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Hydrogen absorption in amorphous and quasicrystalline $Ti_{45}Ni_{17}Zr_{38}$ powders synthesized by mechanical alloying

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Abstract

Hydrogen absorption in amorphous and quasicrystalline $Ti_{45}Ni_{17}Zr_{38}$ powders, obtained both directly by mechanical alloying (MA) and after subsequent annealing, was studied. MA was performed in a planetary ball mill under protective argon atmosphere. The powders were hydrogenated at 503 and 573 K under initial pressure of 2.9 kPa. Hydrogen absorption of the as-milled amorphous samples led to formation of TiH_2, ZrH_2 and $(ZrTi)H_2$ hydrides. Hydrogenation of quasicrystalline phase resulted in formation of hydrogen solution in quasicrystalline phase and ZrH_2. The maximum registered concentration of H_2 in the samples was 1.38 H/M. Quasicrystalline phase disappeared after partial degassing up to 1.25 H/M. Activation energies of hydrogen absorption and hydrogen evolution were measured, these values were found as 40.4 ± 0.2 and 25.2 ± 0.1 kJ/mol correspondingly.

Keywords: Quasicrystals; Mechanical alloying; X-ray diffraction

1. Introduction

In recent years the quasicrystalline phases due to unique combination of properties have attracted much attention as the promising base for production of new materials. Icosahedral quasicrystals (I-phases) exhibit a new type of translational long-range order in combination with noncrystallographic rotational symmetry, so they presumably may possess the interstitial pores configuration different from normal crystals. I-phase may have better physical properties for hydrogen-storage applications since some atoms of them have an adequate affinity for hydrogen. Thermodynamically stable Ti–Zr–Ni quasicrystals and relate phases, which can be produced by melt-spinning, can store large quantities of hydrogen, indicating their promise as new hydrogen-storage materials [1–5]. It have been previously reported that the amorphous and quasicrystalline phases can be synthesized by the mechanical alloying (MA) a Ti–Zr–Ni powder mixture and that both powders showed ability to store as much hydrogen as the I-phase ribbons obtained by melt-spinning [6].

Besides ability to store large quantities of hydrogen, ability to keep the microstructure stable during hydrogen cycling (repeated absorption–desorption of hydrogen) is necessary at moderate temperature and the relatively low pressure of hydrogen for actual applications as a hydrogen-storage materials. The hydrogen cycling, however, normally generates structure defects and pulverizes the alloys because of changing atomic distances during hydrogen absorption and desorption, having a dramatic influence on the properties of the alloys regarding to their application [7]. The aim of the present work was to investigate phase transformations resulting in icosahedral quasicrystalline Ti–Zr–Ni phase formation during MA and subsequent annealing and to study the hydrogen absorption and desorption in obtained materials.

2. Experimental procedure

MA of Ti, Zr and Ni high purity powders (Ni: 99.99%, Zr: 99.99%, Ti: 99.96%) was carried out in AGO-2U high-energy planetary ball mill with cylindrical vials (volume 160 cm^3 each) of hardened carbon-chromium steel and steel balls of 7 mm in diameter. Plate rotation speed was 685 revolutions per minute (rpm). The ball-to-powder mass ratio was 10:1.

A DRON-4 X-ray diffractometer with Co Kα radiation was used to study the crystalline structure of the samples and phase composition. Manometric equipment with constant volume was used to study the sorption and desorption of hydrogen.

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3. Results and discussion

The powder mixture of Ti, Zr and Ni in the atomic proportion of $Ti_{45}Zr_{38}Ni_{17}$ was milled for 1, 2, 3, 4, 5 and 6 h. After MA the samples were annealed in vacuum at temperature varied from 400 to 600 °C. Fig. 1a shows the X-ray diffraction pattern of the sample after 6 h of MA and subsequent annealing during 3 h in vacuum at $T_a = 600$ °C. Obtained samples mainly consist of the I-phase and the cubic Ti_2Ni-type phase with the lattice parameter $a = 12.04$ Å.

