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Calorimetric investigation of the hydrogen interaction with $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$

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Abstract

The interaction of hydrogen with $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$ compound was studied by means of calorimetric and *P–C* isotherm methods. The obtained results allow to propose the existence of two hydride phases in the $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ system in the temperature range 72–116°C.

Keywords: Intermetallic compounds; Calorimetry; $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ systems

1. Introduction

The AB_2 Laves phase intermetallic compounds (IMC), with hexagonal structure C14 on Ti–Mn-based multicomponent alloys, formed by the partial substitution of transition metals such as zirconium or hafnium for titanium and vanadium, chromium, iron, cobalt, nickel, copper for manganese are a promising class of materials for hydride applications. Some of these compounds exhibit fast kinetics, appropriate H_2 gas pressure at or near ambient temperature, large hydrogen storage capacities and resistance to degradation during cycling through the hydride phase changes, which are necessary for hydrogen storage, heat pumping, etc.

It is known that binary system Ti–Mn_x with hexagonal structure type C14 ($MgZn_2$) Laves phase can exist over a wide range of non-stoichiometry, i.e. from $x=1.25$ to 2.0 [1,2].

We present in this paper a calorimetric investigation of the $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ system. $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$ belongs to the C14 Laves phase with hexagonal structure.

2. Experimental details

The materials were prepared with high purity components such as titanium (purity 99.99%), zirconium (purity 99.99%), electrolytic manganese (purity 99.99%), and electrolytic vanadium (purity 99.99%). The sample was obtained by arc melting in the furnace with non-spending tungsten electrode on a copper water-cooled boat in a purified argon atmosphere under 2 atm pressure. Because of the high volatility of manganese, 4 wt.% extra Mn was added.

The sample was turned over and remelted several times to ensure homogeneity, and then annealed at 1100–1150 K for 240 h in a quartz ampoule filled with 0.1 Pa argon. After annealing, the alloy was cooled at room temperature at a rate of 0.5°C per min.

A twin-cell heat differential calorimeter of Tian-Calvet type connected to a volumetric device was used in this study. A schematic diagram is shown in Fig. 1. The calorimeter is operable in the range from 20 to 400°C. The two identical stainless steel cells are designed to carry out

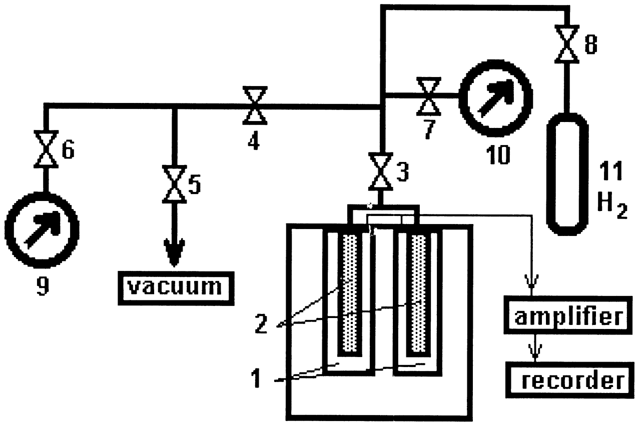

Fig. 1. Scheme of the calorimetric installation: (1) calorimetric chambers; (2) calorimetric cells (reaction and blank); (3–8) needle valves; (9) vacuum gauge; (10) pressure gauge; (11) hydrogen source.

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investigations in the pressure range from 1×10^{-1} to 1×10^{7} Pa. The cells are close-slip fits to the calorimetric chambers and both connected to the apparatus for gas dose feeding. The hydrogen reservoir containing $LaNi_5$ hydride was employed as a hydrogen source of high purity. The volumes of the system and the cells were calibrated. The reaction volume was 3.09 cm^3. Volumetric device can be evacuated to 5×10^{-1} Pa.

The alloy was crushed and placed into the calorimetric cell. Twin cells were connected to volumetric device and evacuated by a vacuum pump for about 0.5 h at room temperature. The sample was then exposed to hydrogen at 50 atm. No special activation treatment was employed. After several cycles of hydriding–dehydriding process calorimetric measurements started. As we studied the desorption process firstly the sample was completely saturated at room temperature and then twin cells were inserted into their calorimetric chambers. The desorption and calorimetric measurements were then carried out in a definite isothermal regime by means of withdrawing a small portion hydrogen gas from the sample into a calibrated volume. The time interval over which the heat was liberated and after which the recorder returned to its baseline, was generally about 1–1.5 h. In order to calculated the heats of the reactions from the areas of the voltage–time plots we used heat–area calibration relationship determined from an electrical calibration. The electrical calibrations we carried out twice per day before and after the calorimetric measurements. The current employed during calibration was measured by a digital multimeter (accuracy 0.01 mA). The measured heats correspond to enthalpies of reaction when expressed per mol H_2 or $1/2H_2$. In a twin-cell calorimeter corrections are not required for the work of expansion of the gas [3].

