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Characteristics of titanium-based C14-type Laves phase alloys and their hydride electrodes

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Abstract

The pressure–composition–temperature (PCT) isotherms, lattice parameters and electrode properties of titanium-based Laves phase alloys with various compositions were studied in this work. The as-cast pseudobinary $Ti_{1-x}Zr_xFe_{0.15}Mn_{1.21-y}V_{0.64}Ni_y$ alloys ($x=0$–0.2, $y=0$–0.6) were found to have the same crystal structure of the C14-type Laves phase by analysis of X-ray diffraction patterns. The equilibrium characteristics of their hydrides obtained by measuring PCT isotherms at 30 °C were attributed to both geometric and electronic factors. The electrode properties of the hydrides were dependent on both the plateau pressure of the PCT curves and the electrocatalytic activity of their alloys.

1. Introduction

Metal hydrides are promising materials for the negative electrode in rechargeable nickel–hydrogen batteries since they provide a high electrochemical capacity without causing environmental pollution. Many studies have been carried out on AB_5-type and Ti(Zr)–Ni system alloys as potential electrodes [1, 2].

Recently Laves phase metal hydrides have been studied because of their large hydrogen-absorbing capacity and relatively long electrochemical charge–discharge cycle. Much research has been focused on zirconium-based Laves phase metal hydrides, which have the disadvantage of requiring many charge–discharge cycles for activation [3]. However, the performance of zirconium-based Laves phase metal hydrides has been improved by increasing the equilibrium pressure of the hydrides. Titanium-based Laves phase metal hydrides have a large hydrogen-absorbing capacity, easy activation behaviour and high equilibrium pressure [4]. By substituting some of the components, the equilibrium pressure required for good electrochemical performance can be decreased.

In this work we have concentrated on Ti–Fe–Mn–V alloys, whose hydrides exhibit a larger reversible absorption of hydrogen than that of $LaNi_5$. The alloys have the C14-type Laves phase structure. By substituting and optimizing some of the components, their hydride plateau pressure was decreased and the electrochemical capacity of the hydride electrode was increased. We also investigated the geometric and electronic effects on titanium-based Laves phase hydriding behaviours.

2. Experimental details

$Ti_{1-x}Zr_xFe_{0.15}Mn_{1.21-y}V_{0.64}Ni_y$ alloys with the Laves phase structure were prepared by arc melting in an argon atmosphere. $TiFe_{0.15}Mn_{1.21-y}V_{0.64}Ni_y$ alloys ($y=0$–0.6) were obtained by modifying the ratios of manganese and nickel, while $Ti_{0.8}Zr_{0.2}Fe_{0.15}Mn_{0.61}V_{0.64}Ni_{0.6}$ alloy was obtained by substitution of titanium by zirconium in $TiFe_{0.15}Mn_{0.61}V_{0.64}Ni_{0.60}$ alloy. The alloys were crushed and ground mechanically to below 300 mesh. In order to identify their crystal structure and lattice parameters, X-ray diffraction measurements were performed. The hydrogen storage performance of the alloys was measured by determination of their pressure–composition–temperature (PCT) characteristics at 30 °C and their hydride electrode characteristics were also evaluated.

The electrodes were prepared by pressing the alloy powder after mixing it with nickel powder and polyvinyl alcohol (PVA), *i.e.* 0.6 g of alloy powder, 0.1 g of nickel powder and 0.01 g of PVA were mixed and then pressed into a foamed nickel plate.

The characteristics of these negative electrodes were examined using a sintered nickel electrode as counterelectrode and an Hg/HgO (6N KOH) electrode as reference electrode. The electrodes were charged with

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a current density of 50 mA g^{-1} for about 12 h in 6 N KOH electrolyte. The discharge capacities were then measured under conditions of a constant current density of 50 mA g^{-1} at room temperature and a discharge end potential of -0.740 V.

3. Results and discussion

X-Ray diffraction analysis of the Ti$_{1-x}$Zr$_x$Fe$_{0.15}$Mn$_{1-y}$V$_{0.64}$Ni$_y$ ($x=0$–0.2, $y=0$–0.6) alloys showed that their structures were the hexagonal C14-type Laves phase irrespective of the composition. The lattice volume of the TiFe$_{0.15}$Mn$_{1-y}$V$_{0.64}$Ni$_y$ alloys ($y=0$–0.6) decreased as the amount of nickel increased (see Table 1). In the case of the Ti$_{1-x}$Zr$_x$Fe$_{0.15}$Mn$_{0.61}$V$_{0.64}$Ni$_{0.60}$ alloys ($x=0$–0.2), in contrast, replacing titanium by zirconium led to the alloy lattice volume increasing.

