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Nitrogen absorption behaviors of ZrVFe and related alloys

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ABSTRACT

For the future use of hydrogen storage alloys for ammonia synthesis, nitrogen absorption behaviors of ZrVFe, ZrVFe (Ti) and ZrVFe (Ti-Al), where the elements in parentheses were added or substituted, were volumetrically investigated by successively adding nitrogen at selected temperatures between 593 and 653 K. Nitrogen contents of ZrVFe (Ti-Al) were the highest among the tested three alloys and reached 5.4 mass% under 1 MPa of nitrogen at 653 K. Variations of nitrogen contents with nitrogen pressures showed plateau-like features, that is, the nitrogen contents rapidly increased with the pressures maintained at around 0.01 MPa. Only ZrVFe (Ti-Al) showed additional plateau-like features under approximately 0.0001 MPa. Supplementary addition of aluminum brought about nitrogen absorption ability under very low pressures to maximize the nitrogen absorption capacity of ZrVFe (Ti-Al). While X-ray diffraction peaks from ZrVFe and ZrVFe (Ti) did not substantially change on nitrogenation, those from nitrogenated ZrVFe (Ti-Al) shifted to the lower angles, became broad and contained the peaks from separated phases. Supplementary addition of aluminum would impart thorough nitrogen absorption ability to ZrVFe. Absorbed nitrogen would exist on the surfaces or in the vicinity of the surfaces of the alloys, and significant pulverization of ZrVFe (Ti-Al) during proposed activation treatment would provide reactive surfaces to absorb large amounts of nitrogen.

1. Introduction

Hydrogen storage alloys such as $LaNi_5$ and FeTi absorb hydrogen through gas–solid reactions, which comprise dissociation of hydrogen molecules on the surfaces and uptake of hydrogen atoms inside the crystal lattices. Hydrogen is able to be reversibly desorbed by adjusting temperatures and/or pressures. Some alloys absorb nitrogen through similar gas–solid reactions [1–5], and R_2Fe_{17} (R = Y, Ce, Sm) are regarded as “nitrogen storage alloys”. Absorption of nitrogen is typically carried out at elevated temperatures, and desorption of nitrogen as ammonia is observed at the same temperatures under hydrogen atmosphere.

Nitrogen absorption behaviors of rare earth-iron alloys have been reported in detail to develop permanent magnets, and among them, Sm_2Fe_{17} has preferable nitrogen absorption and desorption properties, and $Sm_2Fe_{17}N_3$ has been gathering attentions as a prominent permanent magnet [5–8]. From viewpoints of storage and utilization of nitrogen, alloys based on practically available metals, such as $ZrFe_2$, FeTi and $LaNi_5$ [9,10] as well as Ca-Fe and Ca-Co alloys [11,12], have been prepared and assessed. Since dissociated hydrogen on a palladium membrane promotes particular reactions [13,14], atomic nitrogen would be also highly reactive. If an alloy absorbs both hydrogen and nitrogen to accumulate atomic hydrogen and nitrogen, some novel reactions are expected to take place.

While relationships between temperatures and nitrogen contents were often reported, variation of nitrogen contents with pressures were scarcely measured with an exception of Sm_2Fe_{17} [8]. Further, nitrogen absorption properties of ternary alloys are left unclear. In the present study, nitrogen pressure dependence of nitrogen absorption behaviors of a promising ternary alloy, ZrVFe, and modified alloys were studied. ZrVFe has a C14 Laves phase structure and absorbs large amounts of hydrogen under mild pressures [15]. Hydrogen desorption temperature as determined by temperature programmed desorption *in vacuo* is able to be lowered by adding titanium and/or aluminum. If ZrVFe and/or modified alloys are able to absorb nitrogen at elevated temperatures (593–653 K), there is a chance that ammonia synthesis under mild

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conditions will be realized. Nitrogen pressure dependence of nitrogen absorption behaviors of the Zr-based alloys was thus studied for potential use of them in ammonia synthesis.

2. Experimental

$Zr_{1.0}V_{1.0}Fe_{1.0}$ (ZrVFe), $Zr_{0.9}V_{1.0}Fe_{1.0}Ti_{0.1}$ (ZrVFe (Ti)) and $Zr_{0.9}V_{1.0}Fe_{1.0}Ti_{0.1}Al_{0.15}$ (ZrVFe (Ti-Al)), where the elements in parentheses were added or substituted, were prepared by Taiyo Koko Co., Ltd. by means of arc melting method using grains of vanadium (99.9%), iron (99.9%) and zirconium (98%), together with reagent grade titanium and aluminum powders. The alloy lumps were milled into powders in a mortar under a nitrogen atmosphere. Activation treatment prior to hydrogenation or nitrogenation was carried out as follows. About 0.5 g of each alloy was put in a stainless reactor, evacuated with simultaneous heating to 653 K, and kept at that temperature for 1 h. After the sample was cooled to room temperature, 1.1 MPa of hydrogen was admitted to be absorbed for 2 h. Desorption of hydrogen was then carried out by evacuation at 653 K for 1 h.

Characterization of the alloy samples was performed using HITACHI TM3000 scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) and Rigaku MultiFlex Cu Kα X-ray diffractometer (XRD). The alloys were handled without exposing to air, and nitrogen absorption behaviors were assessed immediately after the activation treatments. Absorbed amounts of nitrogen were volumetrically measured by use of Suzuki Shokan PCT-2ST. Nitrogen was admitted every 15 min with pressure gradually increased. The alloy once assessed at an intended temperature between 593 and 653 K was not employed for any successive measurements at other temperatures, since absorbed nitrogen was not entirely removed from the sample by evacuation at that temperature. Relationships between temperatures and nitrogen contents were also measured by thermogravimetric–differential thermal analysis (TG-DTA) under a nitrogen atmosphere using Rigaku Thermo plus TG-8120. The heating rate was 10 K per minute.

