Abstract

Ti-Cr-V series is being extensively studied, because of its high hydrogen storage capacity. In the present work, we have studied the hydrogen absorption-desorption properties of the Ti$_2$CrV alloy. The alloy and its hydrides have been characterized for the structure, and the pressure composition of isotherms, kinetics of hydrogen absorption, hydrogen storage capacity, cyclic hydrogen absorption properties and desorption temperature have been studied in detail. The Ti$_2$CrV alloy shows a maximum hydrogen storage capacity of 4.37 wt% at room temperature. From the cyclic hydrogen absorption study it was seen that the hydrogen storage capacity decreases progressively with cycling initially, but the alloy can maintain steady cyclic hydrogen absorption capacity of 3.5 wt% after the 5th cycle. The DSC measurement of both saturated hydrides show, that the cycled hydride desorbs hydrogen at lower temperature as compared to the hydride not subjected to cycling.

Introduction

Though in the recent years hydrogen storage has attracted many new materials such as carbon nanotubes, porous metal-organic frameworks, complex hydrides, alanates, etc.\textsuperscript{1-3}, but still alloys and intermetallic based hydrides, continue to be the most important materials for practical applications\textsuperscript{4}. The conventional AB$_2$ and AB$_5$ type of alloys, exhibit low gravimetric hydrogen storage capacity of ~1.2 to 1.4 wt%. The new series of Ti-V and Ti-Cr-V-based body-centered cubic (bcc) alloys are being explored extensively, due to their high hydrogen absorption capacity of ~3 wt%, which is almost twice that of conventional alloys. These alloys are considered to be promising third generation hydrogen storage materials\textsuperscript{5}. \textsuperscript{6}. The body centered cubic solid solution alloys show high reactivity with hydrogen at room temperature\textsuperscript{5}. Due to the higher gravimetric storage capacity, these alloys are preferred over the conventional AB$_5$ alloys, used in the Ni-MH batteries. The hydrogen storage properties such as reversibility, desorption capacity hydrogen storage capacity, and desorption temperature of the alloys can be improved, by changing the composition\textsuperscript{5-8}.

Recently, we studied stoichiometric TiCrV alloy and Zr-substituted TiCrV alloys, for their hydrogen storage properties. The 5 at% Zr-substituted TiCrV alloy is found to show maximum hydrogen storage capacity of 3.53 wt% with less hysteresis loss and good cyclic stability\textsuperscript{8}. In the present study, the cyclic hydrogen absorption-desorption properties of the Ti$_2$CrV alloy has been
investigated. The alloy has been characterized for the structure, pressure composition isotherms, hydrogen storage capacity, hydrogen absorption kinetics and the desorption temperature. The cyclic hydrogen absorption properties of Ti$_2$CrV alloy is systematically investigated upto 10$^{th}$ cycle.

**Experimental**

The Ti$_2$CrV alloy was prepared by arc-melting the high purity elements, in a water-cooled copper hearth, under argon atmosphere. For achieving homogeneity, the alloy button was turned over and remelted 4 times. The crystal structure of the as-cast alloy and hydride was examined by X-ray Diffraction (XRD) technique, using monochromatic Cu K$_\alpha$ radiation.

The hydrogen absorption and desorption studies were done, using a Sieverts set up described in our earlier studies. The activation procedure involved heating the alloy under vacuum (10$^{-6}$ mbar) for 2 hours at 673 K. Pressure-composition isotherms were studied in the temperature range 298 K and up to a hydrogen pressure of 2 MPa, using a Sievert’s type set up. The kinetic study was done at room temperature and a hydrogen pressure of 2 MPa after one absorption-desorption cycle. The cyclic hydrogen absorption study was also done. For cyclic hydrogen absorption study, the alloy was activated after each cycle as described above. The hydride sample was surface-poisoned before being taken out. The hydrogen desorption behavior of the saturated hydride sample was studied by DSC measurement. The DSC measurement was done by using DSC823$^{+}$ Mettler-Toledo instrument under argon flow, at a heating rate of 10K/min for both the samples of uncycled and cycled Ti$_2$CrV hydrides.

