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Pressure–composition isotherms and reversible hydrogen-induced phase transformations in Ti–6Al–4V

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Abstract

Reversible stepwise phase transformations induced by the addition and removal of hydrogen in pure Ti and Ti–6Al–4V (Ti64) were examined by means of pressure–composition (P–C) isotherm measurement from 550 to 700 °C. Both Ti–H and Ti64–H systems exhibit two pressure plateaus in the P–C isotherms which indicate phase transformations. Phase transformations take place at lower hydrogen content and higher hydrogen pressure in Ti64 than in Ti due to the effect of substitutional elements Al and V. Upon hydrogenation, the Ti–H system exhibits the sequence of phase transformation $\alpha \leftrightarrow \alpha_H \leftrightarrow \alpha_H + \beta_H \leftrightarrow \beta_H \leftrightarrow \beta_H + \delta \leftrightarrow \delta$, whereas the Ti64–H system shows a sequence of $\alpha + \beta \leftrightarrow \alpha_H + \beta_H \leftrightarrow \beta_H \leftrightarrow \beta_H + \delta \leftrightarrow \delta$ because of the presence of the original β phase. Partial phase diagrams for Ti–H and Ti64–H were established based on their P–C isotherms. Modification of microstructure of Ti64 occurs after cyclic hydrogenation. This can be ascribed to hydrogen-induced atomic migration during the sequential phase transformations.

Keywords: Ti–6Al–4V; Hydrogen; Pressure–composition isotherm; Phase transformation; Phase diagram

1. Introduction

Recently, novel thermal hydrogenation processing (THP) has been widely applied to Ti-based alloys. Many interesting features, such as grain refinement, improvement in superplastic forming and reduction of flow stress in forging, have been obtained [1–7]. In this field of study, Ti64 in particular attracts the greatest attention since it is a well-known structural material, accounting for over half of the titanium market. Due to its excellent mechanical properties, good corrosion resistance and low density, Ti64 is widely used in the aerospace, surgical implantation and chemical industries.

In view of the improvement of structure and properties by THP, knowledge on the phase diagram of Ti64 and hydrogen is of importance. Based on a metallographic method, several phase diagrams (temperature vs. hydrogen content) for the Ti64–H system have been reported with a hydrogen content of 30–40 at.% in the temperature ranges 500–1000 °C [1,8] and 0–1000 °C [9]. However, THP is recognized as a gas–solid reaction, so it is necessary to define the phase diagram with thermodynamic variables such as hydrogen pressure, temperature and hydrogen content simultaneously. The best approach to accomplishing this is the measurement of pressure–composition (P–C) isotherms. The occurrence of phase transformation could be characterized by the shapes of P–C isotherms, such as pressure plateaus [10]. Ishiyama et al. first showed P–C isotherms for the Ti64–H system at 100–400 °C up to 60 at.% H [11]. However, the temperatures studied were too low to be applied for THP, and the information relating to phase transformations in the region of hydrogen pressure below 10^3 Pa was not available.

In this study, a Sievert's system capable of measuring hydrogen pressure in the range of 10^2–10^6 Pa was

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established to study the behavior of phase transformations in the Ti64–H system. The study of the Ti–H system was also conducted as a reference. In addition, phase identification and microstructrual characterization were also made to investigate the phase transformation behavior in the Ti64–H system.

2. Experimental

A Sievert's apparatus capable of measuring hydrogen pressure in the range of 10^2–10^6 Pa, modified from that used in a previous study [12], was established. The hydrogen pressure above 10^4 Pa was monitored by a pressure transmitter (Nagano Keiki, Model-KH15) and below this level it was recorded by a capacitance manometer (MKS, Type-626A). The volume of sample reactor was $V_s = 51$ ml. Reservoirs with three different volumes ($V_{r1} = 120$ ml, $V_{r2} = 135$ ml and $V_{r3} = 438$ ml) were equipped to improve the resolution of measurement due to the wide range of hydrogen pressure tested. Based on the ideal gas law, the effective hydrogen pressure was calculated since there was a big difference in temperature between the reservoir and sample reactor. The amount of hydrogen was then calculated by a volumetric method in which a resolution of 8×10^{-6} mol of hydrogen in the specimen could be obtained. By comparing the result of P–C isotherms for Ti obtained in this study with those reported previously [13], the reliability and accuracy of this system was proved.

