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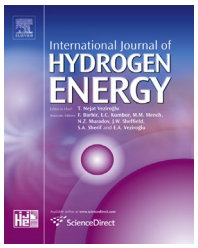

Investigation of the hydrogen interaction with $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ by means of the calorimetric method

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ABSTRACT

In the present work we studied the hydrogen interaction with the stoichiometric $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ Laves phase compound C14 at pressure up to 50 atm and the temperature range from 52 to 130 °C by means of calorimetric method and plotting of pressure-composition isotherms. The processes of hydrogen absorption and desorption were carried out. The findings enabled us to draw the following conclusions: 1) the experimental temperature influences the thermodynamic parameters of studied processes and 2) depending on reaction conditions the formation of one or two hydride phases takes place.

Introduction

Multicomponent intermetallic compounds (IMC) AB_2 with hexagonal structure C14 Laves phase are very important and used for storage, transportation and purification of hydrogen. It is well known that such IMCs absorb significant amount of hydrogen, they possess high rate of hydrogen reaction with IMCs and they are resistant to degradation during cycling. The main thermodynamic parameter characterizing the process of hydrogenation is the change of enthalpy of hydrogen reaction with metallic matrix at absorption/desorption processes (ΔHabs.(des.)). The value of ΔHabs.(des.), character of its change depending on hydrogenation rate, the temperature of the experiment permit us to understand the mechanism of the hydrogen reaction with the intermetallic alloy better. A lot of works are devoted to the investigation of the hydrogen interaction with IMCs. Generally the experimental method which is applied for determination of enthalpy change ΔH and entropy change ΔS is a calculation of the thermodynamic parameters on the basis of the Van't Hoff equation though the values of enthalpy and entropy calculated in such a way may significantly deviate from real characteristics as this method supposes that the enthalpy and the entropy are independent from the temperature which is not always the case, therefore, this assumption may leads to the errors. There are few works, in which thermodynamic properties of intermetallic compound – hydrogen system (IMC-H_2 system) were investigated by the calorimetric method [1–6]. The application of the twin-cell heat conducting calorimeter permits us to determine directly the heat reaction of hydrogen interaction with IMC. As it was shown in Ref. [7] in this case the measured heats

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correspond to enthalpy of reaction when expressed per mole H_2 or ½ H_2.

In the present work we continue our study of the (Ti,Zr)(MnV)$_{2\pm X}$-H_2 system where (Ti,Zr)(MnV)$_{2\pm X}$ are intermetallic compounds (IMC) with Laves phase structure C 14 by means of the calorimetric method. Earlier we studied the IMC-H_2 systems in which IMCs had nonstoichiometric compositions [3–6]. Now we have chosen the $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ compound with stoichiometric composition as the subject under the investigation.

Materials and methods

The initial intermetallic compound $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ was prepared by arc melting of a stoichiometric mixture of pure metals in a furnace with a non-consumable tungsten electrode on a water-cooled boat in a purified argon atmosphere under pressure 2 atm. The purity grade of starting metals was better than 99.9%. As a high volatility of manganese in comparison with another metals used for preparing initial compound 4 mass% extra Mn was added to compensate a weight loss during melting. Titanium sponge was used as a getter for purification of argon from admixtures. For that reason it was melted in the furnace before alloying of the starting metals. The button of sample was tuned over and re-melted four times and then annealed in a sealed quartz vessel at 1100 °C for 240 h to ensure homogeneity. The phase composition and unit-cell parameters of initial intermetallic compound $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ and its hydrides were determined by X-ray diffraction on a DRON-2 powder diffractometer (Cu Kα radiation) and XRD data showed that the parent sample was single-phase compound with the hexagonal Laves phase structure C 14 ($MgZn_2$) with refined units lattice parameters a = 4.922 Å, c = 8.040 Å, c/a = 1.633, V = 168.82 Å^3. The refinement of diffraction profiles was performed using the RIETAN-2000 software [8]. To prevent of a hydrogen losses from the hydride phases during their X-ray study under ambient conditions we should passivate synthesized hydrides. Therefore at first we cooled autoclave with hydrogenated sample to the liquid nitrogen temperature, further we depressed of hydrogen pressure to atmospheric pressure, opened autoclave and exposed it to air at 77 K for 2 h [9].

