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Study of cyclic performance of V-Ti-Cr alloys employed for hydrogen compressor

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ABSTRACT

The development of a suitable hydrogen compressor plays one of the key roles to realize the fuel cell vehicle as well as for many other stationary and mobile applications of hydrogen. V-Ti-Cr BCC alloys are considered as promising candidates for effective hydrogen storage. The cyclic durability of hydrogen absorption and desorption is very important for these alloys to be realized as practical options. In connection to this, two alloys of V-Ti-Cr, (1) $V_{40}Ti_{21.5}Cr_{38.5}$ and (2) $V_{20}Ti_{32}Cr_{48}$, were selected and their cyclic hydrogen absorption-desorption performance was evaluated up to 100 cycles for temperature and pressure ranges of 20–300 °C and 5–20 MPa, respectively. It has been found that the cyclic hydrogen storage capacity continuously decreased for one composition while it was stable after 10 cycles for another composition. This performance difference of the alloys was studied in terms of their structural and microscopic properties and the results are presented in this paper.

Introduction

Hydrogen compression using metal hydride has been considered as a potential application for hydrogen energy systems [1]. Although several mechanical compressors, such as ionic liquid piston compressor, electrochemical compressors, are available commercially, they suffer from several difficulties and complicated operation. Whereas, metal hydride compressor offers safe, simple, and reliable option for the hydrogen compression. As mentioned in a recent review by Lototsky et al. [1], hydride compressor utilizes reversible heat driven interaction of metal and hydrogen to form a metal hydride. In a typical hydride compressor, a metal absorbs low-pressure hydrogen gas at an ambient temperature and releases high-pressure hydrogen gas at higher temperatures. In order to realize metal hydride compressor, the material should possess several properties namely: (i) high reversible H-content, (ii) Fast kinetics, (iii) Low plateau slope, (iv) Low

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hysteresis, (v) good overall Pressure Composition Temperature (PCT) properties in order to get high pressure from low initial pressure in reasonable temperature range [2,3]. Numerous efforts have been made in order to achieve the above properties and several materials have been developed as an outcome of these researches [4–7]. Among the considered materials, BCC vanadium based hydrides have attracted attention of scientific community, owing to their suitable PCT data, high H_2 capacity (~4 wt%), fast kinetics at ambient temperature, and steep dependence of equilibrium sorption pressure on temperature due to high enthalpy and entropy of VH_2 formation [8–10]. Despite of having such a large capacity and fast kinetics, vanadium can not be employed for practical applications due to its difficult activation, strong pulverization, low cyclic capacity (~2 wt%), very stable β-phase monohydride [11,12], high hysteresis, high slope of absorption isotherm, and increase of hysteresis during sorption cycling [13]. Several works have been reported to resolve these issues by adding other elements, with a special focus on Ti [14–23]. Introduction of titanium in vanadium makes it suitable for compressor application as a significant variation of pressure from 0.02 to 1 MPa could be achieved at 60 °C [17]. Although Ti-V alloy presents favorable hydrogenation characteristics, the cyclic stability still remained a challenge. In a recent work by Kim et al. [24], atomic pair distribution functional analysis has been used to explain this poor cyclability. They found a direct relation between this cyclic decay and the amount of generated dislocation defects in the crystal lattice. It was observed that with the increasing number of cycles, the density of these dislocation defects was increased. To improve the cyclic stability of these V based alloys it is suggested to develop the alloys having BCT monohydride with a large tetragonal distortion. The presence of dislocation and defects has also been confirmed by a microscopic study performed by Washio et al. [25] on $V_{40}Ti_{24}Cr_{36}$ alloy. It was suggested in this work that the presence of nanometer size particles can have good degradation resistance because of less accumulation of dislocations and defects in the lattice during cycling. Chromium addition to Ti-V system has been explored widely, as the addition of Cr improves the cyclic stability as well as the resistance of material towards pulverization without affecting the effective H_2 storage capacity [16,26–28]. Till date, several Ti-Cr-V alloys have been studied for their structural, hydrogenation and cyclic properties [29–44]. Tsukahara et al. found the highest effective capacity 2.62 wt% for $V_{60}Ti_{15}Cr_{25}$ alloy out of several studied combinations [32]. Shen et al. [40] have shown the cyclic stability of $Ti_{25}V_{35}Cr_{40}$ alloy and found that it retains 83% of initial hydrogen capacity after 500 cycles, whereas C doping in this alloy slightly improve the capacity retention to 90% after 500 cycles. The slight decrease was suggested due to precipitation of TiH_2 formation during cycling. Itoh et al. [31] studied the cyclic durability of $V_{40}Ti_{24}Cr_{36}$ alloy and find it quite stable after 100 cycles with absorption and desorption plateau pressure at around 0.1 and 0.04 MPa, respectively. In another work, Kazumi et al. [29] and Tamura et al. [30] have shown 2.4–2.5 wt% desorption capacity of $V_{20}Ti_{32}Cr_{48}$ alloy with absorption/desorption plateau pressure at around 0.3 and 0.09 MPa at 313 K. Inspired from suitable PCT window of these two alloys for compressor, recently our group developed a two-stage high pressure (80 MPa) compressor [45], where these two alloys were employed at first stage compression. Although near ambient temperature properties of these alloys are well established, the effect of high temperature and high pressure on these properties have not been studied yet. To realize these materials as a potential candidate for hydrogen compressor, their cyclic performances are quite important. This motivated us to study the effect of high temperature and pressure conditions on the performance of these alloys over a number of cycles in details. In this work, two kinds of BCC alloys i.e. $V_{40}Ti_{21.5}Cr_{38.5}$ and $V_{20}Ti_{32}Cr_{48}$ have been studied for their structural, morphological and sorption properties up to 100 cycles. The difference in their performance over a number of cycles has also been clarified in details.

