Journal of Alloys and Compounds 293–295 (1999) 433–436

New V-based alloys with high protium absorption and desorption capacity

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Abstract

The hydrogen absorption properties of V–Zr–Ti–M(M=Fe, Mn, Ni) alloys were examined in order to develop the alloys with high hydrogen capacity. It was found that the best composition among the studied alloys is the V–Zr–Ti–Ni system. A suitable amount of the vanadium in the V–Zr–Ti–Ni system was studied in correlation with its hydrogen absorption properties, and turned out to be around 75 at.%V. Substitution with Zr improved the hydrogen absorption properties in forming the grain boundary network phases of C14 Laves phase. Heat treating the alloys (homogenize and quench) drastically improves the plateau region of *PCT* curves. Zr addition also improves the properties for V–Zr–Ti–Cr alloys. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Hydrogen storage alloy; V-based alloy; Multi-phase alloy; Heat treatment; C14 Laves phase

1. Introduction

Recently, alloys with a high density of protium (hydrogen atoms) were enthusiastically studied not only for high-performance negative electrodes, but also for future fuel cells or for other applications. Vanadium or V-based solid solution type alloys with BCC crystal structure are known to have a high capacity for protium [1–4]. V forms two types of hydride, monohydride, $VH_{\approx 1}$ and dihydride, $VH_{\approx 2}$, and the equilibrium pressure of hydrogenation between V and $VH_{\approx 1}$ is too low at room temperature for utilization. But the equilibrium pressure of hydrogenation between $VH_{\approx 1}$ and $VH_{\approx 2}$ is appropriate for various applications and the theoretical capacity of protium per mass of alloy during this reaction is higher than that of $LaNi_5$ transforming with $LaNi_5H_6$. But one of the problems in use of V-based alloys is difficulty of activation, and heat treatment (i.e. homogenization) has been reported to be ineffective or harmful [1,2] for hydrogen desorption properties. The hydrogen capacity of those reported alloys still remains smaller than that of theoretical value [1,2]. It was reported that V–Ti–Ni alloys can be used as the electrode for secondary batteries through the formation of the TiNi(d)-rich grain boundary network phases that will act as catalysts [2]. It is well known that the Laves phases undergo easy activation treatment. Then it may be possible that the activation of BCC phases will be easier if the alloys contain such Laves phases.

The purpose of the present study is to explore a way to improve the hydrogen absorbing properties by forming the Laves phase in V-based BCC alloys. In particular Zr substitution was tried in the alloys since Zr is known to be a strong former for Laves phase [5]. In addition, it is known that the addition of Ti to V alloys improves the hydrogen absorbing properties. The present study adopts the V–Ti–Zr alloys as the starting alloy system. It was found that Zr addition is effective in forming Laves phase as grain boundary phases in V–Ti–Zr–Ni alloys, and in improving the plateau region, especially after heat-treatment.

2. Experimental procedures

All the alloys used in this study were prepared by arc-melting under purified argon atmosphere from pure metals, with a purity of better than 99 mass%. The alloy was melted into a button form. The buttons were remelted several times in order to improve the homogeneity. The buttons were cut into two pieces. Half of the samples are heat-treated at 1473 K for 18 h in Ar atmosphere, and quenched into water. Phases of samples were determined by X-ray diffractometer (XRD) with a Cu-Kα radiation. The pressure–composition isotherm (*PCT*) curves of the

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PII: S0925-8388(99)00325-4

specimen were measured at 313 K by Sieverts-type apparatus.

3. Results and discussions

The selected studied compositions were V–11.1%Zr–11.1%Ti–11.1%M (M=Fe, Mn, Ni). Fig. 1 shows the PCT curves of 3rd cycle heat-treated V–11.1%Zr–11.1%Ti–11.1%M alloys (M=Fe, Mn, Ni). The figure indicates that plateau pressures of the samples with Mn and Fe turned out to be low, and that with Ni absorbs the highest amount of hydrogen as well as resulting in best flatness of plateau region. As a result, the V–Ti–Zr–Ni alloy system is chosen for further study.

