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Cyclic hydrogenation stability of γ-hydrides for $Ti_{25}V_{35}Cr_{40}$ alloys doped with carbon

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ABSTRACT

An automatic Sievert's apparatus equipped with a temperature-programmed desorption spectrometer was constructed to study the stability of annealed $Ti_{25}V_{35}Cr_{40}C_x$ (x = 0 and 0.1) alloy under cyclic hydrogenation at 6 N H_2. The specimens were tested at 30 °C with a hydrogen loading of around 1.00 H/M, which enabled the phase transformation from β-to γ-hydrides. After 500 cycles, 83% and 90% of the initial hydrogen capacities were preserved for $Ti_{25}V_{35}Cr_{40}$ and $Ti_{25}V_{35}Cr_{40}C_{0.1}$, respectively. Therefore, a small amount of C doping was effective in reducing the hydrogenation degradation of $Ti_{25}V_{35}Cr_{40}$. The hydrogenation degradation of $Ti_{25}V_{35}Cr_{40}$ was examined by measuring the P–C isotherms, temperature-programmed desorption spectra, and X-ray diffraction patterns. The degradation was ascribed to intrinsic disproportionation, *i.e.*, $Ti_{0.25}V_{0.35}Cr_{0.40} + 0.88H_2 \rightarrow yTiH_2 + Ti_{0.25-y}V_{0.35}Cr_{0.40}H_{1.76-2y}$, where the coefficient y indicates the amount of Ti-rich precipitate. The better cyclic hydrogenation stability of $Ti_{25}V_{35}Cr_{40}C_{0.1}$ was related to the suppression of intrinsic disproportionation by the presence of carbon atoms in the body-centered-cubic lattice.

1. Introduction

TiV-based body-centered-cubic (BCC)-type alloys have been explored as advanced hydrogen storage materials because of their excellent maximum hydrogenation capacities of 3.5 wt%. It is important to investigate the stability of the TiV-based alloys under repeated hydrogenation–dehydrogenation applications, such as hydrogen storage tanks, Ni–MH batteries, metal hydride heat pumps, separation of hydrogen isotopes, and H_2 purification membranes [1–9].

To date, few studies have described the cyclic hydrogenation properties under the gas-phase for TiV-based alloys [10–16]. Kamegawa et al. reported that the annealed $Ti_{40}Cr_{57.5}Mo_{2.5}$ alloy maintained only 43% of its initial maximum protium capacity after 300 cycles, which was ascribed to the formation of protium trapping sites caused by an increase in lattice defects that formed during cycling [10]. By alloying with a high vanadium content, the annealed $Ti_8Cr_{12}V_{80}$ alloy lost only 0.8% of the initial hydrogenation capacity after 500 cycles [11]. On the other hand, the cast $Ti_{35}V_{31}Cr_{34}$ alloys were susceptible to hydrogenation degradation within five cycles via the formation of irreversible TiH_2, probably due to microsegregation in the specimen [12]. Similar phenomena have been observed in other cast TiVCr alloys [13]. Only about 23% of the initial hydrogenation capacity of the cast $V_{55}Ti_{20.5}Cr_{18.1}Fe_{6.4}$ alloy remained after 150 cycles. Impurities in the H_2 gas were responsible for some of the degradation because of the presence of metal oxides and adsorption of hydrocarbons onto the surfaces of the specimens [14]. Therefore, the hydrogenation degradation mechanism of TiV-based alloys by either intrinsic and/or extrinsic factors requires closer examination. Approaches that replace the use of the expensive vanadium element in alloys but maintain their cyclic hydrogenation properties are also required [11,16].

