

Short communication

A low-cost BCC alloy prepared from a FeV80 alloy with a high hydrogen storage capacity

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Abstract

A $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy prepared from a FeV80 master alloy is reported. It has a high hydrogen absorption/desorption capacity, good activation performance and kinetics. Heat-treatment at 1673 K is an effective way to increase the capacity and flatten the plateau due to the homogenization of the compositions in the alloy and the disappearance of Laves phase after heat-treatment. The heat-treated alloy can absorb 3.76 wt.%H at 298 K. It desorbs 2.35 wt.%H at 298 K and 2.56 wt.%H at 373 K. The development of this alloy could be of great significance to the application of V-based BCC hydrogen storage alloys.

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1. Introduction

BCC alloys have high hydrogen storage capacities (about 3.8 wt.%H) and good hydrogen desorption properties at moderate conditions [1–4]. However, their applications are reduced mainly due to the high cost of vanadium. A FeV80 master alloy is a low-cost vanadium source. Some researchers [5,6] have attempted to prepare BCC alloys from FeV80, but high capacities were not obtained (as shown in Table 1). In this paper, we report a $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy, which was prepared from a FeV80 master alloy and which has high hydrogen absorption/desorption capacities.

2. Experimental

The purities of the raw materials Ti and Cr used were 99.6 and 99.9 wt.%, respectively. An FeV80 master alloy (bought from PZHSTEEL) contains 78.14 wt.%V, 19.16 wt.%Fe and minor amounts of Al, Si, C and O, etc. The alloy was re-melted five times under argon atmosphere (purity: 99.999 wt.%). In addition to Ti and Cr, 3 wt.%Ce was added to the alloy to remove the oxygen and improve the activation performance. Half of the

alloy was heat-treated at 1673 K for 30 min followed by cooling to room temperature in the furnace.

The alloy was crushed into powder directly in air. Powders with particle diameters of 1–3 mm were put into a stainless steel reactor, which was evacuated with a rotary pump at 298 K for 30 min. Then 3 MPa pressure of hydrogen (purity: 99.999 wt.%) was introduced into the reactor. The variation of the pressure with time was recorded to describe the initial activation curves in absorption process. PCT (pressure–composition–temperature) curves in the desorption process were measured subsequently in the pressure range of 0.01–3 MPa.

Powders with about 75 μm in size were used for X-ray diffraction (XRD, DX-2000 type with Cu $K\alpha$ radiation) analysis. The microstructure was observed under scanning electron microscopy (SEM, JSM-5900LV).

3. Results and discussion

3.1. Hydrogen absorption–desorption properties

The initial activation curves of $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy are shown in Fig. 1. After a short incubation of about 1 min, both as-cast and heat-treated alloy reacted fast with hydrogen and reached maximum capacities in ~ 5 min, which shows good activation performance and kinetics. The maximum capacities are

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Table 1
Hydrogen absorption/desorption capacities of some alloys prepared by FeV80 master alloy at moderate conditions

Alloys	Hydrogen capacity (wt.%)		Reference
	Absorption	Desorption	
Ti ₄₀ V _{48.8} Fe _{11.2} Al _{3.5}	3.5	0.5	[5]
Ti ₄₀ V _{47.3} Fe _{7.5} Al _{3.6}	2.2	0.5	[5]
TiCr _{1.2} (V–Fe) _{0.6}	3.2	2.0	[6]

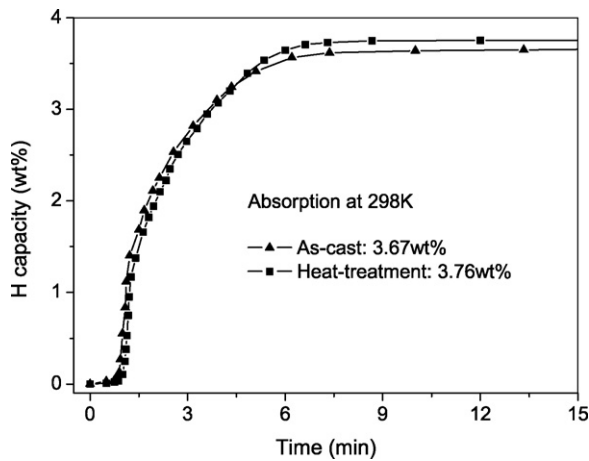


Fig. 1. Initial activation curves of V₃₀Ti₃₂Cr₃₂Fe₆ alloy.

