

EFFECT OF HYDROGEN ON THE PHASE-STRUCTURE TRANSFORMATIONS IN ZrCrNi ALLOY

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Introduction

Electrochemical properties of alloys based on intermetallic compounds greatly depend on their phase composition. This, also, applies to zirconium-based alloys, which are used as active material for negative electrodes of nickel-metal hydride power sources. As a rule, these materials are multiphase and except the C14 and C15 type Laves phase, which are main and determine the electrode capacity, include different portion of Zr-Ni binary phase. Availability of these phases can enhance the hydrogen sorption-desorption rate and capacity [1] and improves electrochemical properties of metal hydride electrodes of nickel-metal hydride power sources.

Investigation using metal-hydride technologies as the hydrogenation, disproportionation, desorption, recombination (HDDR) process for the formation of electrode materials morphology were begun. Conditions and peculiarities of the HDDR process in ZrCr₂ intermetallic compounds have been investigated [2].

In this work investigation results of the HDDR process in ZrCrNi alloy are presented.

HDDR process was investigated using the differential thermal analysis (DTA) and measuring the pressure change in the temperature range from room temperature to 968 °C at the initial hydrogen pressure 0,1 and 5,0-5,2 MPa. A sample was put into the autoclave, and then autoclave was vacuumized and filled with hydrogen to the given (initial) pressure and heated.

Phase-structure analysis – X-ray phase analysis (XPhA) – was carried out by means of the diffractometer DRON-4 with Cu K_α radiation.

Results and discussion

Heating thermogram of the ZrCrNi sample in hydrogen at the initial pressure $P_{H_2} = 5,2$ MPa and the maximum heating temperature 946°C is shown in the Fig. 1. Except the hydrogen absorption peak at the room temperature, four thermal effects at 535, 675, 791 and 819 °C were registered. For the study of the character of phase transformations, which determine peaks in the DTA curve, ZrCrNi-H₂

system was heated to 608, 751 i 810 °C, i.e. higher the temperature of peaks in the thermogram.

The base of the initial alloy is C14 type Laves phase. Zr₉Ni₁₁ compound and minor amount of chromium were registered in the alloy (Fig. 2a).

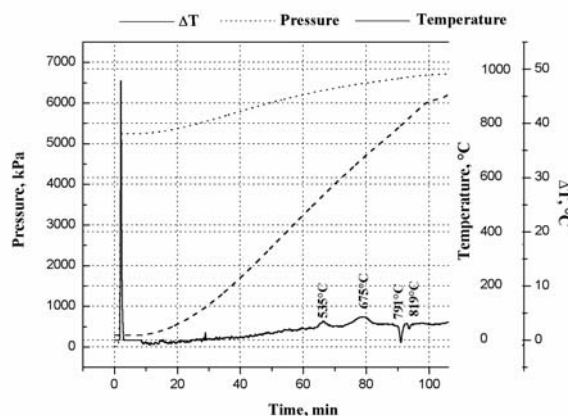


Fig. 1. Heating thermogram in hydrogen of the ZrCrNi alloy.

A hydride of the initial C14 phase is formed after heating of the ZrCrNi alloy to the temperature 938 °C in hydrogen at the initial pressure 0,1 MPa (Fig. 2b).

According to XPhA, which was carried out after heating of the ZrCrNi-H₂ system to 608 °C ($P_{H_2} = 5,2$ MPa) and cooling to the room temperature (Fig. 2c), decomposition (disproportionation) of the initial phase begins at 535 °C. Among disproportionation products a hydride of the initial phase, zirconium hydride and chromium were registered.

The complete disproportionation of the initial C14 phase is occurred at the temperature higher 675 °C. But a phase composition of interaction products with hydrogen depends on the maximum heating temperature (Fig. 2d-f).

The initial alloy was decomposed into ZrH_x, Cr and Ni with the hexagonal lattice after heating to 751 °C (Fig. 2d). An increase of a maximum temperature to 810 °C leads, as we suppose, to precipitation of the Zr₂Ni₇ compound among

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disproportionation products instead of nickel (Fig. 2e) (ZrH_x and Cr are remained). The initial alloy is decomposed into ZrH_x , Cr, Zr_2Ni and Zr_2Ni_7 after heating of the *alloy-hydrogen* system to 946 °C (Fig. 2f).

