuterium and the completion of the transition only after the stoichiometric deuterium concentration is attained, give evidence for the chemical nature of the structural transition observed.

The analysis of spectra for deuterium thermodesorption from titanium (see Fig. 1) with due account for the above-mentioned structural changes has revealed a well-defined correlation between the gas release peaks in the spectra and phase transitions in the Ti-D system.

The $T_m \sim 800$ K peak appears at the decay of the TiD_2 hydride, and the $T_m \sim 1100$ K peak is almost exactly coincident with the phase transition temperature of titanium $\alpha\text{-Ti} \rightarrow \beta\text{-Ti}$. As it follows from the phase diagram of the Ti-H system [4], at $T > 1100$ K hydrogen may be present in titanium only in the form of a solid β -solution. Hence, the $T_m \sim 1350$ K peak corresponds to the decay of deuterium solid solution into β -Ti, and is due to the full emission of deuterium into the gaseous phase, this being testified by the absence of deuterium gas liberation after this peak with a further heating of the specimen up to its melting. The $T_m \sim 200$ K peak is determined by the presence of the loosely bound deuterium in the target (the activation energy of desorption is $E=0.12$ eV). The $T_m \sim 200$ K peak appears and grows with the dose after the stoichiometry at $\text{D/at/Ti}=2$ is attained. It is quite reasonable to suggest that the fraction of deuterium released in the peak is associated with the presence of superstoichiometric deuterium concentration in the implanted layer. For the latter, the ratio of the number of deuterium-to-lattice atoms does not exceed 2.2.

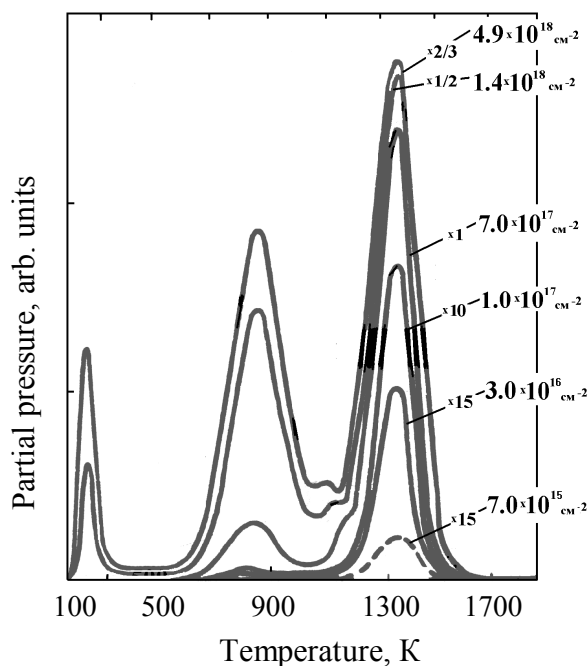


Fig.1. Thermodesorption spectra of deuterium implanted into bulk Ti at $T_{irr} \approx 110$ K for different irradiation doses.

Taking the temperature of peak maxima in the thermodesorption spectra as an upper boundary of phase existence in the Ti-D system, it appears possible to indicate the temperature ranges of phase existence of the Ti-D system.

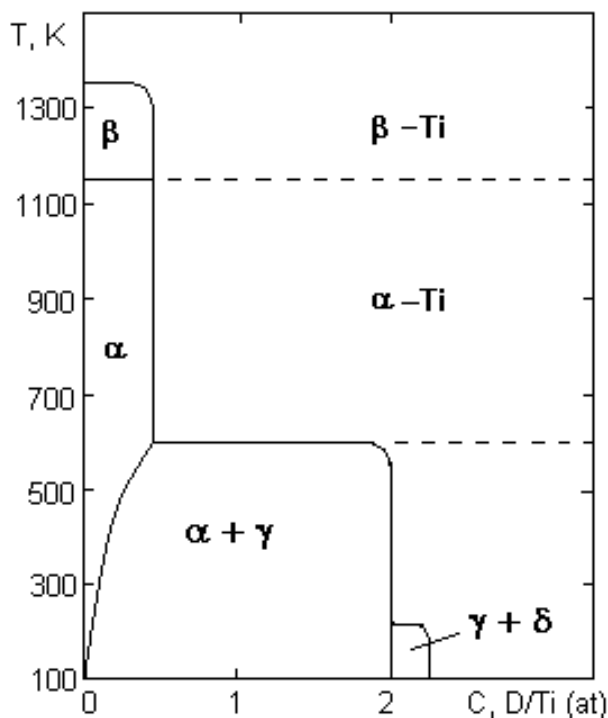


Fig. 2. T-c phase diagram for the Ti-D system.

- α -Ti(D) – solid solution exists up the phase transition temperature of pure titanium α -Ti $\leftrightarrow$ β -Ti

(~ 1100 K). In the phase transition, a part of deuterium is desorbed from titanium, and the remaining hydrogen is dissolved to form the solid solution β -Ti(D).

- γ -Ti(TiD₂) is formed at temperatures below 300 K, and exists up to 600 K.
- β -Ti(D) - solid solution is formed at the phase transition temperature of pure titanium α -Ti $\leftrightarrow$ β -Ti (~ 1100 K), and decays at ~ 1350 K. The decay is accompanied by a full release of deuterium from titanium.
- δ – solid solution of deuterium in titanium hydride decays at ~ 200 K.

Relying on the estimates of temperature ranges for existence of different phases, the T-c diagram of the Ti-D system was constructed (see Fig. 2).

Conclusions

The present work has demonstrated the possibility of constructing, in principle, the T-c diagram of the Ti-D system by the thermodesorption spectrometry method. Among the advantages of this method we should mention the possibility of determining both the total quantity of dissolved gas in the metal, and its content in each separate component (phase) with the determination of temperature ranges of phase existence.

Acknowledgments

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