3.67 and 3.76 wt.% at $T=298\text{ K}$ and $P=3\text{ MPa}$ for the as-cast and the heat-treated alloy, respectively.

PCT curves of V₃₀Ti₃₂Cr₃₂Fe₆ alloy are shown in Fig. 2. The as-cast alloy shows a very inclined plateau region and desorbs 2.10 wt.%H at 298 K. After being heat-treated at 1673 K for 30 min, the alloy gets a much flatter plateau and increased hydrogen desorption storage capacity of 2.35 wt.%, which is higher than those of the alloys listed in Table 1. Additionally, the plateau pressure at 298 K reached 0.13 MPa, which is beneficial for the applications of the hydrogen storage alloys.

Fig. 3 shows the PCT curves of the heat-treated alloy at different temperatures. When the temperature rose, the curves moved to the left, indicating that residual hydrogen capacity in the alloy

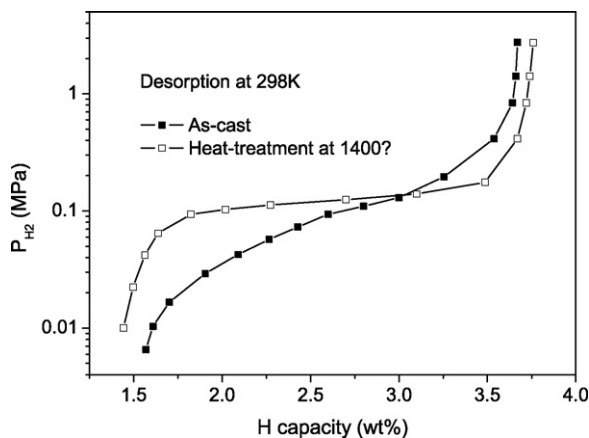


Fig. 2. PCT curves of as-cast V₃₀Ti₃₂Cr₃₂Fe₆ alloy.

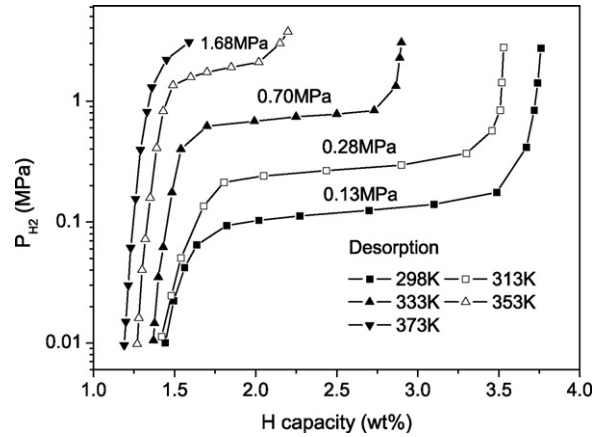


Fig. 3. PCT curves of heat-treated V₃₀Ti₃₂Cr₃₂Fe₆ alloy.

decreases gradually. Usually, in applications, absorption and desorption is not an isothermal process. To obtain a higher hydrogen desorption capacity and good efficiency, absorption often happens at a lower temperature and desorption a higher temperature. From Fig. 3, we can calculate that the alloy can desorb 2.56 wt.%H at 373 K and 2.50 wt.%H at 353 K after absorbing at 298 K.

