TiCr\(_{1.2}(V–Fe)_{0.6}\)—a novel hydrogen storage alloy with high capacity

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Abstract

To develop a new alloy with high hydrogen storage capacity, partial Cr in TiCr\(_{1.8}\) was substituted by V–Fe alloy. X-ray diffraction and metallography observation proved that the substitution did not change the phase constitution of TiCr\(_{1.2}(V–F)_{0.6}\). It still remained in its initial Laves phase related body centred cubic structure. Pressure–composition–temperature tests showed that the hydrogen storage capacity could reach up to 3.2 wt% and its reversible capacity to about 2.0 wt%. TG-DSC tests showed that there are two kinds of tetrahedral site for hydrogen atoms to locate.

Keywords: TiCr; Hydrogen storage alloy; X-ray diffraction; Pressure–composition–temperature; TG-DSC

1. Introduction

With the development of modern industry and worsening environment pollution, hydrogen as the representative of green fuels has been given more attention. However, the storage and transport of hydrogen throw obstacles on the way of its wide application. Hydrogen storage alloy is one of the most promising methods for the resolution of the problem. Many kinds of hydrogen storage alloys have extensively been studied in the past decades [1–6]. LaNi\(_5\) based alloys are the first generation of hydrogen storage material and are mainly used as the active substance of negative electrode in rechargeable nickel–metal hydride (Ni–MH) cells. Their hydrogen storage capacity is about 1.4 wt%. TiFe and TiMn based alloys are usually classified as the second generation and their capacities approximate to 1.8 wt%. The greatest obstacle for the application of TiFe alloy is its inertness of the activation before hydrogen absorption, yet TiMn based alloy has the shortcoming of short cycle life and can be poisoned with ease by the impurity gases such as O\(_2\), CO etc. that usually contained in hydrogen. Magnesium based alloys and TiCr based alloys are categorized as the third generation but the operation temperature of magnesium based alloys are over 300 °C, which limited their wide applications.

TiCr based alloy was first found in Brookheaven National Laboratory in 1978 [7]. Johnson prepared TiCr\(_{1.4}H_{5.3}\) at 195 K and 200 MPa hydrogen pressure [8]. Such critical condition made it non-sense for practical application though the alloy has high hydrogen storage capacity. After the discovery of TiCr alloy with hydrogen storage performance it was not given enough attention for its execrable hydrogen storage condition in the consecutive 20 years. But recently, with the imminence increase of hydrogen storage alloy with high capacity, TiCr based alloys have been interested again for its potential of high capacity. The present work developed a kind of novel TiCr based hydrogen storage alloy with high capacity as well as mild application conditions.

2. Composition design and preparation of alloy

To design a kind of TiCr based hydrogen storage alloy with high capacity vanadium and iron were introduced into the matrix. Vanadium, as an important element for hydrogen storage reacted with hydrogen and formed hydride with the composition of V\(_2\)H, VH and VH\(_2\). The hydrogen capacity of VH\(_2\) approximates to 3.8 wt% [9,10]. But, vanadium alloy with high purity has a high price and is not economical.
for practical application especially on a large scale. On the other hand, VH₂ has large hysteresis during the course of hydrogen absorption and desorption. Iron is usually used as an activate element in hydrogen storage alloys. Its occurrence usually reduces the hysteresis and enhances the activation characteristics of the matrix. To reduce the expense of raw material, vanadium and iron with high purity was replaced by cheap V–Fe alloy. The price of V–Fe alloy is rather low compared to that of pure vanadium and iron. The composition of the V–Fe alloy in the study is 82.6 wt% of vanadium and 16.9 wt% of iron. The composition of the new alloy was designed as TiCr₁.₈₋ₓ(V–Fe)ₓ (X = 0, 0.3, 0.6, 0.9). V–Fe alloy was added as substitute for the partial Cr of the matrix. The purity of Ti and Cr was over 99.5 wt%. Each composition of alloys was weighed according to the molecular formula. The crude material was melted in a vacuum arc-melt furnace. In order to prevent the segregation of elements, the ingot was turned over and remelted for five times. Then the liquid alloy rapidly solidified in a vacuum melt-spinning machine with argon atmosphere protection, the cooling rate was estimated about 10⁵ K s⁻¹. The thickness of alloy ribbons was about 60–70 μm.