Pressure was measured by a 1–60-atm pressure gauge for the high pressure and a 0.01–1-atm vacuum gauge for the low pressure.

Finally, the twin cells were taken out from the calorimeter chambers and evacuated to about 5×10^{-1} Pa at 350°C in order to eliminate any hydrogen that remained in the sample.

Desorption relative molar enthalpies $|\Delta H_{a(d)}|$ were determined from the heat effect of the reaction

$$Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}H_x + y/2H_2 \Leftrightarrow Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}H_{x+y}$$

The hydrogen contents of the sample were determined from the volumes of the apparatus and pressures before and after desorption of H_2 and the hydrogen concentration in the sample was calculated using the Van-der-Waals equation of state for pressure below 20 atm and using the modified Van-der-Waals equation [4] for pressure above 20 atm. The accuracy of the measurement was taken as square of average value $\delta = \Sigma\Delta^2[n(n-1)]^{-1}$ (Δ, deviation from average value; n, number of measurements).

X-ray data (DRON-2, Cu Kα radiation, Ni-filter) showed that $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$ sample is hexagonal Laves phase $MgZn_2$ type with cell parameters $a=4.93$, $c=8.063$.

The amount of desorbed hydrogen was $(200–900)\times10^{-6}$ mol. The same sample ($15\,532.4\times10^{-6}$ mol $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$) has been used in all experiments.

3. Result and discussion

$Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$ system has been studied at 72, 88, 103 and 116°C and a hydrogen pressure $0<P<50$ atm.

Figs. 2 and 3 show the P–X ($X=$H/IMC) and $|\Delta H_d|$–X dependencies. For all temperatures the desorption isotherms are presented. The desorption isotherms have significant sloping plateaus, that agree with previously published data. Thus, as stated in Ref. [5], this phenomenon is a peculiarity of ternary IMCs and non-stoichiometric binary IMCs. Pourarian and Wallace [5] assumed that this behaviour can be attributed to the complexity in lattice energetics.

Another feature of the studied system is an anomalous large α-region for all measured P–X isotherms, which decreases with increasing temperature, but remains significant over the investigated temperature range.

In Fig. 3 the enthalpy data show two distinct regions with a constant value of desorption enthalpy in the temperature range from 72 to 103°C. Apparently, this is due to the existence of two hydride phases, $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}H_{\sim1.0}$ and $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}H_{\sim2.0}$, corresponding to β_1- and β_2-hydrides. This assumption agrees with the results of Grant et al. [6] who carried out calorimetric studies on the $Zr(Cr_{0.25}Fe_{0.75})_2$–H_2 and $Zr(Cr_{0.45}Fe_{0.55})_2$–H_2 systems at 273 K. These authors [6] proposed the existence of two hydride phases in both systems. An analogous phenomenon was found also in the ZrCrFe–H_2 system at 380–497 K [7]. In this case the

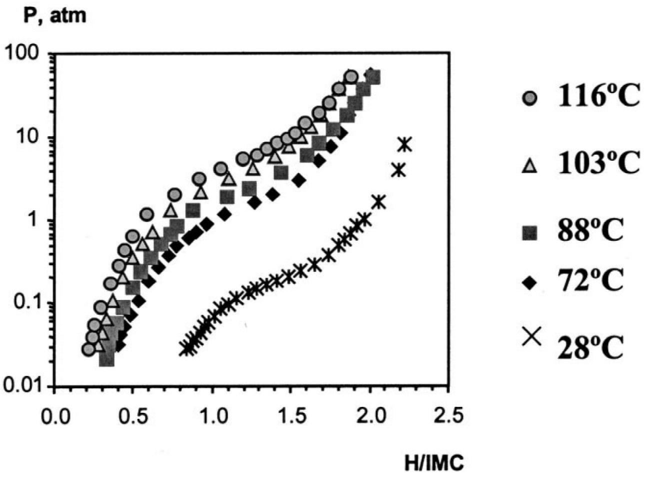

Fig. 2. Desorption isotherms for the $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ system.