The plateau pressures increase and the plateau regions become narrow with the increase of temperature. The Van't Hoff curve is displayed in Fig. 4, from which the Van't Hoff equation is obtained as follows:

$$\ln p_{\text{H}_2} = -\frac{4904.8}{T} + 28.2 \quad (1)$$

From the above equation, the hydride formation enthalpy (ΔH) is calculated to be $-40.8\text{ kJ mol}^{-1}\text{H}_2$ and the entropy (ΔS) $-223.6\text{ J K}^{-1}\text{ mol}^{-1}\text{H}_2$. From Eq. (1), the plateau pressure at 373 K is calculated to be 3.5 MPa, which is beyond the pressure limitation in this experiment, thus leading to an incomplete plateau region.

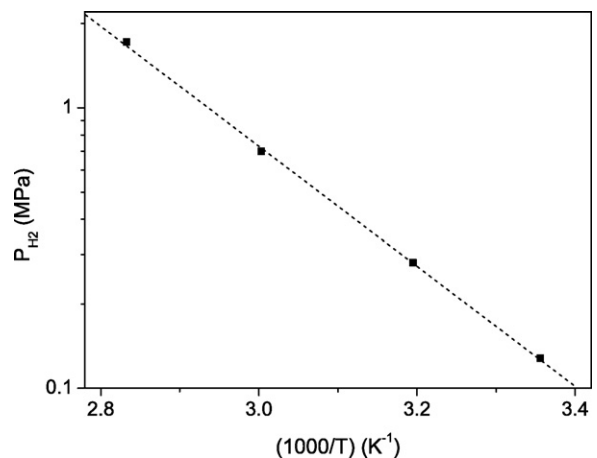


Fig. 4. Plateau pressures of heat-treated V₃₀Ti₃₂Cr₃₂Fe₆ alloy at different temperatures.

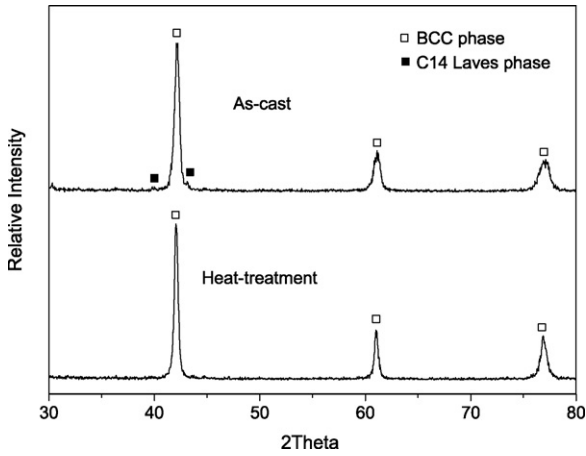


Fig. 5. XRD patterns of as-cast $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy.

Table 2
Crystalline parameters of $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy by XRD

State	Phase	Lattice parameter (nm)	FWHM of (110) peak
As-cast	BCC C14 Laves	0.30334 (a)	0.519
Heat-treated	BCC	0.30331(a)	0.371

3.2. Structure of the phases

Fig. 5 shows the XRD patterns of the $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy. Two phases, including BCC and C14 Laves phase, are found in the as-cast alloy, while only a BCC phase is observed in the heat-treated alloy. Table 2 displays the crystalline parameters of the alloy. Both the as-cast and heat-treated alloys have nearly the same lattice parameters. However, the diffraction peaks of the BCC phase become sharper and narrower after heat-treatment. The above phenomena indicate that heat-treatment at 1673 K for 30 min is an effective way to improve the homogeneity of the compositions in the alloy. As a result, the absorption capacity and desorption capacity at 298 K are improved to 3.76 and 2.35 wt.%, respectively. The structures of heat-treated $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy hydride are shown in Fig. 6. The alloy has

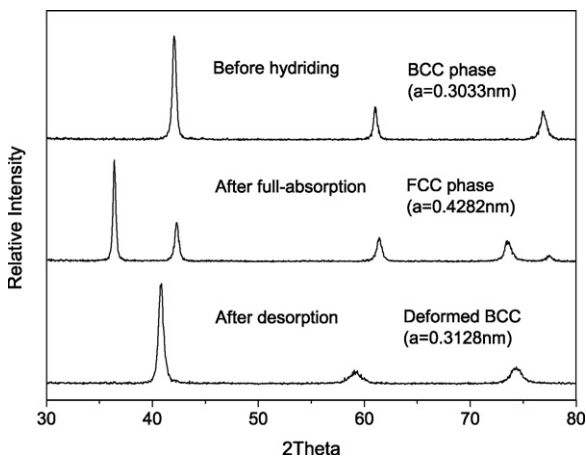


Fig. 6. XRD patterns of heat-treated $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy.