Based on the pressure–composition–temperature (PCT) and hydrogen absorption and desorption capacity tests, it was found that TiCr₁.₂(V–Fe)₀.₆ alloy had the best comprehensive performance of the series alloys. It was thoroughly studied in this paper. The regularity between hydrogen storage capacity and composition of TiCr₁.₈₋ₓ(V–Fe)ₓ (X = 0, 0.3, 0.6, 0.9) will be reported in other papers.

3. Results and discussions

3.1. Structure analysis of the TiCr₁.₂(V–Fe)₀.₆ alloy

The sample was ground into powder and sieved through the sieve of 200 mesh for X-ray diffraction (XRD) measurements. XRD tests were performed by X’Pert-MPD instrument (graphite filtered Cu Kα radiation) from 20 to 80° of 2θ. The diagram of XRD is showed in Fig. 1. XRD patterns of TiCr₁.₈ are also illustrated for comparison. The XRD patterns of TiCr₁.₂(V–Fe)₀.₆ indicated that the main phase composition of the alloy is TiCr₂ with Laves phase related body centred cubic (BCC) structure, which coincides with the deduction of Thoma [11]. The relative amount of Laves phase and BCC phase changes with the variation of composition of Laves phase related BCC alloys. As Fig. 1 indicated, Laves phase is predominant in TiCr₁.₈, while it can hardly be seen in TiCr₁.₂(V–Fe)₀.₆. Peaks of BCC phase were so strong that they almost thoroughly sheltered the peaks of Laves phases. The radii of Ti, Cr, V and Fe atoms are 144.8, 124.9, 131.1 and 124.1 pm, respectively. It could be deduced that the alloy has symmetrical phase constituent according to the principle of geometric space filling principle. Ritvield analysis of XRD indicated that an unknown alloy phase existed in the alloy, which accounts for only a small portion in the whole body.

The metallography photograph of TiCr₁.₂(V–Fe)₀.₆ also embodied the phase constituent. It could be seen from Fig. 2 that the alloy’s metallography photograph presented a lamellar microstructure, which is the representative of TiCr₂ alloy. It could be deduced that Fe, V formed homogenous alloy with Ti and Cr. TiCr₁.₈ is an interesting compound in the sense that C₁₅ Laves phase is formed only in the non-AB₂ stoichiometric form, which leads to a substitution of Ti atoms onto the Cr sites [11]. V and Fe atoms substituted for Ti or Cr atoms onto the corresponding sites and further led to the increase in hydrogen storage capacity. Based on these discussion it could be deduced that TiCr₁.₂(V–Fe)₀.₆ alloy was consisted of C₁₅ Laves phase and BCC phases.

3.2. PCT tests of TiCr₁.₂(V–Fe)₀.₆ at different temperatures

PCT tests of TiCr₁.₂(V–Fe)₀.₆ were conducted at 273, 303 and 333 K by using Gas Reaction Controller of Advanced Materials Corporation US. Samples were fully activated prior to PCT measurement. Three grams of the
sample powder was put into the reaction chamber of the equipment. Then the chamber was evacuated to $10^{-3}$ Pa and simultaneously heated to 600 K and kept for 30 min. After that, hydrogen with a pressure of 5 MPa was filled into the chamber, which was subsequently cooled into water. The activation course should be repeated several times for full activation of the sample. Before PCT tests, the chamber was evacuated to $10^{-3}$ Pa while heating to 700 K for 30 min to repel the absorbed hydrogen. The PCT tests were performed in the sequence of absorption first followed by desorption. The diagrams of PCT tests at 273, 303 and 333 K are displayed in Fig. 3. For the sake of comparison, the PCT testing results of TiCr$_{1.8}$ are also presented.