Recombination of disproportionation products obtained in hydrogen at 608 (sample **I**), 741

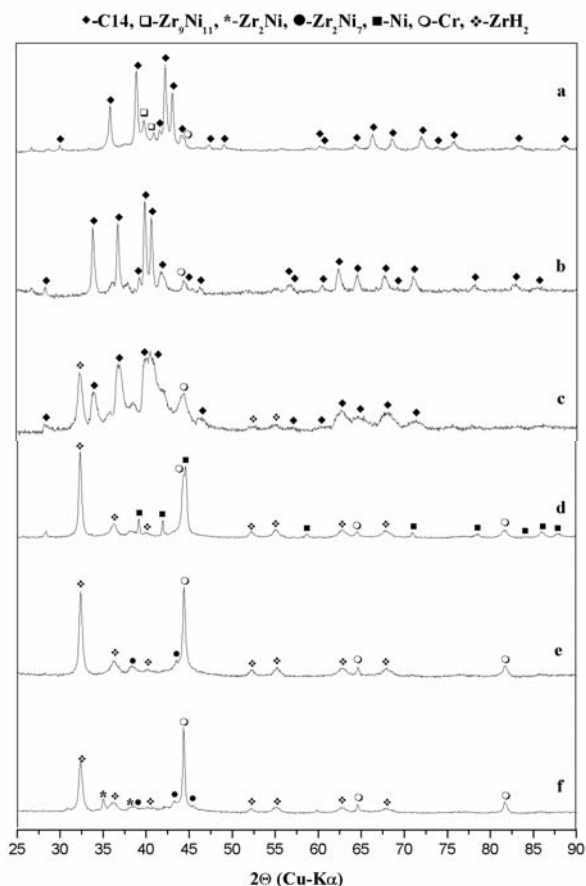


Fig. 2. X-ray powder patterns of the initial $ZrCrNi$ alloy (*a*) and of interaction products in $ZrCrNi-H_2$ system after heating at $P_{H_2}=0,1$ MPa to 938 °C (*b*); at $P_{H_2}=5,0-5,2$ MPa to 608 °C (*c*); to 751°C (*d*); to 810 °C (*e*); to 946 °C (*f*).

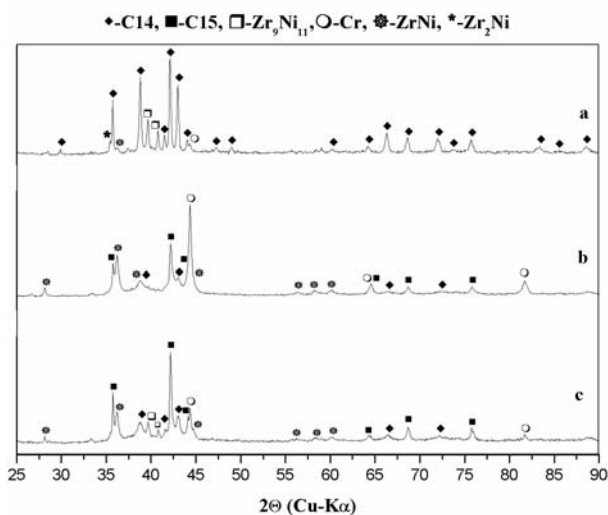


Fig. 3. X-ray powder patterns of recombination products in $ZrCrNi-H_2$ system: *a* – sample **I**; *b* – sample **II**; *c* – sample **III**.

(sample **II**) and 810 °C (sample **III**) was carried out by heating in vacuum to 940-970 °C.

Recovery of the main phase (C14) of the initial alloy occurs only in case of the sample **I** (Fig. 3*a*). Zr_2Ni , Zr_9Ni_{11} and $ZrNi$ phases were also registered in the X-ray powder patterns. Recombination of the sample **II** is finished with a formation of the mixture of C14, C15, $ZrNi$ and Cr phases (Fig. 3*b*). Mixture of C14, C15, $ZrNi$, Zr_9Ni_{11} and Cr phases were obtained after recombination of the sample **III** (Fig. 3*c*). The relative intensity of peaks of the C15 phase was considerably increased.

Conclusions

Application of hydrogen as a technological medium and a reagent (HDDR process) for the treatment of alloys based on zirconium enables to change their phase composition. It was determined that a disproportionation in the $ZrCrNi$ *alloy-hydrogen* system at the initial pressure $P_{H_2}=5,2$ MPa begins at 535 °C. Disproportionation products are ZrH_x , Ni, Cr, Zr_2Ni and Zr_2Ni_7 depending on the temperature. After HDDR process alloy with C14, C15, $ZrNi$, Zr_9Ni_{11} and Cr phases depending on realization conditions was obtained.

References

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