Fig. 2 shows *PCT* curves of 3rd cycle heat-treated V_x–$(Zr_{0.33}$–$Ti_{0.33}$–$Ni_{0.33})_{100-x}$ (x=75, 77.78, 80) alloys. It turned out that 77.78%V alloy curve shows the best properties such as high hydrogen absorbing capacity and best plateau slope. But increment of V content above 80%V yields the 2 stepped plateau region in the *PTC* curve, and reduces its hydrogen capacity. Presently obtained optimum composition of V is much higher than the reported value by Tsukahara [2,6]. The *PCT* curve for as-cast V–7.4%Zr–7.4%Ti–7.4%Ni alloys (77.78%V) is also shown in Fig. 2 for comparison with that of heat-treated alloys. This illustrates that heat-treatment improves the hydrogen absorbing characteristics. An advantage of this alloy is obviously its high capacity for protium (about

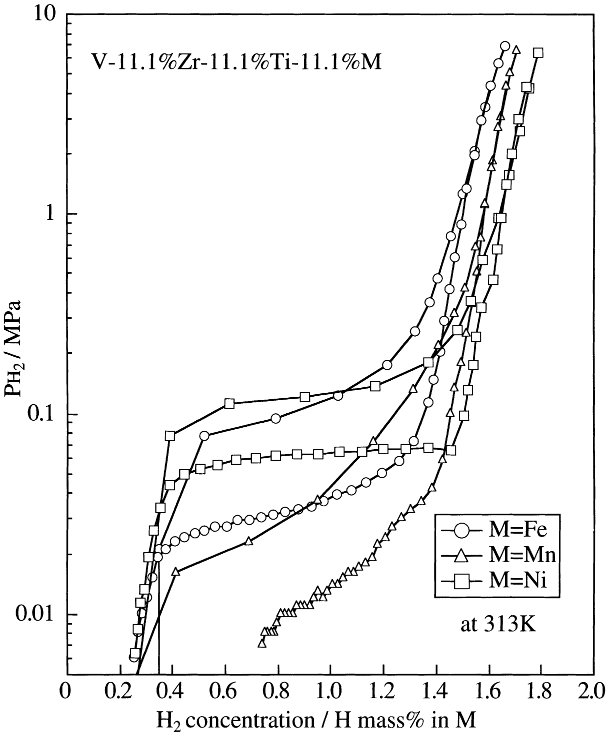

Fig. 1. *PCT* curves of V–11.1%Zr–11.1%Ti–11.1%M (M=Fe, Mn, Ni) heat-treated samples. (3rd cycle, absorption/desorption process).

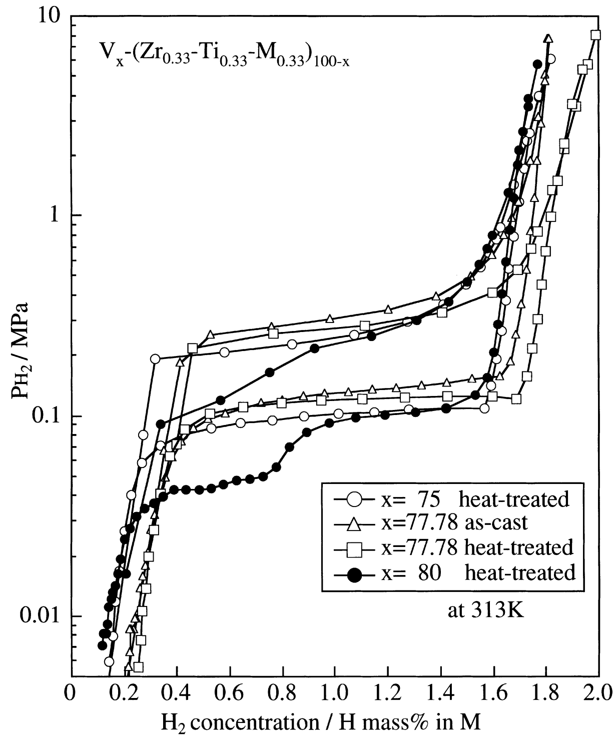

Fig. 2. *PCT* curves of V_x–$(Zr_{0.33}$–$Ti_{0.33}$–$Ni_{0.33})_{100-x}$ (x=75, 77.78, 80) samples. (3rd cycle, absorption/desorption process).