The higher portion of each curve enunciates hydrogen pressure of absorption and corresponding hydrogen content for hydrogen absorption. The lower portion is for enunciate hydrogen desorption. The culmination of each curve indicates the maximum absorbed hydrogen content and corresponding pressure. Each point of the curve presented a balance between hydrogen pressure and hydrogen content in the alloy. It could be seen that the hydrogen storage capacity of TiCr$_{1.2}$(V–Fe)$_{0.6}$ was greatly increased with contrast to that of TiCr$_{1.8}$. According to Fig. 3, the maximum of hydrogen absorption content (H/M) increased with the decrease in temperature. The maximum values of H/M 4.54, 3.62 and 2.51 corresponds to 273, 303 and 333 K, respectively. The minimum of desorption at the three temperatures are 1.7, 1.5 and 1.4. The difference between the maximum and the minimum are usually named as reversible hydrogen storage content. The maximum hydrogen content reaches up to 4.54 at 273 K corresponding to 3.2 wt%, which surpassed double capacity of LaNi$_5$ alloy; and the reversible hydrogen content also reaches up to about 2 wt%. When hydrogen first contacts with the alloy it easily occupies the site favourable to hydrogen storage in the BCC crystal cell and forms stable metal hydride. With the increase of absorbed hydrogen content the hydrogen atom occupy sites with less stability in the alloy and hydrogen atoms in the adjacent crystal cells exclude mutually. As a result, with the increase of absorbed hydrogen content the pressure of hydrogen also increases. Ekiba [10] proposed the concept of Laves phase related BCC solid solution with high hydrogen storage capacity. He deduced that the capacity of TiCr$_X$V$_Y$ system might reach up to 2.2 wt%. The introduction of iron resulted in great improvement of hydrogen storage capacity. Our PCT results also proved that Laves phase related BCC solid solution has high storage capacity.

3.3. TG-DSC tests of TiCr$_{1.2}$(V–Fe)$_{0.6}$ Hydride

As mentioned above, quite a lot of absorbed hydrogen did not release from the metal hydride even at 333 K. In order to determine the condition under which hydrogen could be fully released differential scanning calorimetry (DSC) and thermogravimetry (TG) technology coupling thermal analyses were applied.

About 20 mg fully activated samples thoroughly absorbed hydrogen under the pressure of 1 atm were quickly put into the crucible of the NETSCH STA 449C TG-DSC instrument. The working temperatures were between ambient temperature and 500 °C and the heating rate was 10 °C/min. The flowing gas Ar was used as the carrier gas with the rate of 20 ml/min. As showed by TG curve in Fig. 4, the mass losses of the sample increase with the increasing of temperature.

![Fig. 3. PCT curves of TiCr$_{1.8}$ and TiCr$_{1.2}$(V–Fe)$_{0.6}$ at 273, 303 and 333 K.](image)

![Fig. 4. DSC-TG test of TiCr$_{1.2}$(V–Fe)$_{0.6}$ hydride.](image)
When the temperature is over 480 °C the mass of the sample was not decreased anymore but showed a stable weight. The total mass change is about 1.8 wt%. This is in good agreement with the test of PCT curves at 30 °C, which corresponds to 2.5 H/M of hydrogen desorption under the pressure of 1 atm. Based on this test it could be deduced that only when the metal hydride is heated to about 500 °C, the absorbed hydrogen could be released thoroughly.

The peaks of DSC curve embodied heat exchange between the sample and the environment. Two main peaks appeared on DSC curve, which corresponds to thermal absorption at 302.8 and 397.7 °C, respectively. The decomposition course of metal hydride is heat absorbing. Both the endothermic peaks are probably related to the decomposition of two kinds of metal hydride. Hydrogen atoms located at different sites of the crystal cell with different combination energies were released at different temperatures. Beeri presented similar results on research with TiCr1.8 [12]. There are two types of interstitial site for hydrogen atoms. Most of the hydrogen atom occupation takes place with 96 g sites (forming a tetrahedron of 2Ti + 2Cr), with only a minor fraction occupying the 32e sites (forming a tetrahedron of Ti + 3Cr). TiCr1.2(V–Fe)0.6 has similar structure to TiCr1.8 except V, Fe atoms substituted partial Ti or Cr atoms on some interstitial positions.

4. Conclusions

In this paper, partial Cr of TiCr1.8 was substituted by V–Fe alloy, which resulted in great improvement of hydrogen storage of the matrix. The patterns of both XRD and metallography proved that TiCr1.2(V–Fe)0.6 has the Laves phase related BCC structure of TiCr2. PCT tests of the alloy showed that initial hydrogen storage capacity of alloy can reach up to 3.2 wt% at 273 K and the reversible capacity also to about 2.0 wt%. The TG-DSC results imply the alloy probably has two main tetrahedron sites for hydrogen storage. These two positions have different combination energy with hydrogen.

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