Synthesis of Ti-V-Ni Alloys with Mixed Phase Structure and its Hydrogenation and Dehydrogenation Characteristics

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1. Introduction

Vanadium hydride VH_2 has a hydrogen storage capacity of 3.8 mass%, which is greater than that of LaNi_5H_6 of 1.4 mass% and $\text{Zr Mn}_2\text{H}_{3.46}$ of 1.7 mass%. Vanadium seems to be one of the most promising candidates for the hydrogen storage materials to support the coming new hydrogen energy systems. However, VH_2 has the difficult point for practical use that the monohydride VH only desorbs its hydrogen under 0.1 Pa at 313 K. In the case of Ti-V-Ni alloys, the secondary phase of inter-metallic compound TiNi was formed around the main vanadium solid solution phase through metallurgical peritectic reactions^{1)~2)}. While the vanadium monohydride could not be discharged, TiNi phase acted as a good electrochemical catalyst, and the effective hydrogen could be discharged smoothly in electrochemical cell.

We took notice of these electrochemical results. Moreover, we made a plan to form inter-metallic compound Ti_2Ni as the secondary catalytic phase in Ti-V-Ni ternary alloy. Ti_2Ni has a preferable crystallographic coherency with main vanadium solid solution phase to transfer the stored hydrogen with each other.

2. Experimental detail

It is well known that $\text{TiV}_{1.4}$ alloy forms $\text{TiV}_{1.4}\text{H}_{4.6}$ hydride of 3.8 mass% hydrogen concentrations. In this study, $\text{Ti}_{0.73}\text{V}_{1.4}\text{Ni}_{0.27}$ alloy, in which a part of titanium was substituted by nickel, was prepared by the mechanical alloying (MA) of the mixtures of titanium, vanadium and nickel powders. The MA was carried out at 300 rpm for 30 hours in the argon atmosphere. The alloy was heat-treated at 973 K for 1 hour under argon gas flow in order to form the new mixed phase structure.

The structural analysis was carried out by X-ray diffraction (XRD) and scanning electron microscope (SEM). Dehydrogenation characteristics were evaluated by electrochemical equipment* at 298 K and differential scanning calorimeter (DSC). (*Electrochemical equipment was composed of 6 M KOH, metal hydride working electrode, platinum counter electrode and Hg/HgO reference electrode)

3. Results and discussion

3. 1 Structure of the alloys

The XRD results are shown in Fig. 1. Diffractions from the source metals were disappeared, and new broad peaks originated from bcc vanadium of slightly expanded lattice were observed. We confirmed the synthesis of meta-stable vanadium solid solutions supersaturated titanium and nickel. In the profile of the alloy after heat treatment, diffraction peaks indexed in two phases, solid solution of vanadium (bcc, space group #229) and inter-metallic compound Ti_2Ni (Ti_2Ni type structure, space group #227), were observed. Cross-sectional SEM observation indicated that the heat-treated alloy was the new mixed phase of highly dispersed small Ti_2Ni precipitates in the vanadium matrix. This structure was quite different from that of the alloy solidified through the peritectic reactions^{1)~2)}.

3. 2 PCT characteristics of the alloy

The hydrogen storage capacity of the heat-treated alloy was about 2.3 mass% (about 600 Ah/kg) and the effective hydrogen capacity at discharge rate of 20 A/kg was about 1.1 mass% (about 280 Ah/kg). The effective hydrogen seems to be attributed to the discharge from vanadium dihydride to monohydride.

Fig. 2 shows the PCT curve of $\text{Ti}_{0.73}\text{V}_{1.4}\text{Ni}_{0.27}$ alloy in the desorption process. Two plateaus, which were peculiar

Fig. 1 X-ray diffraction profiles of mechanically synthesized $\text{Ti}_{0.73}\text{V}_{1.4}\text{Ni}_{0.27}$ alloy (a) and the alloy after heat treatment (b).

