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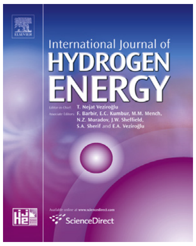

Influence of Ta and Nb on the hydrogen absorption kinetics in Zr-based alloys

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ABSTRACT

The kinetics of hydrogen absorption in Zr alloys containing Nb and Ta admixtures (10 wt% Nb, 12 wt%Ta and 10 wt%Nb&12 wt%Ta) is addressed. Hydrogen absorption is measured in the temperature range 400–700 °C at hydrogen pressure 1 bar using the volumetric method, and a kinetic analysis is performed to determine the mechanisms and rates of hydrogen absorption. To get further insight into hydrogen diffusivity in zirconium hydride, ^{1}H NMR spectroscopy is used to provide the activation energies for proton jumping in the studied samples. The tantalum is found to dominantly influence the surface reactivity, while niobium influences large decrease of the activation energy for hydrogen diffusion in the bulk of zirconium hydride. This behavior is linked to the information on the structure of the alloys obtained by XRD.

Introduction

Interaction of zirconium and zirconium alloys with hydrogen has been investigated for a long time, due to their application as materials in nuclear [1] and hydrogen energy applications [2]. The expectations from metals and alloys used in these two energy - related applications are, however, very different. While the hydrogen absorption in Zr alloys at high temperatures presents critical, life-limiting degradation mechanism for nuclear claddings [3,4] fast absorption of hydrogen in metal hydrides is advantageous for the hydrogen storage systems [2]. For any of the numerous applications of zirconium alloys, as well as from fundamental point of view, kinetics of hydrogen absorption and diffusivity of hydrogen in zirconium are topics of great interest.

Zirconium forms different types of hydrides, classified based on the amount of hydrogen absorbed [5–7]. Various metals, such as Nb, Ta, Ni, V, Fe, Al are added to zirconium in order to improve mechanical or storage properties [3,8–12]. Additionally, bcc-Nb greatly improves properties of hydrogen permeability membranes [13]. Mechanisms and kinetics of hydrogen absorption by zirconium and its alloys are widely investigated [14–18]. Alloying zirconium with small percentage of tantalum and niobium was demonstrated to affect mechanical properties as well as thermodynamics and

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kinetics of hydrogen absorption in these systems [15,16,19]. It was shown that alloying with Ta and Nb improves hydrogen absorption kinetics by lowering activation energy some reaction stages, particularly for hydrogen diffusion [20,16]. In order to further improve Zr-alloys for various applications, the fundamental understanding of how each metal contributes to various steps of hydride formation reaction, including the surface related processes as well as diffusion of hydrogen through bulk is, therefore, imperative.

In this paper we continue the study of influence of Nb and Ta to the changes in hydrogen absorption process in zirconium, reported in our previous work [16]. It was earlier shown that both the amount of the additives and temperature have major influence on the mechanism of the reaction. Also, as the amount of the absorbed hydrogen approaches capacity limit for the given temperature, the rate of hydrogen absorption in the zirconium containing small amount of Ta and Nb was found to be limited by hydrogen diffusion [16]. In this study we address the possibility of improving hydrogen absorption kinetics in zirconium by alloying it with larger amounts of Ta and Nb (10–12wt% of Ta and Nb). To gain further insight into diffusion of hydrogen in these alloys we employ ^{1}H NMR measurements, which has proven to be advantageous method for the study of bulk diffusion as compared to the common volumetric and weight change methods [21].

Experimental

Three zirconium alloys, containing 12wt%Ta (labeled as Zr–12Ta in further text), 10wt%Nb (labeled further as Zr–10Nb) and 10wt%Nb & 12wt%Ta (labeled further as Zr–10Nb–12Ta) were prepared by melting a mixture of pure elements (purities >99%) in the RS induction furnace. Preparation was done in argon atmosphere; to ensure homogeneity, melting was repeated several times.