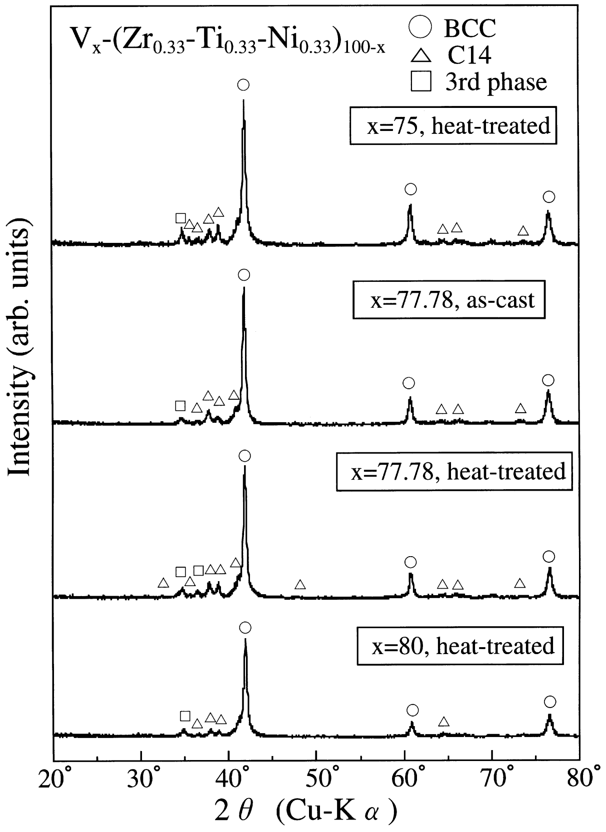

Fig. 3. XRD patterns of V_x–$(Zr_{0.33}$–$Ti_{0.33}$–$Ni_{0.33})_{100-x}$ (x=75, 77.78, 80) samples.

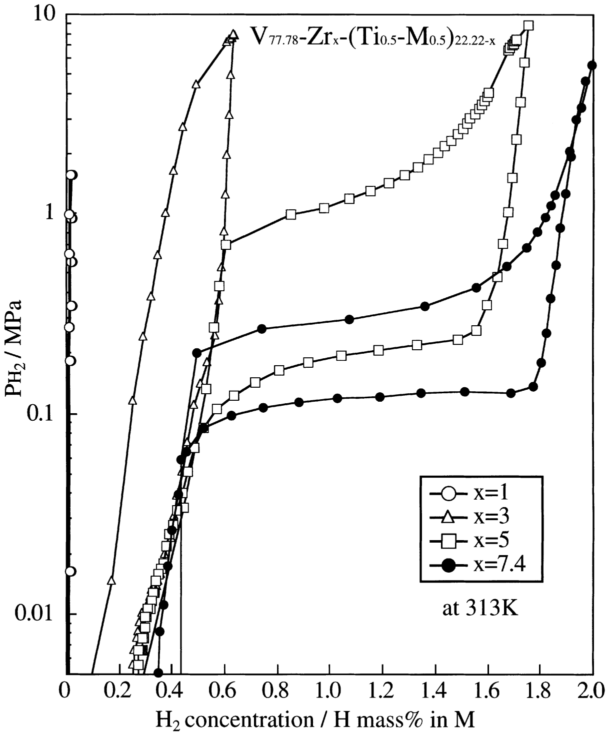

Fig. 4. *PCT* curve of $V_{77.78}$–Zr_x–$(Ti_{0.5}$–$Ni_{0.5})_{22.22-x}$ (x=1, 3, 5, 7.4, 8) heat-treated samples (3rd cycle, absorption/desorption process).