3. Results and discussion

3.1. Properties of nitrogen absorption

Fig. 1 shows nitrogen absorption behaviors of ZrVFe, ZrVFe (Ti) and ZrVFe (Ti-Al) in nitrogen gas at 653 K. ZrVFe and ZrVFe (Ti) reached maximum nitrogen content of 2.8 mass%, and ZrVFe (Ti-Al) absorbed more nitrogen to reach 5.4 mass% under 1.0 MPa. In other words, each of ZrVFe and ZrVFe (Ti) absorbed 0.39 and 0.38 mol of nitrogen per 1 mol of alloys, and ZrVFe (Ti-Al) absorbed 0.76 mol of nitrogen per 1 mol of alloy. Reported nitrogen contents observed on nitrogen gas absorption were 0.1 mol of nitrogen per 1 mol of alloy at 773 K for $TiFe_2$ [9], and 0.8 mol of nitrogen per 1 mol of alloy at 873 K for $LaNi_5$ [10], and their nitrogen to metal ratios, N/M's, were 0.03 and 0.13, respectively. Since the referred values were obtained under 0.1 MPa of nitrogen, the nitrogen content of 0.73 mol of nitrogen per 1 mol of ZrVFe (Ti-Al), or $N/M = 0.24$ was to be employed for comparison. The superiority of ZrVFe (Ti-Al) was evident.

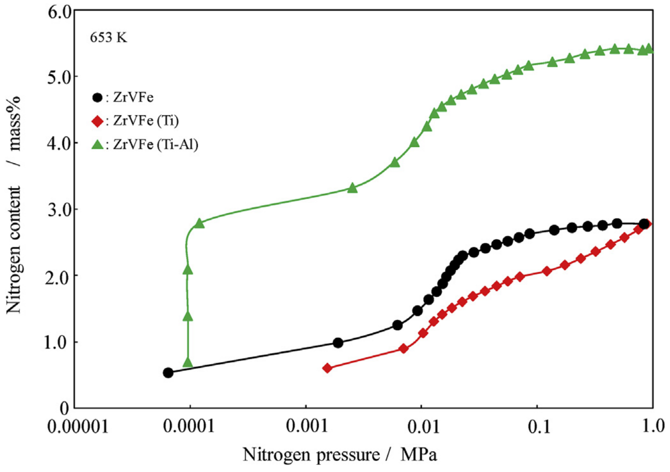

Fig. 1. Variation of nitrogen absorption amounts with increased pressures at 653 K for ZrVFe, ZrVFe (Ti) and ZrVFe (Ti-Al).

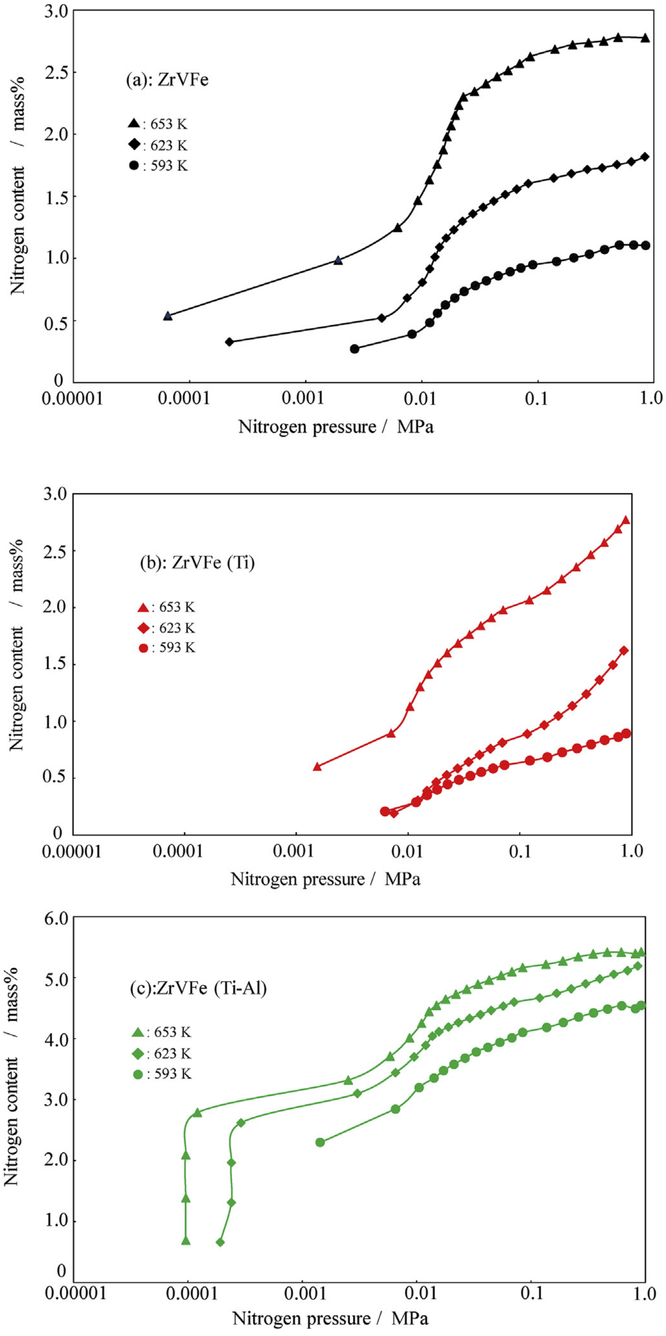

Fig. 2. Variation of nitrogen absorption amounts with increased pressures at varied temperatures for (a) ZrVFe, (b) ZrVFe (Ti) and (c) ZrVFe (Ti-Al).