Recently, Chandra et al. investigated the effect of interstitial carbon on the improvement in the stability of vanadium hydrides during thermal cycling. After 1000 cycles, the degradation of effective hydrogen capacity was reduced from 20% for VH_x to 5% for $V_{0.995}C_{0.005}H_x$. In addition, a significant reduction in both the plastic deformation of γ-VH_2 and premature fracture of vessels can be obtained by adding a small amount (0.5 at%) of interstitial carbon into the vanadium [17,18]. Kim et al. also suggested that using an

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interstitial nitrogen element could slow down the hydrogenation degradation of annealed $Ti_{33}V_{37}Mn_{30}$ alloys [19]. These results encouraged us to investigate whether a carbon element has the same positive effect for TiV-based alloys. Our previous study showed that the effective hydrogen desorption capacities (desorption pressure $\geqq 0.1$ MPa) at $T = 30$ °C increased from 0.80 H/M for the annealed $Ti_{25}V_{35}Cr_{40}$ to 0.87 H/M for the annealed $Ti_{25}V_{35}Cr_{40}C_{0.1}$ due to the destabilization of the γ-hydride [7]. Therefore, the aim of this study was to investigate the cyclic hydrogenation behavior of the annealed $Ti_{25}V_{35}Cr_{40}$ and $Ti_{25}V_{35}Cr_{40}C_{0.1}$ alloys.

Based on the strong similarities in composition between $Ti_{25}V_{35}Cr_{40}$ and other TiVCr-based specimens, reversible phase transformations of $Ti_{25}V_{35}Cr_{40}$ occurred during hydrogenation and dehydrogenation, as described in equation (1). The phases α, β, and γ represent the solid solution (BCC), the mono-hydride (BCT), and the dihydride (FCC), respectively [20–22].

$$\alpha \leftrightarrow \alpha + \beta \leftrightarrow \beta \leftrightarrow \beta + \gamma \leftrightarrow \gamma \tag{1}$$

At room temperature, only the hydrogen storage capacity discharged from γ to β of the $Ti_{25}V_{35}Cr_{40}$ alloy can be utilized. Thereby, this study focused on the hydrogenation stability of $Ti_{25}V_{35}Cr_{40}$ alloys subjected to hydrogen loading under β ↔ γ cyclic transitions. An automatic Sievert's apparatus equipped with a temperature-programmed desorption (TPD) spectrometer was constructed to study the stability of annealed $Ti_{25}V_{35}Cr_{40}C_x$ ($x = 0$ and 0.1) alloys under cyclic hydrogenation. A TPD technique was employed to examine whether the cycled specimen was degraded extrinsically via surface contamination by impurities in the H_2 gas [14,15,22]. Additional measurements, including hydrogenation kinetics, P–C isotherm curves, maximum hydrogenation capacities, and the changes in phase structure for the specimens, were also included to determine the hydrogenation degradation behaviors of the specimens.

2. Material and methods

$Ti_{25}V_{35}Cr_{40}$ and $Ti_{25}V_{35}Cr_{40}C_{0.1}$ alloys were prepared. Elemental powders of Ti (purity 99.7%), V (purity 99.9%), Cr (purity 99.5%), and C (purity 99.5%) were mixed at the desired stoichiometries, and arc-melted on a water-cooled copper hearth in an argon atmosphere with a flow rate of 15 L/min. The ingots were turned and re-melted five times for homogenization. They were further sealed in a quartz tube under vacuum (10^{-2} Torr), followed by annealing at 1200 °C for 2 h to eliminate segregation [7]. The carbon contents in the specimens were measured by a combustion method using an infrared absorption carbon–sulfur analyzer. Previous report has shown that the carbon concentrations in $Ti_{25}V_{35}Cr_{40}$ and $Ti_{25}V_{35}Cr_{40}C_{0.1}$ were 0.063(4) at% and 0.156(4) at%, respectively [23].

