

Short communication

Structure of the secondary phase and its effects on hydrogen-storage properties in a $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy

Q.A. Zhang^{*}, Y.Q. Lei, C.S. Wang, F.S. Wang, Q.D. Wang

Department of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, China

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Abstract

The phase structures and hydrogen storage properties of a $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy are studied. It is found that this alloy consists of a matrix and a secondary phase. The matrix is a B2-type compound with bcc structure and the secondary phase is a C14-type Laves phase with hexagonal structure. This alloy electrode has a larger charge–discharge capacity than stoichiometric TiNi electrodes but shows poorer activation behaviour. Optimizing the content of secondary phase is necessary for improving the overall hydrogen-storage properties of substituted Ti–Ni system alloys. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconium- and vanadium-substituted TiNi alloy; Phase structure; Hydrogen absorbing–desorbing capacity; Activation

1. Introduction

TiNi alloy of stoichiometric composition has been widely studied for its superior shape memory property. Moreover, the hydrogen-storage property of the same alloy has also attracted the attention of scientists. Ti–Ni system electrodes were first studied by Justi et al. [1] because of their relatively low specific weight and good oxidation resistance. These electrodes did not, however, exhibit sufficiently long cycle lives and high-rate capacities. At low constant-current discharge rates, the reversible electrochemical capacity was 210 to 250 mAh g⁻¹ [2], but the useful capacity decreased to 180 mA g⁻¹ at a rate of 50 mA g⁻¹ [3]. Further research [4,5] revealed that the electrochemical properties of hydride electrodes could be greatly improved by using polyphasic alloys. The investigations of Gutjahr [5] showed that alloys containing TiNi and Ti₂Ni phases have a larger charge–discharge capacity than TiNi electrodes.

The electrochemical properties of a $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy, in which Ti is partly substituted by Zr and V in TiNi alloy, was studied by Jordy et al. [6]. They found that this alloy has a high charge–discharge capacity and can be considered as a potential electrode material in nickel/metal hydride (Ni/MH) batteries. Their investigations also

showed the $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy to have a main phase with B2 structure and a minor precipitated grain boundary phase. Nevertheless, the structure of the precipitated phase and its effects on hydrogen-storage properties are not yet clear. The aim of the present paper is to study these features in more detail.

2. Experimental details

Samples of a $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy were prepared by arc melting under an argon atmosphere and were subsequently sealed in evacuated quartz tubes. They were annealed at 1273 K for 5 h followed by quenching in water to ensure homogeneity. The samples were crushed into powder of 300 mesh [7]. Test electrodes were prepared by mixing alloy powder with copper powder in a weight ratio of 1:2 and then cold-pressing the mixture to form pellets.

Prior to electrochemical testing, all alloy electrodes were activated by immersion for 1 day in 6 M KOH solution. The characteristics of these negative electrodes were examined by using a sintered Ni(OH)₂/NiOOH positive counter electrode and a Hg/HgO (6 N KOH) reference electrode. All potentials are reported with respect to this reference electrode. The alloy electrodes were charged with a current density of 100 mA g⁻¹ for 6 h and discharged with a current density of 50 mA g⁻¹ to –0.6 V at 298 K.

^{*} Corresponding author. Fax: +86-571-795-11-52.

Each phase was subjected to metallographic examination and composition analysis by means of scanning electron microscopy (SEM) with a Philips-XL30 microscope equipped with an energy dispersive X-ray (EDX) spec-

trometer. For metallographic studies, samples were etched in a solution of 10% HF, 40% HNO₃ and 50% H₂O (by volume). To evaluate the crystal structure of the alloy, X-ray diffraction (XRD) was performed with a Rigoku