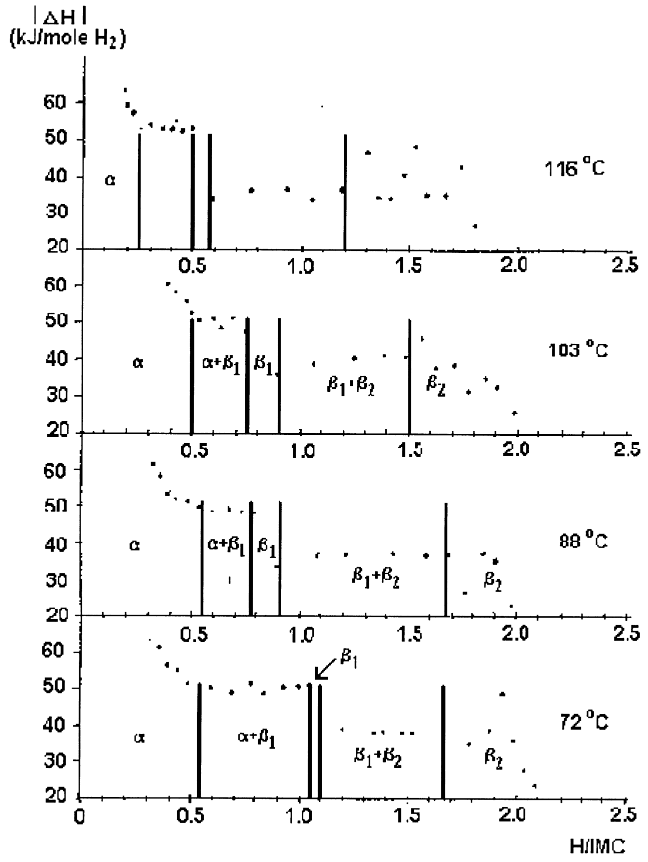

Fig. 3. Desorption enthalpy versus composition for the $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ system.

hydride phase compositions were ZrCrFe–$H_{2-\delta}$ and ZrCrFe–$H_{3-\delta}$.

It can be seen from Fig. 3 that, moving from 72 to 103°C, the β_1-hydride domain decreases, whereas the β_2-hydride region expends at the same time from $1.10<x<1.67$ at 72°C to $0.90<x<1.50$ at 103°C. Meanwhile the ΔH_d values remain almost constant (see Table 1).

However, as can be seen in Fig. 3 the 116°C study shows drastic changes in the $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ system. From the results it can be assumed that 103°C is close to the critical temperature for β_1-hydride, above which temperature it does not exist. Thus we can assign three regions with constant values of desorption enthalpy at 116°C. In a range $0.25<x<0.50$ hydrogen dissolution is accompanied by significant large enthalpy values ($|\Delta H_d| = 54.17 \pm 0.53$). Then, in the range $0.58<x<1.20$ enthalpy values are less exothermic than the values correlated for β_2-hydride, while in the range $x>1.2$ at 116°C the constancy of concentration dependence of $|\Delta H_d|$ values is not so clearly manifested.

Table 1
Temperature dependence of reaction enthalpy for the $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ system

Temp. (°C)	Range	$|\Delta H_d| \pm \delta$ (kJ/mol H_2)
72	$1.10 \leq x \leq 1.67$	38.17 ± 0.23
	$0.53 \leq x \leq 1.05$	49.78 ± 0.31
88	$0.90 \leq x \leq 1.68$	37.50 ± 0.11
	$0.55 \leq x \leq 0.78$	49.14 ± 0.53
103	$0.90 \leq x \leq 1.50$	39.79 ± 1.28
	$0.50 \leq x \leq 0.75$	49.69 ± 0.77
116	$0.58 \leq x \leq 1.20$	35.57 ± 0.75
	$0.25 \leq x \leq 0.50$	54.17 ± 0.53

In the region of very low hydrogen concentrations, hydrogen desorption is accompanied by drastic increasing of $|\Delta H_d|$ values. However, because of very low equilibrium pressure the sample could not be fully desorbed in the calorimeter.

The above-described complex character of interaction in the $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$–$H_2$ system could be connected with ordering hydrogen in the tetrahedral holes formed by different metals, as well as with possible structural changes in the metal matrix.

In spite of its multicomponent nature, the isotherms and the calorimetric data for the alloy $Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}$ are very reproducible, i.e. there is no change in behaviour with cycling due to atomic rearrangements although we carried out all experiments with the same sample of alloy.

The conclusions given in this work were made on the basis of only calorimetric data and P–X measurements and, undeniably, should be tested by other experimental methods.

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