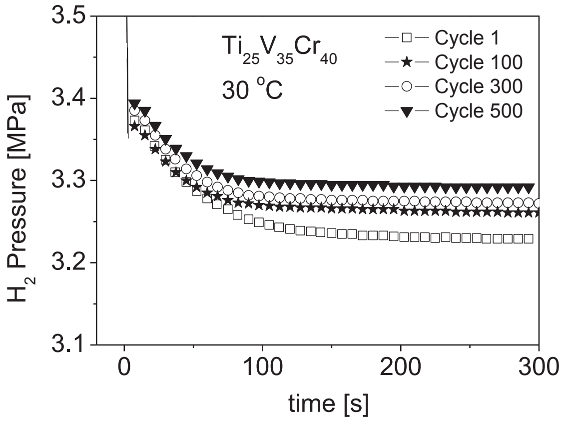
A modified automatic Sievert's apparatus equipped with a TPD spectrometer was constructed for the cyclic hydrogenation test [22,24]. High-purity (99.9999%) hydrogen gas was used. All specimens were activated at 400 °C under a hydrogen pressure of 0.50 MPa. To completely remove the residual hydrogen, the hydrided specimens were heated under vacuum at 600 °C for 1 h. After two cycles of hydriding and dehydriding (*i.e.*, pulverization), P–C isotherm measurements at a maximum hydrogen pressure of 4 MPa were conducted. Cyclic hydrogenation of the alloy was conducted with as many as 500 cycles at 30 °C, and the hydrogen loading in equilibrium was controlled at 1.15 H/M by the volumetric method. The H concentration was conducive to the β to γ phase transformation. Dehydrogenation via the transition from γ to β was accomplished by outgassing the hydrided specimens under vacuum using a rotary pump. Hydrogen absorption for 300 s and hydrogen desorption for 900 s were performed each cycle. The TPD test was conducted under a vacuum in which the pressure of H_2 desorbed from the hydrided specimen was monitored as the temperature increased from 30 °C to 600 °C at a heating rate of 7 °C/min. The phase structures of the annealed and cycled specimens, which had been dehydrided under vacuum at 600 °C for 2 h, were examined by X-ray diffraction (XRD) at two scanning rates (4°/min and 1°/min). Si was added as an internal standard for the XRD measurements.

3. Results and discussion

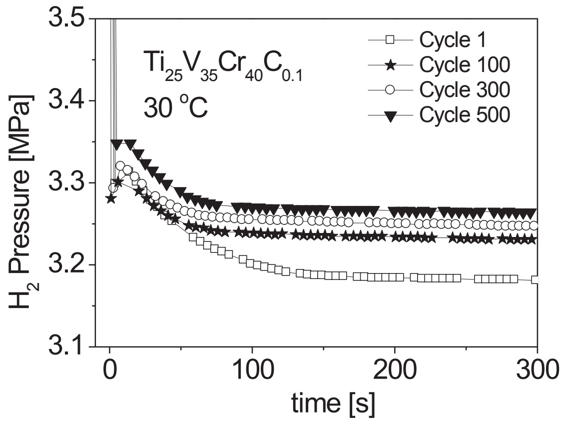
3.1. Hydrogenation kinetics and capacity

The kinetics of hydrogen absorption for $Ti_{25}V_{35}Cr_{40}$ and $Ti_{25}V_{35}Cr_{40}C_{0.1}$ at 30 °C was recorded after each cycle, as shown in Fig. 1(a) and (b), respectively. For each cycle, hydrogen loading of around 1.00 H/M into the specimen was achieved within 100 s. However, the absorption pressures that were required to reach a saturated equilibrium increased with the cycle number.

Fig. 2 shows the variations in the cyclic hydrogenation capacities at 30 °C for $Ti_{25}V_{35}Cr_{40}$ and $Ti_{25}V_{35}Cr_{40}C_{0.1}$. Both specimens displayed a similar tendency toward degradation of the hydrogenation capacity. Rapid degradation was observed within the first 100 cycles, followed by a gradual leveling-off. This phenomenon was correlated with the increase in the final pressures, as observed in Fig. 1. After 500 cycles, 83% and 90% of the initial hydrogen capacities were preserved in $Ti_{25}V_{35}Cr_{40}$ and $Ti_{25}V_{35}Cr_{40}C_{0.1}$, respectively.



(a)



(b)

Fig. 1. Comparison of hydrogen absorption kinetic curves at 30 °C for various cycles. (a) $Ti_{25}V_{35}Cr_{40}$, and (b) $Ti_{25}V_{35}Cr_{40}C_{0.1}$ alloys.