**Results and Discussion**

**Crystal structure**

Fig.1 shows the XRD pattern of Ti$_2$CrV alloy before and after hydrogen absorption. The Ti$_2$CrV alloy forms pure body centered cubic (bcc) structure, with a lattice parameter of 3.10 Å. After hydrogenation, the alloy forms a hydride with a composition Ti$_2$CrVH$_{9.05}$. The saturated hydride shows face centered cubic (fcc) structure with a lattice parameter of 4.35 Å. Contrary to the TiCrV alloy, on cycling, the hydride of Ti$_2$CrV does not show phase separation, indicating good cyclic stability of the hydride.

**Hydrogen Absorption Study**

The hydrogen absorption and desorption properties have been studied, using a Sievert’s type set up. Fig. 2a shows the room temperature pressure-composition isotherms of Ti$_2$CrV alloy. The absorption isotherm measured at room temperature shows quite a flat plateau and the plateau pressure is less than 0.02 atm. The Ti$_2$CrV alloy shows a maximum hydrogen storage capacity of 4.37 wt% at room temperature and a hydrogen pressure of 2.5 MPa.

The rate of hydrogen absorption has been measured at room temperature, after one cycle of absorption-desorption. The rate of hydrogen absorption as a function of time is shown in Fig. 2b. The kinetics of hydrogen absorption is found to be fast for the Ti$_2$CrV alloy. As can be seen from Fig. 2b, Ti$_2$CrV alloy absorbs hydrogen without any incubation time. The alloy Ti$_2$CrV reaches the 2/3$^{rd}$ of the saturation value in about 290 seconds.
Fig. 3 shows the cyclic absorption isotherm of Ti$_2$CrV alloy at room temperature, studied using Sievert’s type setup. In this figure, we have plotted the pressure composition isotherm of some selected cycles viz. 1$^{st}$, 2$^{nd}$, 3$^{rd}$, 4$^{th}$, 6$^{th}$, 8$^{th}$ and 10$^{th}$. It has been found from literature, that upon cycling, the hydrogen absorption capacity decreases initially, however, after a few cycles it remains the same. The Ti$_2$CrV alloy absorbs a maximum of 9.05 H/ formula unit. All the absorption isotherms show the same plateau pressure below 0.02 atm. The plateau pressure remains unaltered with cycling. The alloy shows maximum absorption of 7.21, 7.19 and 7.21 H/Formula unit in the 6$^{th}$, 8$^{th}$ and 10$^{th}$ cycles, respectively. After a few cycles, a stable absorption capacity of 3.5% is found for the Ti$_2$CrV alloy. The decline in hydrogen absorption capacity may be due to the formation of irreversible stable hydride. Many researchers have found similar cyclic absorption capacity trend in the Ti-Cr-V based alloys $^9,10$.

**Hydrogen desorption Study**

In order to investigate the hydrogen desorption process, and desorption temperature, Differential Scanning Calorimetric (DSC) measurement was performed on the saturated hydride, Ti$_2$CrVH$_{9.05}$ and Ti$_2$CrVH$_{7.21}$. Fig. 4 shows the DSC curve of uncycled and multi cycled hydride. From the figure it can be seen, that both hydrides of the Ti$_2$CrV hydrides
alloy show single endothermic peak. The main dehydrogenation peaks for the multicycle hydride and hydride after one hydrogen absorption desorption cycle, are found at 650 and 695K, respectively. It has been found, that the multi cycled hydride releases hydrogen at slightly lower temperature as compared to uncycled Ti$_2$CrV hydride. The cyclic study reveals, that the hydrogen desorption temperature decreases with cycling of the alloy.

Conclusions

The cyclic hydrogen absorption-desorption properties of Ti$_2$CrV alloy have been studied. This alloy was found have a maximum storage capacity of 4.37 wt%. The kinetics of hydrogen absorption was found to be fast for Ti$_2$CrV alloy without any incubation time. The cyclic hydrogen absorbing ability decreased progressively during the first few cycles and after that it remained almost constant at 3.5 wt% hydrogen absorption capacity. From the DSC analysis, the multicycled hydride showed hydrogen desorption at lower temperature as compared to uncycled hydride of Ti$_2$CrV. The plateau pressure was found to be less than 0.02 atm. at room temperature, indicating that this alloy forms stable hydride at room temperature. Due to the high storage capacity, this alloy could be used in Ni-MH batteries.

References