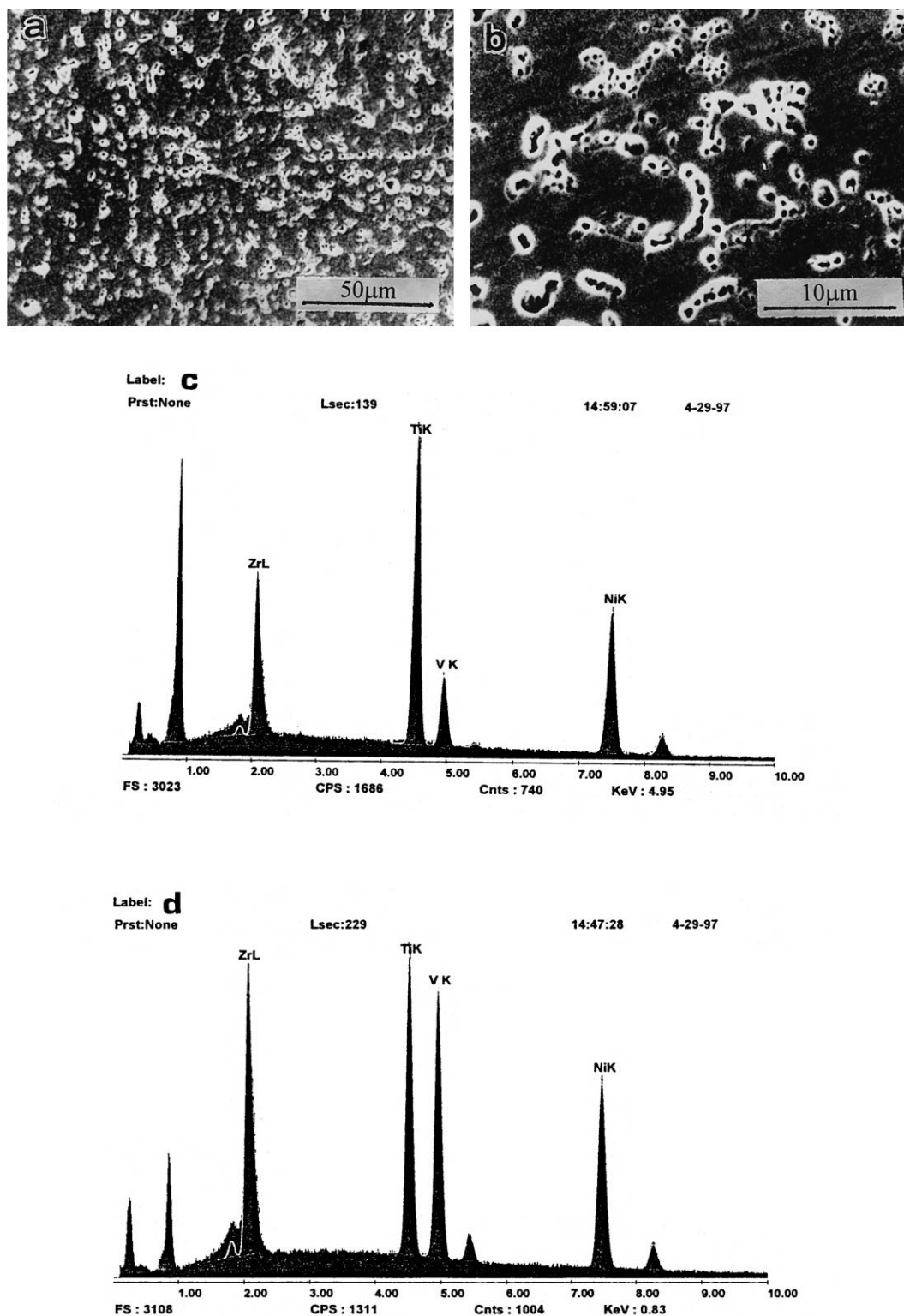


Fig. 1. (a) Electron micrograph showing the morphology of the matrix and the secondary phase in Ti_{0.7}Zr_{0.2}V_{0.1}Ni alloy aged at 773 K; (b) magnified image for (a); (c) and (d) EDX spectra taken from the matrix and the secondary phase, respectively.

D/MAX-3B diffractometer using Cu $K\alpha$ radiation at 40 kV and 30 mA.

3. Results and discussion

3.1. Phase structure

Samples of the heat-treated $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy were first examined with SEM. Electron micrographs are shown in Fig. 1a and b. Martensitic transformation was not observed because of the lowered M_s temperature caused by substitution of Zr and V, yet a fine precipitated phase was found in the matrix. For ascertaining the structure of the secondary phase, powdered samples of the annealed $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy were studied by XRD analysis. The matrix was found to have a B2 structure with a lattice parameter of 0.3052 nm, as shown in Fig. 2a. The secondary phase was indexed to be a C14-type Laves phase with a hexagonal structure with $a = b = 0.5017$ nm and $c = 0.8150$ nm, and not any of the intermetallic compounds, Ti_2Ni , $\text{Ti}_{11}\text{Ni}_{14}$, Ti_2Ni_3 and TiNi_3 , which could be formed according to the phase diagram of the Ti–Ni system. We conclude that the sites of atoms change to a certain degree in the secondary phase. As zirconium atoms are much larger it is difficult for them to replace nickel atoms. Thus, we suggest that zirconium atoms are substituting titanium atoms only, while the smaller vanadium atoms are substituting nickel ones.