To investigate the kinetics of hydrogen absorption, samples were crushed into powders by grinding. Experiments were done using the typical volumetric equipment, constructed in our laboratory [22]. Prior to measurements, samples were activated for two hours by annealing under a 1×10^{-3} mbar vacuum at the temperature 100 °C higher than the measuring one, and slow cooling to the room temperature in the hydrogen atmosphere. All measurements were conducted in the temperature range 400–700 °C (673–973 K) under isothermal conditions and at 1 bar hydrogen pressure. Experimental conditions were considered isobaric, because of negligible pressure drop due to hydrogen absorption. Samples were prepared for the next measurement cycle by degassing at the measurement temperature, under vacuum of $1 \cdot 10^{-3}$ mbar. Pressure drop was measured as function of time and converted to the number of hydrogen atoms absorbed per atom of metal, H/M.

X-ray powder diffraction (XRD) was done at room temperature, using Ultima IV Rigaku diffractometer, equipped with Cu Kα1,2 radiation, using a generator voltage 40.0 kV and a generator current (40.0 mA). The 2θ range of 20–90° was used in a continuous scan mode with a scanning step size of 0.02° and at a scan rate of 5°/min.

The ^{1}H Nuclear Magnetic Resonance spectroscopy (NMR) measurements were conducted using a 100 MHz Oxford superconducting magnet. ^{1}H (proton) spin-lattice relaxation time (T_1) was measured for all three samples in the temperature range from 80 to 420 K at proton resonance frequency of 100 MHz (corresponding to B = 2.35 T).

Results and discussion

XRD

The X-ray diffraction (XRD) patterns of Zr–12Ta alloy and resulting hydride are presented in Fig. 1. The results for Zr–10Nb and Zr–10Nb–12Ta were reported in our earlier work [16]. In the XRD of the starting alloy the main identified phase is hexagonal α-Zr, while diffraction peaks of Ta phase can be identified as well. This is in agreement with earlier conclusion regarding structure of Ta and Nb containing Zr-alloys, where exceeding metal's solid solubility limit in hexagonal zirconium lattice was shown to lead to the appearance of Ta/Nb phase [16,23,24]. Compared to the XRD of Zr–10Nb and Zr–10Nb–12Ta alloy [16], results point to lower solubility of tantalum than niobium in zirconium.

Changes in XRD pattern after hydrogen absorption indicate the decrease in the particle size, due to mechanical stress in the repeated shrinking/expansion of the crystal lattice [16]. Appearance of new peaks in XRD pattern of the hydride points to the possible coexistence of more than one hydride phase in the sample, which is in accordance with the earlier experimental studies [25,7].

Hydrogen absorption kinetics

Kinetics of hydrogen absorption in Zr–12Ta was studied at isothermal conditions in the temperature range 673–973 K (400–700 °C), following the same procedure as for earlier reported study of Zr–10Nb and Zr–10Nb–12Ta alloys [16].

Obtained isotherms, showing change of hydrogen to metal ratio (H/M) with time due to repeated hydrogen absorption in Zr–12Ta at 673, 773, 873, 973 K are presented in Fig. 2.

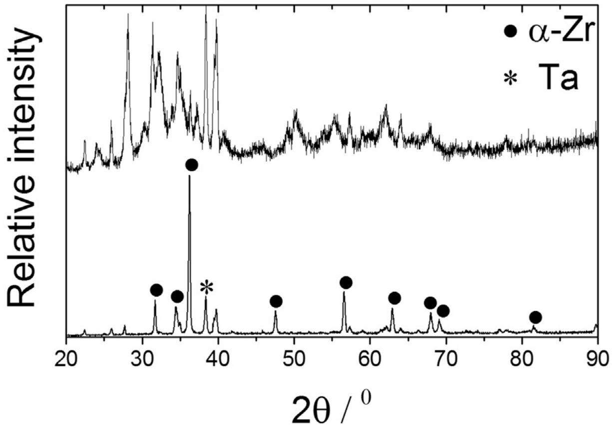

Fig. 1 – X-ray diffraction pattern for Zr–12Ta alloy (bottom) and appropriate hydride (top).