The lattice parameters of the alloys were dependent on the alloy composition, especially on the atomic radii of the metals. The atomic radii of manganese and zirconium are larger than those of nickel and titanium respectively (see Table 2). Therefore the changing tendency of the lattice volume was predictable on the basis of the average radius of A or B atoms in AB$_2$ compounds.

A convenient method for characterizing the properties of any alloy–hydrogen system involves the measurement of PCT curves. A family of such isotherms for the alloys is illustrated in Fig. 1 and characteristic values from Fig. 1 are given in Table 1. All these alloys were activated easily.

Figure 1 and Table 1 show that both the hydrogen equilibrium pressure in PCT measurements and the measured hydrogen storage capacity (H/M) decreased when the amount of nickel was increased in the TiFe$_{0.15}$Mn$_{1.21-y}$V$_{0.64}$Ni$_y$ alloys ($y=0$–0.6). Moreover, the flatness of the plateau pressure of the hydrides decreased as the amount of nickel increased. The measured hydrogen storage capacity (H/M) increased but the hydrogen equilibrium pressure in PCT measurements decreased drastically with the substitution of zirconium in the case of the Ti$_{1-x}$Zr$_x$Fe$_{0.15}$Mn$_{0.61}$V$_{0.64}$Ni$_{0.60}$ alloys ($x=0$–0.2).

According to the geometric model of Burch and Mason [5], a reduction in the lattice volume of an alloy or in the size of the tetrahedral interstices for hydrogen occupation should cause both an increase in the hydrogen equilibrium pressure of the hydride and a decrease in the hydrogen storage capacity. However, the TiFe$_{0.15}$Mn$_{1.21-y}$V$_{0.64}$Ni$_y$ alloys ($y=0$–0.6) showed the opposite tendency, *i.e.* the hydrogen equilibrium pressure of the alloy hydrides decreased gradually with decreasing lattice volume of the alloys, as found in ZrMn$_{2-x}$Ni$_x$ alloys [6]. Besides the geometric factor, an electronic factor also contributes to the hydriding behaviour of the alloys. The electronic factor was the possible reason for the anomalies in the relation between the hydrogen equilibrium pressure and the lattice volume for the above alloys. There is stronger bonding between titanium and B atoms in AB$_2$ compounds with substitution of nickel. Accordingly, the net charge at the hydrogen atom that results from the metal-to-hydrogen charge transfer decreased, while the interaction between the H 1s and B 3d electronic states was weakened [7]. The interaction resulted in a decrease in the hydrogen equilibrium pressure. Therefore the hydrogen equilibrium pressure of the hydrides appears to be governed by electronic rather than geometric factors for a system with a smaller change in alloy lattice volume.

For the Ti$_{1-x}$Zr$_x$Fe$_{0.15}$Mn$_{0.61}$V$_{0.64}$Ni$_{0.6}$ alloys ($x=0$–0.2) the lattice volume of the alloys or the size of the tetrahedral interstices for hydrogen occupation becomes larger without changing the electron density upon zirconium substitution. The decrease in the hydrogen equilibrium pressure of the hydrides arose mainly from the geometric factor. At the same time the affinity of A atoms in AB$_2$ compounds also contributed to the hydrogen storage capacity and the stability of the hydrides.

In the electrochemical tests (see Fig. 2) the electrochemical discharge performance of these alloy elec-

TABLE 1. Structural parameters of Ti$_{1-x}$Zr$_x$Fe$_{0.15}$Mn$_{1.21-y}$V$_{0.64}$Ni$_y$ alloys ($x=0$–0.2, $y=0$–0.6) and characteristics of their hydrides

Alloy	Lattice parameter (Å)		Lattice volume (Å^3)	H/M	Equilibrium pressure (MPa)
	a	*c*			
$x=0$, $y=0$	4.892	8.027	166.35	0.93	0.45
$x=0$, $y=0.2$	4.884	8.036	166.01	0.93	0.34
$x=0$, $y=0.4$	4.881	7.970	164.47	0.90	0.31
$x=0$, $y=0.6$	4.881	7.952	164.03	0.80	0.23
$x=0.2$, $y=0.6$	4.916	8.014	167.77	0.96	0.082

H/M values: ratio of hydrogen atoms in solid to total metal atoms.