The powders milled for 6 h with subsequent annealing in vacuum for 5 h at $T_a = 440$ °C (Fig. 1b) also contains quasicrystalline phase and Ti_2Ni-type phase, but the lattice parameter of the second one is smaller ($a = 11.88$ Å). The content of quasicrystalline phase in this sample is considerably more than in first one. The decrease in the Ti_2Ni phase lattice parameter in this sample in comparison with the sample annealed at $T_a = 600$ °C may be related to the smaller content of Zr in Ti_2Ni-type phase due to the presence of significant amount of the initial unreacted Zr and Ti in this sample. In Fig. 1b ($T_a = 440$ °C) the diffraction lines are wider than in Fig. 1a ($T_a = 600$ °C) because an annealing at higher temperature results in the crystals growth and the decrease in defects density and microstrain in the crystalline lattice.

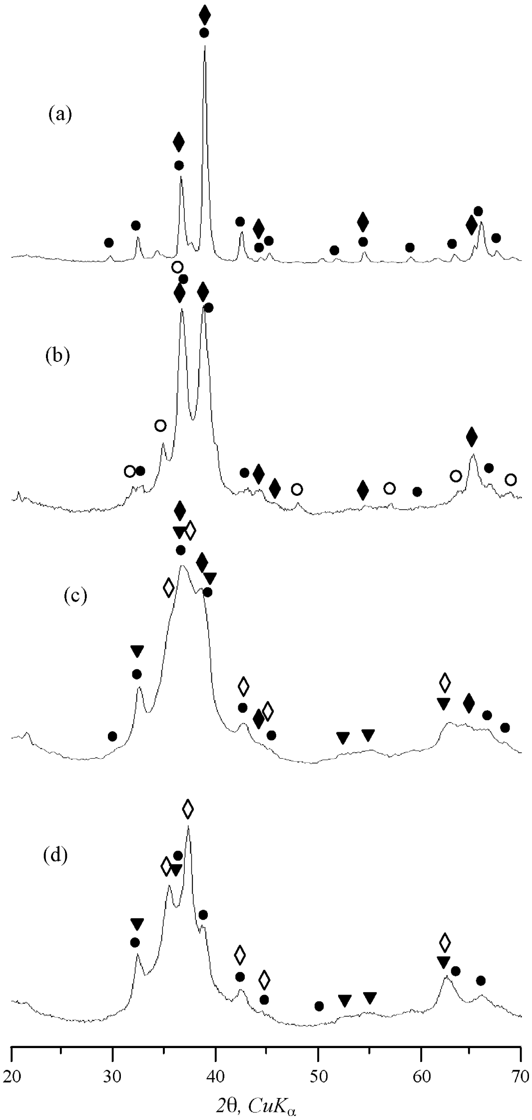

Fig. 1. X-ray diffraction patterns of samples after 6 h of MA and (a) annealing for 3 h in vacuum at 600 °C; (b) annealing for 5 h in vacuum at 440 °C; (c) annealing for 5 h in vacuum at 440 °C and hydrogenation at 300 °C; (d) annealing for 5 h in vacuum at 440 °C, hydrogenation at 300 °C and desorption of H_2 at 300 °C. Symbols: (●) Ti_2Ni-type phase, (○) α-Zr, (◆) I-phase, (▼) ZrH_2, (◊) hydrogen solid solution in I-phase.

Fig. 1c shows the X-ray diffraction patterns of the 6 h MA powder annealed in vacuum for 5 h at $T_a = 440$ °C after hydrogenation at $T_{ha} = 300$ °C. Hydrogen absorption leads to the change of sample phase constitution and results in considerable widening of all peaks because of crystal lattice distortion. Experimental pattern can be described by the superposition of the two quasicrystalline phases with different lattice parameters and Ti_2Ni-type and ZrH_2 phases. One of the quasicrystalline phases possesses the same lattice parameter that initial I-phase in previous cases, the lattice parameter of another one was found to be more than 3% higher. Appearance of the second I-phase may be easily understood in terms of the hydrogen dissolution in the quasicrystalline phase. The amounts of these both phases are nearly equal. The value H/M was estimated to be 1.38. The lattice parameter of Ti_2Ni-type phase remains constant at $a = 11.88$ Å.

