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The equilibrium between hydrogen isotopes and TiVCr alloys

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ABSTRACT

TiVCr alloys are treated as candidate materials for hydrogen isotope separation because of their prominent inverse isotope effects and hydrogen storage properties. In this work, the relationship between the separation factor (α_{H-D}) that characterizes the isotope effects and the ratio of equilibrium pressures (R_p) of the isotopes was investigated. It was found that α_{H-D} in the plateau region was independent on R_p of the α -phase if the phase transitions during hydrogenating are merely dependent on the hydrogen content and not on the type of hydrogen isotopes. In order to deal with the gradient plateau region that originates from the inhomogeneous compositions of TiVCr alloys, a model relating α_{H-D} in the single γ -phase to R_p in the gradient plateau region was formulated. Furthermore, the values of α_{H-D} were also determined by experiments for $Ti_{0.3}V_{0.4}Cr_{0.3}$ -hydrogen systems, and compared with the prediction results, providing validations to the formulated model.

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Introduction

The hydrogen isotope effects in metals can be used for separation of hydrogen isotopes. So far, only palladium has been employed in the large-scale separation due to its remarkable hydrogen isotope effects [1]. However, the application of palladium is limited by its relatively high cost. Recently, inverse isotope effects were observed in TiVCr alloys [2,3], and their good hydrogen storage properties have been reported widely [4–14]. It is thus expected that TiVCr alloys can be promising in the hydrogen isotopes separation.

On the other hand, a reliable description for equilibrium characteristics of the mixed hydrogen isotope in metals is necessary to the design and optimization of the chromatographic separation of the hydrogen isotopes. For this end, separation factor (α_{H-D}) is often applied to describe the hydrogen isotopic partition between the gas and solid phases, and thus reflects the hydrogen isotope effects [15]. In another aspect, since hydrogen isotope effects can be fundamentally reflected by the difference in the equilibrium pressures of protium and deuterium, it can be assumed that α_{H-D} is closely related to the difference in the equilibrium pressures. For instance, Wicke and Nernst [16], Trentin et al. [17] and Luo

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et al. [18] have proposed models that relate α_{H-D} to the ratio of equilibrium pressures (R_p) of single isotope Pd–hydrogen systems. Unlike Pd–hydrogen systems, the α -phase in TiVCr–hydrogen systems contains larger hydrogen amount [3,19], and the equilibrium pressures in the plateau region (α – γ coexisting) are not constant [3–8]. It is therefore doubtful that the models derived for Pd–hydrogen systems [16–18] can be applied in TiVCr–hydrogen systems.

In this work, the previous models [16–18] were discussed and the distinctive equilibrium properties of TiVCr–hydrogen systems were considered. Subsequently, a simple model relating α_{H-D} to R_p of single isotope TiVCr–hydrogen systems was formulated. The predictions of the model were also compared with the measurements of α_{H-D} values for $Ti_{0.3}V_{0.4}Cr_{0.3}$ –hydrogen systems at different temperatures, herein verifying the inverse isotope effects of $Ti_{0.3}V_{0.4}Cr_{0.3}$ alloy [3].

Models relating α_{H-D} to the equilibrium properties of single isotope Pd–hydrogen systems

In this work, α_{H-D} is defined as:

$$\alpha_{H-D} = \frac{X_D(Y_{H_2} + \frac{1}{2}Y_{HD})}{X_H(Y_{D_2} + \frac{1}{2}Y_{HD})} \quad (1)$$

Here, $X_H = H_s/(H_s + D_s)$, $X_D = D_s/(H_s + D_s)$. H_s and D_s are the number of protium and deuterium atoms in the lattice, respectively. Y_{H_2} , Y_{D_2} and Y_{HD} are the mole fraction of H_2 , D_2 and HD in the gas phase, respectively. In this section, the previous models [16–18] were summarily reviewed, and some new insights were also introduced.

Review

When hydrogen isotope molecules dissolve in the lattice, the molecules will dissociate to atoms,



In the same time, there is reaction of homomolecular isotope exchange (HMIE) in the gas phase,



When reaction (2) reaches equilibrium, the chemical potential of H_2 is equal to that of $[H]$. This leads to

$$\mu_{H_2}^g = 2\mu_H^s \quad (5)$$

Here, $\mu_{H_2}^g$ and μ_H^s are the respective chemical potential of H_2 and $[H]$. They can also be written as

$$\mu_{H_2}^g = \mu_{H_2}^o + RT \ln(a_{H_2}) \quad (6)$$

$$\mu_H^s = \mu_H^o + RT \ln(a_H) \quad (7)$$

Here, a_{H_2} and a_H are the activity of H_2 in the mixed gas phase and H in the solid phase, respectively,

$$a_{H_2} = P^{eq} Y_{H_2} \quad (8)$$

P^{eq} indicates the total equilibrium pressure of a mixed H–D system in palladium. If Raoult's law is employed, and hydrogen in the α -phase is neglected, we have

$$a_H = X_H \quad (9)$$

From eqs. (5)–(9), we obtain

$$\mu_{H_2}^o - 2\mu_H^o = RT \ln\left(\frac{X_H^2}{P^{eq} Y_{H_2}}\right) \quad (10)$$

As to pure protium

$$Y_{H_2} = X_H = 1 \quad (11)$$

$$P^{eq} = P_{H_2}^{eq} \quad (12)$$

Here, $P_{H_2}^{eq}$ indicates the equilibrium pressure in the plateau region for Pd H_2 system.

From eqs. (10)–(12), we have

$$P^{eq} Y_{H_2} = P_{H_2}^{eq} X_H^2 \quad (13)$$

Similarly

$$P^{eq} Y_{D_2} = P_{D_2}^{eq} X_D^2 \quad (14)$$

Moreover, the equilibrium constant (K_{HD}) of reaction (4) is given as

$$K_{HD} = \frac{(P^{eq} Y_{HD})^2}{(P^{eq} Y_{H_2} P^{eq} Y_{D_2})} = \frac{(P^{eq} Y_{HD})^2}{P_{H_2}^{eq} P_{D_2}^{eq} X_H^2 X_D^2} \quad (15)$$

Then

$$P^{eq} Y_{HD} = \sqrt{K_{HD} (P_{H_2}^{eq} P_{D_2}^{eq})} X_H X_D \quad (16)$$

By inserting equations (13), (14) and (16) into equation (1), we have

$$\alpha_{H-D} = R_p \frac{2R_X + \sqrt{K_{HD}/R_p}}{2 + R_X \sqrt{K_{HD} R_p}} \quad (17)$$

Here, $R_p = P_{H_2}^{eq}/P_{D_2}^{eq}$, $R_X = X_H/X_D$.

Luo et al. [18] supposed that the approximation of Raoult's law was unreasonable in the plateau region because of the large hydrogen amount in the solid phase. They then employed the isotope activity coefficients, γ_H and γ_D ,

$$a_H = \gamma_H X_H \text{ and } a_D = \gamma_D X_D \quad (18)$$

They also supposed that $\gamma_H = \gamma_D$, since H and D occupy sites with similar surroundings within the Pd lattice. Hence, they have

$$\frac{a_H}{a_D} = \frac{\gamma_H X_H}{\gamma_D X_D} = \frac{X_H}{X_D} \quad (19)$$

Based on this idea, they obtained the same results as Trentin's [17], i.e., equation (17). Since the model given by Trentin et al. [17] is also the same as that by Wicke and Nernst [16], therefore, the models [16–18] are identical with each other.

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