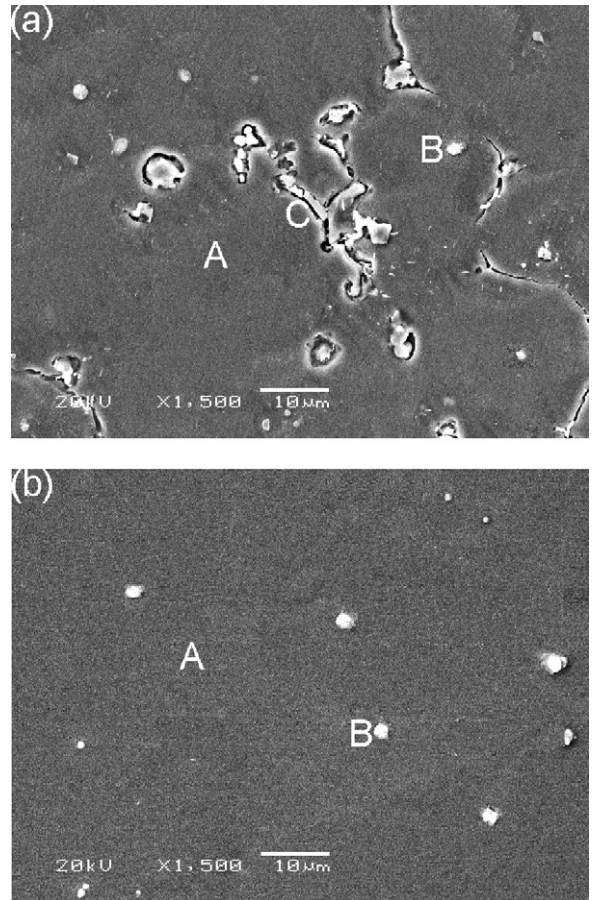


Fig. 7. SEM micrographs of $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy: (a) as-cast, (b) heat-treated. A, BCC phase; B, Ce dispersion phase; C, laves phase.

a BCC structure with a lattice parameter of 0.3033 nm, which transforms to a FCC one and the lattice parameter rises up to 0.4282 nm after full hydrogenation. Then the structure transforms to a deformed BCC one after hydrogen desorption at 298 K, and the lattice parameter was 0.3182 nm.

Fig. 7 shows the SEM micrographs of the $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy. It is clearly seen that the as-cast alloy consists of three phases, BCC (identified as A), Ce (identified as B) and Laves phase (identified as C), among which Ce disperses in the alloy [7] and a Laves phase grows around the grain boundaries [8]. After the alloy was heat-treated, the Laves phase disappears, and only small amount of Ce disperses in the BCC main phase. Ce can't be detected by XRD (as shown in Fig. 5) mainly due to its low content, however, its existence leads to fast activation of both as-cast and heat-treated alloys [7].

4. Conclusions

- (1) A $V_{30}Ti_{32}Cr_{32}Fe_6$ alloy prepared from a FeV80 master alloy had a high absorption/desorption capacity, good activation performance and kinetics.
- (2) Heat-treatment at 1673 K was an effective way to increase the capacity and flatten the plateau due to the homogeneity of the compositions and the disappearance of Laves phase in the alloy. The heat-treated alloy absorbs 3.76 wt.%H at

298 K, and desorbs 2.35 wt.%H at 298 K and 2.56 wt.%H at 373 K, respectively.

- (3) The development of this alloy shows the feasibility to prepare low-cost and high-capacity BCC alloys from a relatively low cost FeV80 master alloy.

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