Fig. 1d presents the X-ray diffraction pattern of 6 h MA powder annealed in vacuum for 5 h at $T_a = 440$ °C and hydrogenated at $T_{ha} = 300$ °C after hydrogen desorption at $T_{hd} = 300$ °C. The annealing results in disappearance of the patterns correspond to the pure quasicrystalline phase, whereas the quasicrystalline phase with increased lattice parameter keeps in sample after annealing. It means that hydrogen can stabilize the quasicrystalline structure in Ti–Zr–Ni system. The lattice parameter of Ti_2Ni-type phase has increased up to $a = 12.04$ Å. The H_2 content in the sample has decreased to 1.25 H/M.

Fig. 2 shows the X-ray patterns of the as-milled powder after MA for 6 h (Fig. 2a) and of the same sample after hydrogenation at $T_{ha} = 300$ °C at the initial pressure of 2.9 kPa (Fig. 2b). The sample after MA consists of amorphous phase and small (less than 10 vol.%) amount of I-phase. In contrast to the I-phase obtained by annealing at $T_a = 440$ °C, which structure maintains stable at hydrogen absorption, the I-phase in the as-milled sample appears to be unstable at hydrogenation and decomposes to ZrH_2, TiH_2, $(Zr,Ti)H_2$ and Ni phases.

From the curve of pressure evolution during hydrogen adsorption we calculated the rate constants of this disproportion process at different temperatures and estimated the activation energy of hydrogen absorption to be of 40.4 ± 0.2 kJ/mol.

Fig. 3 shows the dependence of hydrogen outgassing from the hydrogenated as-milled samples on the experiment temperature. Desorption at 150 °C proceeded slowly and did not reach any equilibrium plateau. Upon increasing the process temperature the dehydrogenation developed easier, but did not result in desorption of the full amount of absorbed hydrogen. In fact

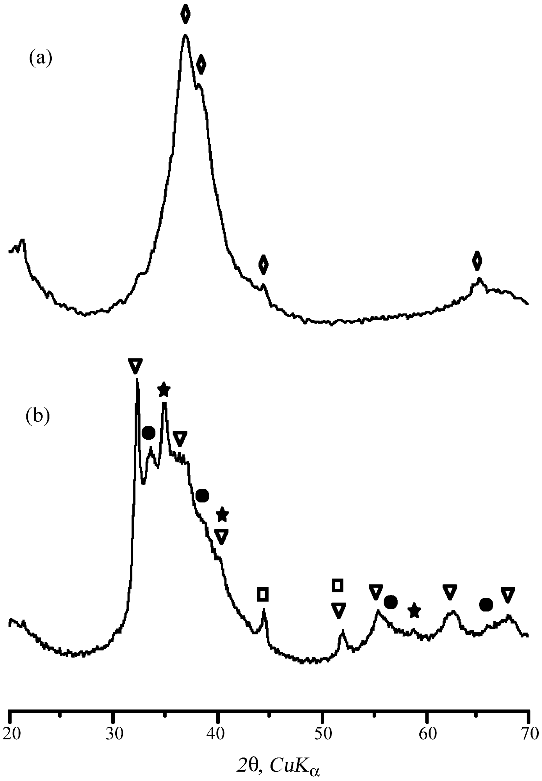

Fig. 2. X-ray diffraction patterns from the as-milled sample after 6 h of MA (a) and after subsequent hydrogenation at 300 °C at initial pressure of 2.9 kPa (b). Symbols: (◊) quasicrystalline phase, (□) Ni, (▽) ZrH_2, (★) TiH_2, (●) (Zr,Ti)H_2.

the hydrides ZrH_2, TiH_2 and (Zr,Ti)H_2 are relatively stable at the temperatures lower than 300 °C and then cannot completely dissociate. The activation energy of hydrogen desorption was estimated as 25.2 ± 0.1 kJ/mol.