○ : V solid solution phase, ● : Ti_2Ni phase, △ : Meta-stable bcc phase

Fig. 2 PCT curve of dehydrogenation process of heat-treated $\text{Ti}_{0.73}\text{V}_{1.4}\text{Ni}_{0.27}$ alloy.

in two kinds of the vanadium hydrides, were observed. Desorption plateau pressure of vanadium dihydride in this research decreased in comparison with the pressure of pure vanadium dihydride of 0.5 MPa, and on the other hand, that of monohydride increased. The pressure of the pure vanadium monohydride is 0.1 Pa. These pressure shifts are desirable for vanadium to release the stored hydrogen.

3. 3 Dehydrogenation of new mixed phase alloys

To discuss the dehydrogenation of the new mixed phase alloy, DSC measurements were carried out both on the $\text{Ti}_{0.73}\text{V}_{1.4}\text{Ni}_{0.27}$ alloy and on the specially prepared Ti_2Ni . The results are shown in Fig. 3.

Profile 1) and 2) in Fig. 3 are the results of the mixed phase alloy before hydrogenation and after full hydrogenation by the electrochemical technique, respectively. Profile 3) and 4) are the results of the alloys after partial dehydrogenation of the effective hydrogen and after full dehydrogenation, respectively.

In profile 2), two peculiar endothermic peaks corresponding to the decomposition of vanadium dihydride and monohydride are observed. The peak at lower temperature mainly came from the hydrogen desorption of vanadium dihydride and the other one at higher temperature was originated from the desorption reaction of vanadium monohydride. The dehydrogenation temperature of monohydride in this research lowered almost 40 K in comparison with that of the pure vanadium monohydride³⁾. As being suggested in the PCT result, the dehydrogenation property of monohydride was improved.

Profile 4) gave us the second information of the improvement. In the profile, no clear peaks are observed. This indicates that the hydrogen stored as vanadium monohydride must be able to be discharged electrochemically even though at unsatisfied slow discharge rate of 2 A/kg.

We took the third notice of the result in profile 3). This profile shows the dehydrogenation after dehydrogenation of the effective hydrogen. Consequently, it was estimated that half of the hydrogen had to remain in the alloy almost as the vanadium monohydride, and an apparent peak had to appear at high temperature zone in

Fig. 3 DSC profiles of heat-treated $\text{Ti}_{0.73}\text{V}_{1.4}\text{Ni}_{0.27}$ alloy (profiles from 1) to 4)) and Ti_2Ni alloy (profile 5) and 6)).

[Profile 1], Before hydrogenation ; Profile 2), After full hydrogenation, Profile 3), After dehydrogenation of the effective hydrogen ; Profile 4), After full dehydrogenation ; Profile 5), After full hydrogenation ; Profile 6), After dehydrogenation of the effective hydrogen]

the DSC profile. However, only two tiny peaks appeared in the profile as shown in Fig. 3.

Profile 5) and 6) show the dehydrogenation of intermetallic compound Ti_2Ni . We noticed that the DSC profile 3) resembled closely the profile 5) and 6). It was considered that the hydrogen stored in vanadium as monohydride once transferred to highly dispersed Ti_2Ni phases and finally discharged.

4. Conclusion

New $\text{Ti}_{0.73}\text{V}_{1.4}\text{Ni}_{0.27}$ alloy of mixed phase structure of vanadium solid solution and secondary highly dispersed Ti_2Ni phase was formed by the heat treatment technique. DSC analyses of the alloy suggested the possibility of the electrochemical dehydrogenation of vanadium monohydride through the hydrogen transfer to the secondary phase Ti_2Ni .

This approach is expected to be new method to overcome the dehydrogenation difficulty of vanadium hydride.

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References

- 1) M. Tsukahara, K. Takahashi, T. Mishima, T. Sakai, H. Miyamura, N. Kuriwa and I. Uehara ; *J. Alloys and Compd.*, 226, 203 (1995)
- 2) C. Iwakura, W. K. Choi, R. Miyauchi and H. Inoue ; *J. Electrochem. Soc.*, 147, 2503 (2000)
- 3) H. Yukawa ; *J. Alloys and Compd.*, 330, 105 (2002)