Experimental

The target alloys $V_{20}Ti_{32}Cr_{48}$ and $V_{40}Ti_{21.5}Cr_{38.5}$ were prepared by arc melting of the starting materials (all > 99.9% purity) in the respective molar ratio. The samples were melted three times under argon atmosphere to ensure homogeneity. To improve the crystallinity and to dissolve some minor phases, the samples were annealed at 1500 K for 24 h. The phase identification was carried out by X-ray Diffraction (XRD) using Rigaku-RINT 2500 equipped with CuKα radiation. The sample was spread on a glass plate and covered by polyimide sheet (Dupont-Toray Co. Ltd., Kapton) in order to protect from oxidation. The powder morphology was observed using Scanning Electron Microscopy (SEM) on JEOL, JSM-6380A instrument. In addition to XRD and SEM, Transmission Electron Microscopy (TEM) experiment was performed on pristine and cycled samples to identify the phases at the microscopic level using 200 kV TEM (JEOL JEM-2010). The sample was dispersed on a Mo TEM grid and then transferred into TEM chamber

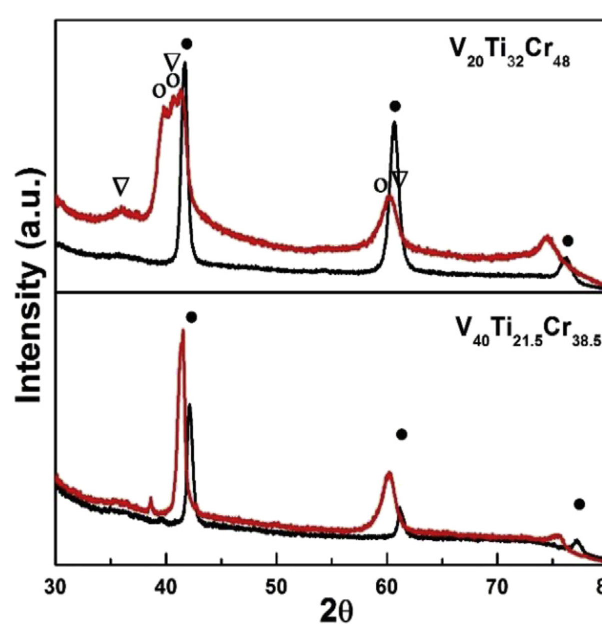

Fig. 1 – XRD profile of pristine and cycled (100 cycles) V-Ti-Cr alloys (•-V; o-$VH_{0.81}$; ∇-$TiH_{0.66}$).