2.0 mass% H_2 at 1 MPa, after 10th cycle). Effective protium mass (defined in this paper as the content of protium in the alloy between 0.01 and 1 MPa) is also high, amounting to 1.6 mass% protium. Further advantages of newly developed V-based alloys are their suitable plateau pressure and easier activation. In particular the flatness of the plateau is comparable to that of $LaNi_5$ homogenized alloys.

Fig. 3 shows XRD patterns of V_x–$(Zr_{0.33}$–$Ti_{0.33}$–$Ni_{0.33})_{100-x}$ (x=75, 77.78, 80) samples. All samples show that the BCC phase is the major phase, with C14 Laves phase and a small amount of 3rd phase as the minor one. The lattice parameter of BCC phase for the heat-treated sample is larger than that of as-cast alloys. This might be the reason for the lower desorption pressure of heat-treated alloy than that of as-cast sample.

Fig. 4 shows *PCT* curves for heat-treated $V_{77.78}$–Zr_x–$(Ti_{1/2}$–$Ni_{1/2})_{22.22-x}$ alloys. The 7.4at.% of Zr addition gives the best hydrogen absorbing and desorbing characteristics. The amount of Zr added below 3% makes the activation difficult. Excess addition of Zr drastically decreases the total amount of absorbing hydrogen.

Fig. 5 shows the SEM photographs of V–7.4%Zr–7.4%Ti–7.4%Ni alloys(a) in as-cast state and (b)with heat-treatment. The BCC matrix phase is surrounded by the grain-boundary (GB)phase, which will be C14 Laves phase, as indicated by the relative X-ray diffraction intensities. The SEM–EDX analysis gives the composition of BCC phase as V–0.5%Zr–5.5%Ti–2%Ni and that of GB phase as V–36%Zr–21%Ti–30%Ni in the as-cast state. The composition of GB 3rd phase is around V–39%Zr–17%Ti–25%Ni. After heat-treatment, the grain size of BCC and C14 GB phase becomes coarsened. The composition of the GB phase will be richer in Zr after heat-treatment. The present works demonstrated that Zr addition to V-based BCC alloys creates the C14 Laves phase as grain boundary network phase, in giving easy activation and smooth plateau region with high amount of absorbing hydrogen. Specially the heat-treatment is very effective in