Fig. 4 shows the dependence of absorbed and desorbed amount of hydrogen after repeated cycles under a hydrogen pressure of 3 kPa at different temperatures. The sample was heated up to the lowest indicated temperature, hydrogenated and then desorbed under vacuum at this temperature, after that it was heated up to the next temperature, hydrogenated, and so forth. This treatment was repeated at 150, 230 and 300 °C. These experiments show that the amount of absorbed hydrogen at a definite temperature does not depends insignificantly on the previous treatment of sample. Nearly the same values of H_2 content in the sample were obtained by hydrogenation of as-milled sample at 300 °C and after hydrogenation–dehydrogenation cycles at three sequentially increasing temperatures. In all cases the hydrogen desorption was not completed.

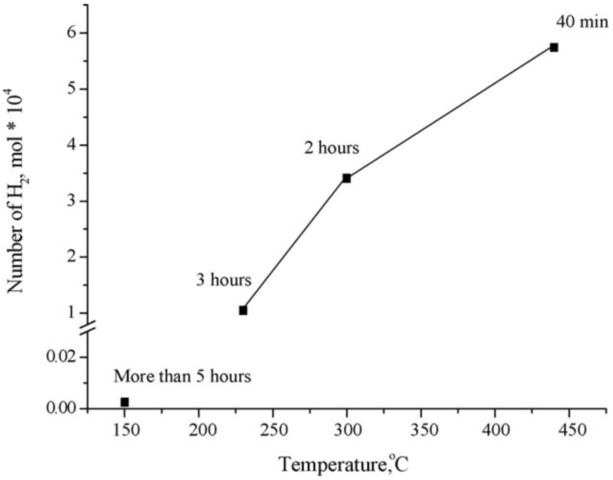

Fig. 3. Hydrogen outgassed from the hydrogenated as-milled sample depending on annealing temperature.

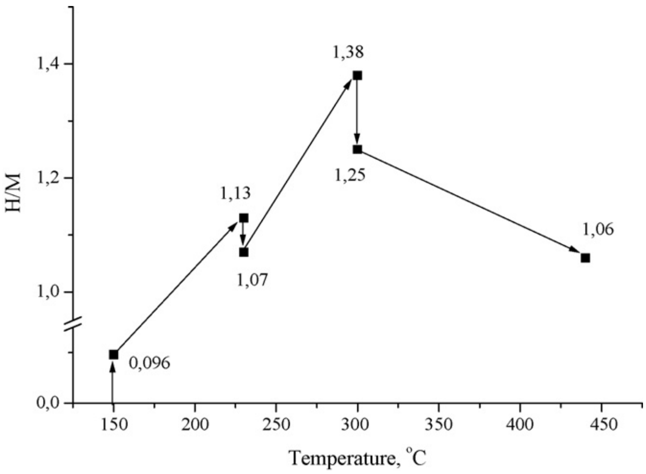

Fig. 4. Dependence of the absorbed and desorbed amount of hydrogen after repeated circles under 3 kPa hydrogen pressure at different temperatures.

4. Conclusions

Amorphous and icosahedral quasicrystalline Ti–Ni–Zr phases were produced by MA and subsequent annealing. The resulting $Ti_{45}Ni_{17}Zr_{38}$ powders were subjected to hydrogen adsorption and desorption. Hydrogenation of the as-milled amorphous samples leads to the formation of TiH_2, ZrH_2 and (ZrTi)H_2 phases. Hydrogenation of quasicrystalline phase results in the formation of hydrogen solution in quasicrystalline phase and ZrH_2 phase. The highest observed solubility of hydrogen in Ti–Zr–Ni alloys was found to be of 1.38 H/M. The hydrogen solid solution in QC state phase disappears after a partial degassing at total solubility magnitude of 1.25 H/M. The activation energies of hydrogen absorption and desorption were evaluated to 40.4 ± 0.2 and 25.2 ± 0.1 kJ/mol, respectively.

Acknowledgment

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