The study of hydrogen interaction with $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ was carried out by a calorimetric method. The twin-cell heat conducting calorimeter Tian-Calvet type connected to a conventional Sieverts'-type volumetric apparatus for measuring by a volumetric method of an amount of absorbed or evolved hydrogen was applied. The apparatus scheme, the experimental procedure and the analysis of the collected data were described elsewhere [3]. As a source of pure hydrogen for hydrogenation of $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ in this study $LaNi_5H_x$ hydride was used. A purity of hydrogen was 99.9999%.

Absorption (desorption) relative molar enthalpy ΔHabs.(des.) was determined from the heat effect of the reaction:

$$Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}\ H_X + y/2H_2 \leftrightarrow Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}\ H_{X+Y} \quad (1)$$

Since $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$ reversibly reacts with hydrogen the same sample (10,831.7 · 10^{-6} mol $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$) was used in all experiments. Before each run the residual hydrogen was desorbed at 350–450 °C under high vacuum outside the calorimeter.

The hydrogen concentration in the sample was calculated from the volumetric measurements using the ideal gas low for pressure < 1 atm, the Van – der – Waals equation of state for pressure below 20 atm and the modified Van – der – Waals equation for pressure above 20 atm [10]. The experimental error in this work was expressed in accordance with recommendations of IUPAC [11] as a standard deviation of the mean value $\delta = \sqrt{\Sigma \Delta^2 [n(n-1)]^{-1}}$, where Δ is the deviation from the mean value and n is the number of data points.

Results and discussion

P-C-T measurements

The $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$-$H_2$ system was studied in the temperature range 52–130 °C and hydrogen pressure up to 50 atm. The P–C (P-equilibrium hydrogen pressure, C=H/IMC) desorption isotherms were measured for 52, 72, 100 and 130 °C and for 52 and 72 °C the P–C absorption isotherms were measured too. Since the overall duration of experiment was about six months it was necessary to check the sample characteristics. For this purpose the runs of hydrogen desorption at 52 °C were repeated from time to time. Despite of the multicomponent composition of the sample under investigation the P–C and ΔHdes. = f(C) dependences measured during these runs provide reproducibility within the present experimental error.

In Fig. 1 from the represented data one can notice that the compound under investigation has a good hydrogen capacity (2.9H/IMC at 52 °C and hydrogen pressure P = 36 atm).

However the reversible hydrogen capacity at this temperature is smaller as the equilibrium hydrogen pressure at the low hydrogen concentration in the IMC is very low. Earlier the authors marked such phenomenon in the work [12] when they studied the effect of different substitutional metals in the $TiMn_2$-based alloys. It has been determined that the increase of the vanadium content in the alloy increased the length of α-region and reduced the reversible hydrogen capacity. V has a strong affinity to hydrogen. The

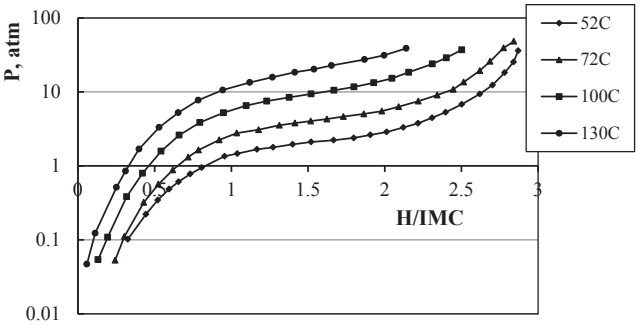

Fig. 1 – Desorption isotherms for the $Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7}$-$H_2$ system.