To verify this assumption, SEM/EDX examinations were made, as shown in Fig. 1c and d. EDX spectra indicate that the formulae (compositions) of the matrix and the secondary phase are $\text{Ti}_{0.74}\text{Zr}_{0.18}\text{V}_{0.08}\text{Ni}$ and $\text{Ti}_{0.65}\text{Zr}_{0.35}\text{Ni}_{1.3}\text{V}_{0.7}$ respectively. Since it is known that TiNi_2 does not exist in the Ti–Ni system, substitution of

Zr and V is responsible for the formation of the $\text{Ti}_{0.65}\text{Zr}_{0.35}\text{Ni}_{1.3}\text{V}_{0.7}$ phase. In this AB_2 -type phase, Ti and Zr atoms occupy site A, and Ni and V atoms occupy site B. It is interesting to find the $\text{Ti}_{0.65}\text{Zr}_{0.35}\text{Ni}_{1.3}\text{V}_{0.7}$ intermetallic compound to be a C14 Laves phase, since such a phase does not usually exist in a Zr–Ni binary system [8] and ZrV_2 is a C15 Laves phase [9]. Perhaps, the simultaneous substitution of Zr and V is the reason for the formation of the C14 phase. According to the model of Elliot and Rostoker [10], $\text{Ti}_{0.65}\text{Zr}_{0.35}\text{Ni}_{1.3}\text{V}_{0.7}$ has an electron:atom ratio of 1.85 which is in the range of stability of the C14 structure (from 1.80 to 2.32).

3.2. Electrochemical characteristics

TiNi alloy with B2 structure has poor activation properties. When pulverized electrochemically, however, it is easier to activate and usually reaches a maximum discharge capacity after two charge–discharge cycles [11]. In order to determine the effect of the precipitation of C14 Laves phase on the activation and the electrochemical capacity of the $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy electrode, the discharge capacity was determined as a function of the charge–discharge cycle number at a discharge current density of 50 mA g^{-1} (see Fig. 3). At 298 K, the activation properties of the electrode were poorer than those of the TiNi electrode. Although the electrode was activated in advance by immersion in 6 M KOH solution, it did not reach a maximum discharge capacity until the fifth cycle.

As the C14 Laves phase is known to have a larger capacity than the C15 phase alloy [12], it is expected that the secondary C14 Laves phase, viz., the $\text{Ti}_{0.65}\text{Zr}_{0.35}\text{Ni}_{1.3}\text{V}_{0.7}$ phase in the $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy, will result in a larger capacity relative to TiNi. In our experiments, the TiNi electrode had a discharge capacity

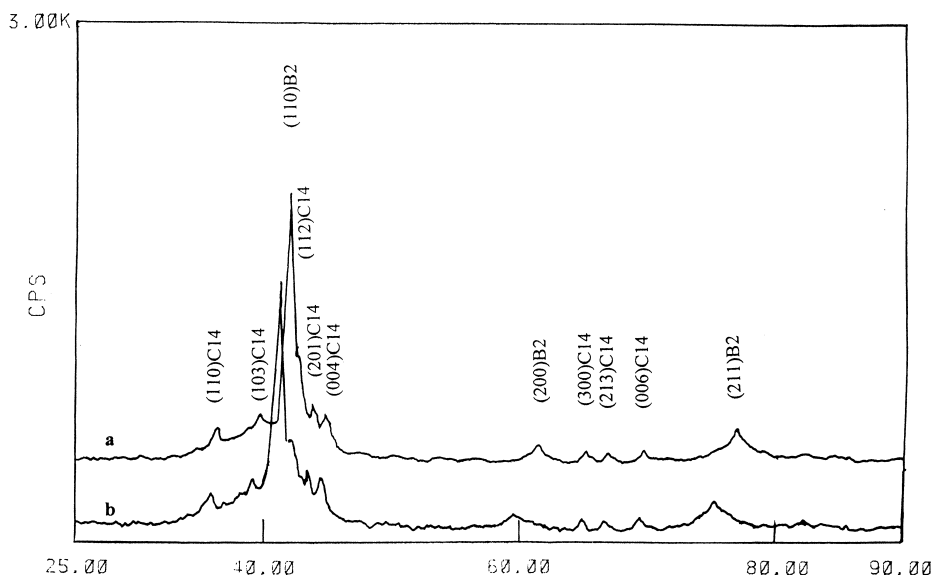


Fig. 2. XRD pattern for $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy powder: (a) before charging; (b) after two charge–discharge cycles.