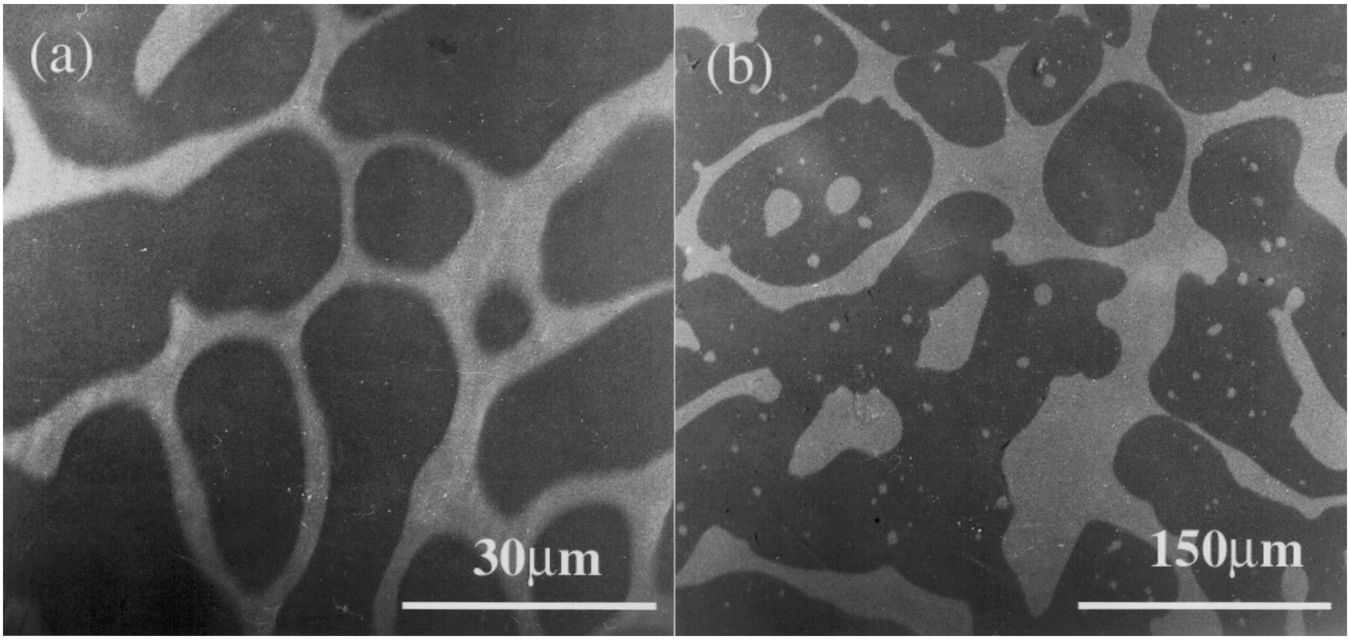

Fig. 5. SEM photographs of V–7.4%Zr–7.4%Ti–7.4%Ni alloys (a) in as-cast state and (b) with heat-treatment.

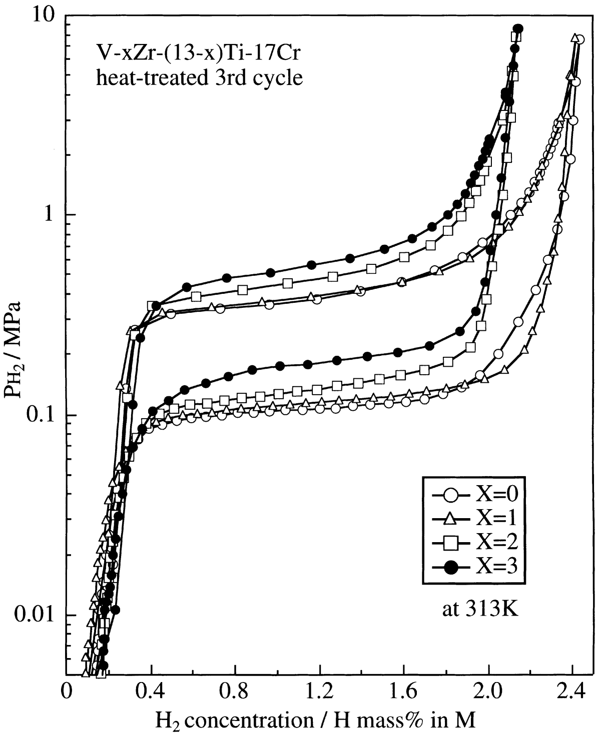

Fig. 6. *PCT* curves of 3rd cycle for heat-treated V–xZr–(13−x)Ti–17Cr alloys (absorption/desorption process).

making the plateau region as flat as that of the $LaNi_5$ alloy.

The Zr addition may also improve the hydrogen absorbing characteristics of V–Ti–Cr alloys reported by Iba [1].

Fig. 6 shows the *PCT* curves of 3rd cycle heat-treated V–xZr–(13−x)Ti–17Cr alloys. The addition of 1%Zr to the alloys improves the flatness of plateau region as well as total capacity of hydrogens. The detailed results on the alloy will be published elsewhere.

4. Conclusion

The hydrogen absorption properties of V–Zr–Ti–M(M=Fe, Mn, Ni) alloys were examined. It was found that the best composition among studied alloys is V–7.4%Zr–7.4%Ti–7.4%Ni alloys. An advantage of this alloy is its high density of protium (absorbs about 2.0 mass% H_2 at 1 MPa, after 10th cycle), at room temperature (at 313 K). Effective protium capacity (defined in this paper as the content of protium in the alloy between 0.01 and 1 MPa) shows also a high amount of 1.6 mass%H. Substitution with Zr improved the hydrogen absorption properties in forming the grain boundary C14 Laves phase network. Homogenizing the alloys significantly improves the flatness of plateau region of *PCT* curves. Zr addition also improves the properties of V–Ti–Cr alloys.

Acknowledgements

This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Area A of 'New Protium Function' from the Ministry of Education, Science, Sports and Culture.

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