The specimens used in this study were pure sponge Ti particles (purity = 99%, diameter = 2–5 mm) and Ti64 extra low interstitial. The chemical composition of Ti64 (wt.%) was 0.006 N, 0.008 C, 0.006 H, 0.2 Fe, 0.13 O, 5.9 Al, 4.0 V and Ti bal. Flakes of Ti64 with a thickness of 100 μm were prepared from the as-received bar to reduce the hydrogen diffusion time in the specimen. They were β-solution-treated at 1000 °C in vacuum for 30 min, followed by furnace cooling for homogenization. Approximately 1 g of specimen was loaded for each test. Prior to measurement of P–C isotherms, it was necessary to make several cycles of activation treatment in which the specimen was exposed to 1.5 MPa of hydrogen gas at 600 °C and then dehydrided completely in vacuum at 750 °C. Measurement of P–C isotherms was conducted in the temperature range 550–700 °C, with intervals of 50 °C. The content of hydrogen in the specimen is expressed as H/M (the ratio of hydrogen to metal atoms). To completely remove residual hydrogen in the specimen after each test of the P–C isotherm, the specimen was dehydrided in vacuum at 750 °C. Phase identification of specimens before and after P–C isotherm measurement was made by X-ray diffraction (XRD, Shimadzu-6000). The specimens hydrogenated with 1.47 H/M and 1.17 H/M in Ti and Ti64, respectively, were prepared to examine whether the single δ phase was formed. Silicon was used as an internal standard for XRD. For microstrucutral characterization, the specimens were etched with Kroll's etching solution and analyzed by scanning electron microscopy (SEM, JEOL 5410).

3. Results

3.1. P–C isotherms

The P–C isotherms of pure Ti and Ti64 from 550 to 700 °C are shown in Fig. 1a and b, respectively. For Ti at 700 °C, for instance, the low-pressure plateau for the coexistence of $\alpha_{H,0.06}$ phase and $\beta_{H,0.17}$ phase occurs at a constant pressure of 845 Pa, where the figure in the subscript displays the hydrogen solubility. In addition, a high-pressure plateau consisting of $\beta_{H,1.01}$ phase and $\delta_{1.48}$ phase occurs at a constant pressure of 305 kPa. The hydrogen content of the δ phase rises to 1.62 H/M when the maximum system pressure 10^6 Pa in this study is reached.

The Ti64–H system also exhibits two pressure plateaus, but the low-pressure one is sloped. At 700 °C, with a hydrogen content of 0.1 H/M, phase transformation from α_H to $\beta_{H,0.14}$ occurs with a sloped pressure plateau at approximately 2.4 kPa. The high-pressure plateau at 466 kPa corresponds to coexistence of $\beta_{H,0.70}$ and $\delta_{1.08}$, and eventually the hydrogen content in the δ phase reaches 1.37 H/M at 10^6 Pa.

When the hydrogen atoms were removed from the specimen in steps, the sequence of phase transformations in the Ti–H and Ti64–H systems was reversed, except that there existed a hysteresis gap, as observed in Fig. 1a and b. For both the Ti–H and Ti64–H systems, the behaviors of phase transformation at 550–700 °C were all similar, except that the compositions and plateau pressures were different.

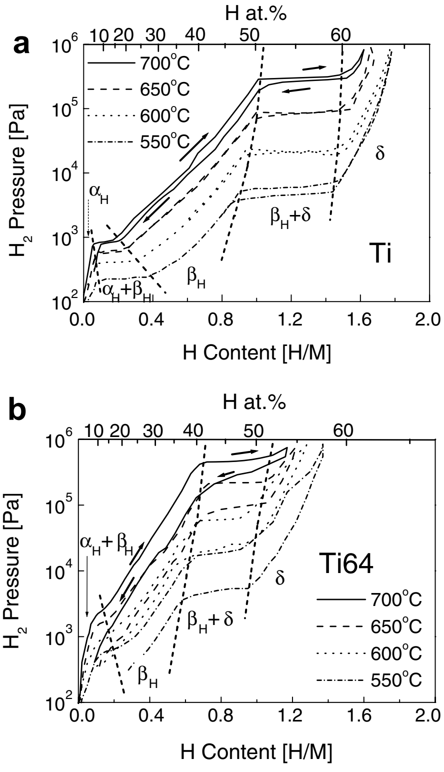

Fig. 1. P–C isotherms for (a) Ti and (b) Ti64.