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On the poisoning effect of O_2 and N_2 for the $Zr_{0.9}Ti_{0.1}V_2$ hydrogen storage alloy

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ABSTRACT

Homogeneously annealed $Zr_{0.9}Ti_{0.1}V_2$ samples are firstly exposed to contamination gases of O_2 and N_2 for 30, 60 and 180 s at the ambient temperature, respectively. Hydrogen absorption properties are examined after poisoning and regeneration. The compositions and valence in the surface and sub-surface are investigated by X-ray photoelectron spectroscopy (XPS). The hydrogen absorption capacity of the alloy has been almost entirely degraded by the oxygen poisoning. After the regeneration, the oxygen-poisoned sample can hardly absorb hydrogen while the nitrogen-poisoned sample re-obtains the hydrogen absorption capacity with the value as 2.85 H A^{-1} (molar ratio of hydrogen to alloy). The activation temperature of the oxygen-poisoned sample is ~100 K higher than the value of the un-poisoned one. With the help of ion etching, it is found the thickness of the passivated surface layer of the oxygen-poisoned sample was ~58 nm. However, the thickness of the passivated surface layer of the un-poisoned sample is only ~36 nm. That is the reason why the oxygen-poisoned sample cannot renew the hydrogen absorption capacity under the same regeneration conditions as in the un-poisoned one.

1. Introduction

Hydrogen storage alloys are susceptible to surface contamination by reactive gases, which are crucial problems in practical applications [1–4]. Poisoning gases adsorbed on the surface of alloys can drastically decrease the hydrogen absorption rate by blocking the dissociation of the H_2 molecules. Even low impurity concentrations in the hydrogen gas can poison surface and destroy the hydrogenation performance [4]. It has been observed the hydrogen absorption kinetics of $LaNi_5$ is strongly influenced by the gaseous impurities including O_2, H_2O and CO [1,4,5]. In addition, the alloys poisoned by gaseous impurities cannot be easily reactivated and the particular reactivation cycles are always required [4]. In the investigations on the poisoning behavior of gaseous impurities, it is normally examined the effect of additives in the hydrogen gas on the reaction rate and the absorption capacity of storage alloys [1–3,5–7]. Research on the poisoning process and the corresponding poisoning mechanism will be valuable for the technical applications of hydrogen storage alloys. Exploring the alloys resistive to poison and searching of the efficient protective method have been the research focus during past decades [6,8,9].

Hydrogenation properties of Zr-based Laves phase alloys have been extensively investigated considering their potential applications in the storage and purification of hydrogen and its isotopes [10–15]. The Zr-based alloys have shown several preferable hydrogenation properties including high storage capacity, rapid kinetics and ease of activation [12,16]. But the hydrides of Zr-based alloys are too stable to be of practical significance [17]. In addition, the large hysteresis between hydrogenation and dehydrogenation make the alloys difficult to be used in practical applications [18,19]. Research efforts have been devoted to improve the shortcomings of Zr-based alloys by substitution of A or B site element in AB_2 phase by alloying elements [20]. The partial substitution of Zr by Ti has been proved to be an efficient way to improve the hydrogenation properties of Zr-based Laves phase alloys [13,16,21]. In our previous work $(Zr_{1-x}Ti_x)V_2$ $(0 \leq x \leq 1)$ alloys have been found to absorb/desorb hydrogen rapidly and preserve an acceptable reversibility [13,22,23]. Twin defects result from titanium substitution significantly improve hydrogen absorption kinetics and the decrease in hysteresis is observed in $(Zr_{1-x}Ti_x)V_2$ Laves phase alloys [13,22,23]. For the practical applications, the hydrogen storage capacity of Zr-based Laves phase alloys is inevitably affected by gaseous impurities which are always concerned in hydrogen storage alloys [1,4,5]. O_2 and N_2 gaseous impurities are of particular concern since they can be present with a small concentration in the hydrogen source or originate from atmospheric sources such as system leaks. The oxygen impurity is also of great importance in the activation processes as it can result from the oxygen-containing species such as carbon oxides and H_2O [3]. It has been reported the properties of

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hydrogen storage alloys are always degraded by gaseous impurities [1,3–5]. However, the available literature is still insufficient to understand the poisoning mechanism of gaseous impurities on the hydrogen absorption properties of Zr-based Laves phase alloys.

In this contribution, a typical $(Zr_{1-x}Ti_x)V_2$ alloy with $x = 0.10$ was selected to investigate the poisoning effect of O_2 and N_2 gaseous impurities on the hydrogen absorption properties of Zr-based Laves phase alloys. The poisoning processes of $Zr_{0.9}Ti_{0.1}V_2$ alloy by O_2 and N_2 and the corresponding mechanism were investigated. Hydrogen absorption properties of regenerated alloys were evaluated after the contamination of gaseous impurities. The compositions and valence in the surface and sub-surface were analyzed with the help of X-ray photoelectron spectroscopy (XPS). The major influence factors of the re-activation are discussed as well. Correspondingly, the poisoning mechanism of Zr-based Laves phase alloys is proposed. The results will shed light on the practical applications of Zr-based hydrogen storage alloys.

2. Experimental procedures

The $Zr_{0.9}Ti_{0.1}V_2$ alloy was prepared by the magnetic induction levitation melting method under argon atmosphere in a water-cooled copper crucible. The purities of the raw materials zirconium, titanium, and vanadium were 99.4 wt.%, 99.8 wt.% and 99.5 wt.%, respectively. The alloy was homogeneously annealed at 1373 K for 100 h under the vacuum of 10^{-3} Pa. The experiments of pre-exposure and hydrogen absorption were conducted in an ultra high vacuum apparatus at the ambient temperature with a volume of 67 cm^3. The purities of O_2, N_2 and H_2 are 99.2, 99.5 and 99.99%, respectively.