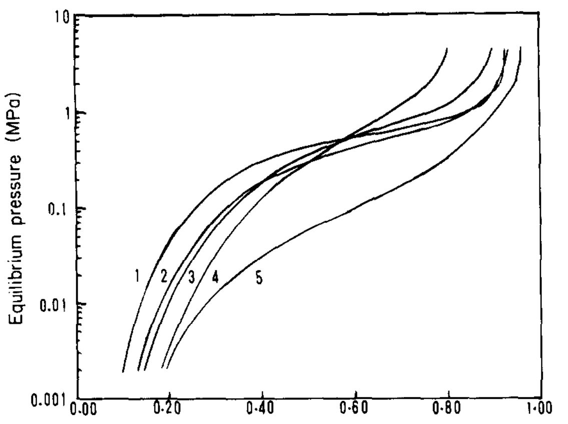

Fig. 1. PCT isotherms of desorption for $Ti_{1-x}Zr_xFe_{0.15}Mn_{1.21-y}V_{0.64}Ni_y$ alloys at 30 °C: 1, $x=0$, $y=0$; 2, $x=0$, $y=0.2$; 3, $x=0$, $y=0.4$; 4, $x=0$, $y=0.6$; 5, $x=0.2$, $y=0.6$.

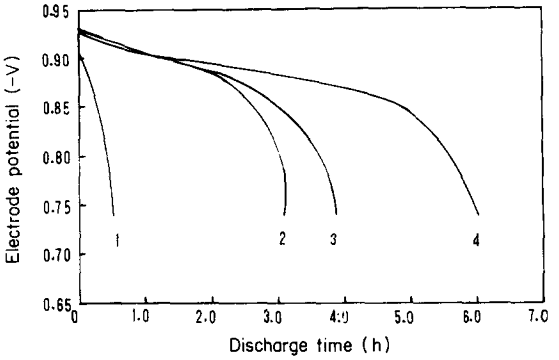

Fig. 2. Discharge curves of $Ti_{1-x}Zr_xFe_{0.15}Mn_{1.21-y}V_{0.64}Ni_y$ alloy electrodes at a current density of 50 mA g^{-1} and room temperature: 1, $x=0$, $y=0.2$; 2, $x=0$, $y=0.4$; 3, $x=0$, $y=0.6$; 4, $x=0.2$, $y=0.6$.

trodes showed some differences. For the $TiFe_{0.15}Mn_{1.21-y}V_{0.64}Ni_y$ alloys ($y=0$–0.6) the discharge capacity of the alloy electrodes increased with increasing amount of nickel. The discharge capacity was negligible for the alloy without any nickel content because of the decrease in the hydrogen equilibrium pressure of the hydride. Besides, the substitution of nickel improved the electrode polarization behaviour, which was attributed to the difference in the electrocatalytic activity between nickel and manganese (the exchange current density i_0 of nickel is larger than that of manganese) [8]. In the application of the electrode materials the materials must also have both better thermal conductivity and a smaller electrical resistivity. Nickel has the dominant position in comparison with manganese in these factors (Table 2). The improved electrochemical performance of the zirconium-substituted alloy was mainly attributed to the lower hydrogen equilibrium pressure of the alloy hydride and had no effect on the electrocatalysis, thermal conductivity and electrical resistivity of zirconium and titanium. Therefore the hydrogen storage alloy for a metal hydride battery must have a suitable hydrogen equilibrium pressure and better electrocatalytic activity. Nickel is an indispensable element for such electrode materials because of the high electrocatalysis.

4. Conclusions

This work has been concerned with the relative importance of geometric and electronic contributions to the hydrogen equilibrium pressure of titanium-based C14-type Laves phase alloy hydrides. The geometric factor is moderately large, especially for a larger change in the lattice volume of the alloys. The electronic factor is dominant for systems with a smaller change in alloy lattice volume. The hydrogen storage alloy for a nickel hydride battery must have a suitable hydrogen equilibrium pressure of the hydride and better electrocatalytic activity.

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TABLE 2. Physical properties of metals and heats of formation of metal hydrides [9–11]

Metal	Atomic radius in metal (Å)	Thermal conductivity at 25 °C (W cm^{-1} K^{-1})	Electrical resistivity at 0 °C ($\mu\Omega$ cm^{-1})	Heat of formation of hydride (kJ $molH^{-1}$)
Mn (γ)	1.366	0.0781	138	−8 ($MnH_{0.5}$)
Ni	1.246	0.909	6.2	−3 ($NiH_{0.5}$)
Ti (α)	1.488	0.219	39	−68 cal (TiH_2)
Zr	1.60	0.226	40	−82 cal (ZrH_2)

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