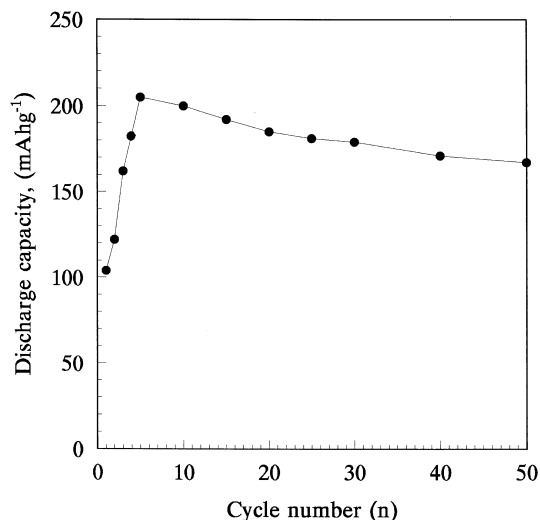


Fig. 3. Discharge capacity vs. cycle number for alloy electrode (charged at 100 mA g^{-1} for 6 h, discharged at 50 mA g^{-1} to -0.6 V in 6 M KOH electrolyte at 298 K).

of about 180 mAh g^{-1} at a current density of 50 mA g^{-1} . The maximum discharge capacity of the $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy electrode was 205 mAh g^{-1} . It is thought that the contribution to the increment of discharge capacity is made both by the matrix and by the secondary phase. The charge–discharge capacity of the matrix was increased due to its enlarged lattice parameters [6]. The B2-type matrix of the annealed $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy has a lattice parameter of 0.3052 nm , which is larger than that of B2-type TiNi ($a = 0.301 \text{ nm}$ [13]). The precipitated C14 Laves phase with high capacity is also considered important for the increase in discharge capacity. The present results show, however, that the annealed $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy does not exhibit a large discharge capacity, as expected from the work of Jordy et al. [6]. The difference in capacity is probably due to the different methods of preparing test electrodes and experimentation. In the experiments of Jordy et al., electrodes were prepared by sintering and the discharge was conducted under potentiostatic conditions at -0.8 V . By contrast, our electrodes were prepared by cold pressing with copper powder and then discharged under galvanostatic conditions at a current density of 50 mA g^{-1} to -0.6 V . Thus, hydrogen in our electrodes was not completely desorbed during discharging. The XRD analysis of an electrode without Cu powder shows that after two charge–discharge cycles the diffraction peaks of the matrix phase after discharging shift to smaller diffraction angles. This indicates that, unlike the experiments of Jordy et al., the electrodes in our experiments were not completely

discharged. From the above results and discussion, it is evident that both the matrix and the secondary phase are important factors in determining the electrochemical properties of Ti–Ni alloy systems.

4. Conclusions

There are two phases, a matrix and a secondary phase, in annealed $\text{Ti}_{0.7}\text{Zr}_{0.2}\text{V}_{0.1}\text{Ni}$ alloy. The matrix is a Zr- and V-substituted TiNi compound with a large lattice parameter compared with stoichiometric TiNi. The secondary phase of $\text{Ti}_{0.65}\text{Zr}_{0.35}\text{Ni}_{1.3}\text{V}_{0.7}$ is a C14-type Laves phase with a hexagonal structure.

The alloy electrode has a discharge capacity of 205 mAh g^{-1} at a 50 mA g^{-1} discharge current density and 298 K . Both the matrix and the secondary phase contribute to this capacity. On the other hand, the secondary phase lowers the activation property of the alloy. To improve the overall hydrogen-storage properties of Zr- and V-substituted TiNi alloys, it is necessary to optimize the compositions.

Acknowledgements

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