Each test was performed by the following procedure. Firstly, a fresh sample was activated by conventional method and then exposed to a defined initial pressure (~1000 Pa) of contamination gas for 30, 60 and 180 s, respectively. After the poisoning treatment, the reactor was evacuated again and the sample was loaded in pure hydrogen. The reaction kinetics was evaluated from the pressure decrease in the reactor. The regeneration process was performed by the out-gassing method in vacuum at 823 K for 10 min. The samples with the diameter of $\Phi 8$ and the thickness around 1.0 mm were used in this work. The weight of samples exposed in N_2 and O_2 is 0.2073 and 0.1820 g, respectively. In order to maintain the initial condition, the sample was continuously used for the poisoning experiments after the same regenerating treatment. The absorbed hydrogen amount of the sample was determined by calculating the pressure variation during the reaction while maintaining constant temperature of the reaction chamber. The hydrogen content was calculated as the hydrogen-to-alloy mole ratio ($H A^{-1}$).

To characterize the surface and subsurface of the $Zr_{0.9}Ti_{0.1}V_2$ alloy before and after exposure to the gaseous impurities, the XPS experiment was performed in an ultra-high-vacuum chamber equipped with an XPS spectrometer ESCALAB 250 (multi-channel hemispherical energy analyzer) and a dual Al/Mg X-ray source using the Al Kα excitation (1486.6 eV, 300 W). The area of the ion etching is 4 mm^2 (2 mm × 2 mm). The parameters of the ion gun are: 2 kV beam, 2 μA sample current, depth by 2 nm per second. The base pressure of the chamber is 5.5×10^{-6} Pa. In each ion etching cycle, the XPS spectra were not recorded until the sample has been kept in a specific time. The binding energy (BE) scale was calibrated by measuring the carbon (C 1s, 284.6 eV) core level signal before and after the measurements.

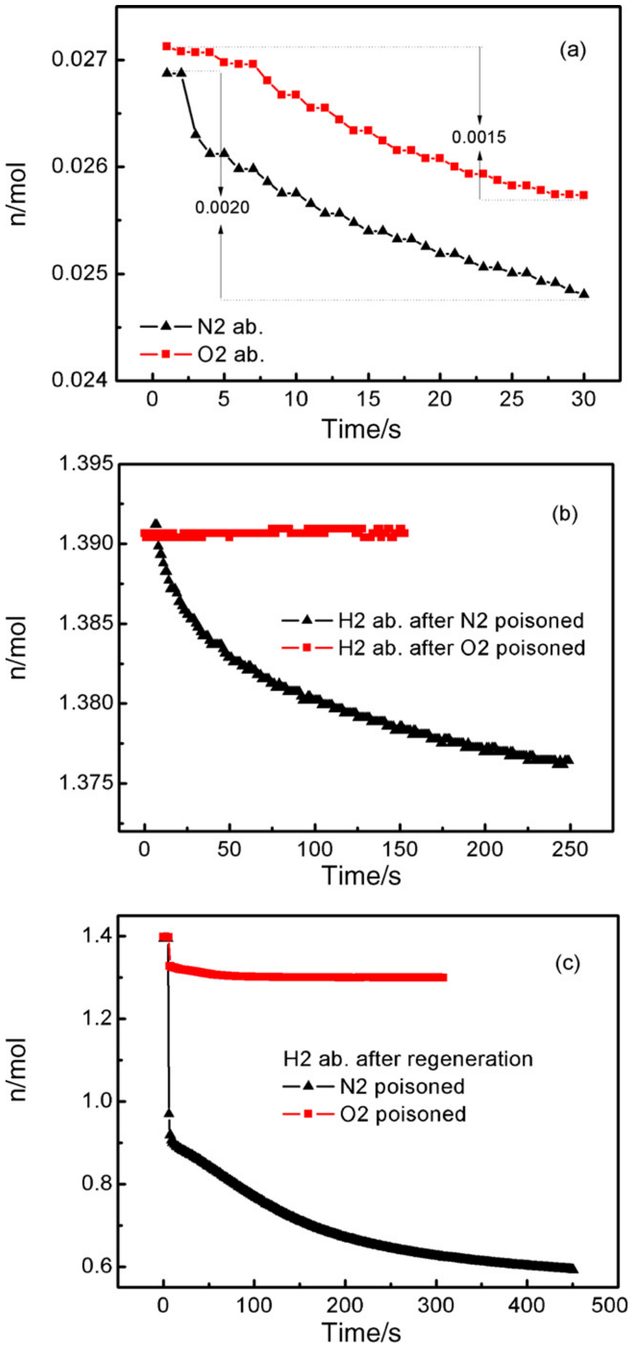

Fig. 1. The comparison of the alloys pre-exposed in the O_2 and N_2 for 30 s, and the hydrogen absorption properties of the regenerated samples. (a) Variations of absorbed gaseous impurities versus time, (b) the hydrogen storage amount versus time of the poisoned samples, and (c) the hydrogen storage amount versus time of the regenerated samples.

3. Results and discussion

3.1. Hydrogenation properties of the poisoned alloy

Fig. 1 shows *P*–*t* curves of the samples pre-exposed in the O_2 and N_2 for 30 s, and the poisoned samples before and after the regeneration. The system pressure decreases as the full activated sample exposed in the oxygen or nitrogen environment. The pressure decrease of the oxygen is about 55 Pa while the data of the nitrogen is around 77 Pa and the sample can rapidly absorb oxygen and nitrogen within 30 s. From Fig. 1a, the calculated amount