Journal of Alloys and Compounds 737 (2018) 337–346

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Effect of gradient-structure versus uniform nanostructure on hydrogen storage of Ti-V-Cr alloys: Investigation using ultrasonic SMAT and HPT processes

Kaveh Edalati [a, b, *], Marc Novelli [c, d], Shota Itano [e], Hai-Wen Li [a, f, g], Etsuo Akiba [a, e, f], Zenji Horita [a, b], Thierry Grosdidier [c, d, **]

[a] WPI, International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, 819-0395, Japan
[b] Department of Materials Science and Engineering, Faculty of Engineering, Kyushu University, Fukuoka, 819-0395, Japan
[c] Université de Lorraine, Laboratory of Excellence on Design of Alloy Metals for low-mass Structures (DAMAS), Metz, F-57045, France
[d] Université de Lorraine, Laboratoire d'Etude des Microstructures et de Mécanique des Matériaux (LEM3 UMR 7239), 7 rue Félix Savart, BP 15082, Metz, F-57073, France
[e] Department of Mechanical Engineering, Faculty of Engineering, Kyushu University, Fukuoka, 819-0395, Japan
[f] International Research Center for Hydrogen Energy, Kyushu University, Fukuoka, 819-0395, Japan
[g] Kyusyu University Platform of Inter/Transdisciplinary Energy Research, Fukuoka, 819-0395, Japan

ARTICLE INFO

Article history:
Received 6 September 2017
Received in revised form
5 December 2017
Accepted 6 December 2017
Available online 7 December 2017

Keywords:
Beta titanium alloys
Metal hydrides
Severe plastic deformation (SPD)
Surface mechanical attrition treatment (SMAT)
High-pressure torsion (HPT)

ABSTRACT

Lattice defects can have contradicting effects on the hydrogen storage behavior of titanium-vanadium-chromium alloys: they may facilitate the surface activation, or they may deteriorate the hydriding/dehydriding reversibility. In this study, two types of microstructure containing different structural defects were investigated to gain further insights on the impact of lattice defects on the hydrogen storage performance of beta Ti-V-Cr alloys: (i) a gradient-structure with high density of surface defects processed by ultrasonic surface mechanical attrition treatment (SMAT), and (ii) a uniform structure containing highly-strained nanograins processed by high-pressure torsion (HPT). Because of the effect of surface lattice defects on initial activation, both the SMAT- and HPT-processed materials readily absorbed hydrogen at room temperature. However, while the SMAT-processed samples showed good hydrogen storage reversibility, the HPT-processed materials exhibited poor reversibility because of the effect of bulk defects on hindering the hydrogen transport to/from the hydride. The results clearly demonstrate that the engineering of structural defects on the surface is an effective approach to achieve both easy activation and good reversibility.

1. Introduction

Although titanium and vanadium are thermodynamically immiscible at room temperature [1,2], they can keep their high-temperature solid solution β phase with the BCC (body-centered cubic) structure at room temperature within a wide range of binary and ternary alloying compositions because of the slow atomic diffusion in the Ti-V system [3,4]. In 1975, Nagel and Perkins [5] conducted some of the first experiments on the hydrogenation behavior of the metastable Ti-V alloys. This pioneering work [5] and several following studies [6–10] showed that the hydrogenation in the Ti-V system occurs through two steps: (i) formation of a very stable hydride with the BCT (body-centered tetragonal) structure and a hydrogen/metal ratio of ~1, and (ii) formation of a less-stable hydride with the FCC (face-centered cubic) structure and a hydrogen/metal ratio of ~2. Following these studies, the Ti-V-based alloys with the addition of a third element as destabilizer of FCC hydride such as Fe [11], Ni [12], Mn [13] and Cr [14] were investigated for solid-state hydrogen storage. Among the ternary Ti-V-based alloys, the Ti-V-Cr alloys with large fractions of V received appreciable attention because they could reversibly absorb and desorb ~2 wt% of hydrogen at room temperature [15].

---

* Corresponding author. WPI, International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, 819-0395, Japan.
** Corresponding author. Université de Lorraine, Laboratory of Excellence on Design of Alloy Metals for low-mass Structures (DAMAS), Metz, F-57045, France.
E-mail addresses: kaveh.edalati@zaiko6.zaiko.kyushu-u.ac.jp (K. Edalati), thierry.grosdidier@univ-lorraine.fr (T. Grosdidier).

https://doi.org/10.1016/j.jallcom.2017.12.053

Although the room-temperature dehydrogenation capability of Ti-V-Cr alloys is an important point to employ them for hydrogen storage without using a heating system [16], the Ti-V-based alloys usually suffer from two main drawbacks: (i) they need an initial thermal activation process to react with hydrogen in the first hydrogenation cycle (they are usually activated by exposure to vacuum or hydrogen at high temperatures up to 673 K) [17–19], and (ii) their reversibility is degraded with the formation of lattice defects [20–22] (there is no general agreement which type of lattice defects has the most significant effect on the reversibility). Despite the reported negative effects of lattice defects on reversibility of Ti-V-Cr alloys, several studies on severe plastic deformation (SPD) (see the principles of SPD in Refs. [23,24]) of pure Mg [25,26], Mg-based composites [27,28], Mg-based alloys [29,30], Mg_2Ni intermetallics [31,32], TiFe intermetallics [33,34], TiFeMn intermetallics [35] and binary Ti-V alloys [36] suggested that large fraction of lattice defects can act as hydrogen diffusion pathways to enhance the hydrogenation kinetics and facilitate the activation. Since the activation for hydrogenation is mainly a surface-related issue involving the dissociation of H_2 molecules into create H atoms which subsequently diffuse from the surface towards the bulk [37], it may be sufficient - and easier from an engineering point of view - to create the lattice defects only on the surface to (i) have the effect of surface lattice defects on easy activation and (ii) avoid the effect of some bulk lattice defects on degradation of hydrogen storage reversibility.

Compared to the SPD techniques [23,24] such as the high-pressure torsion (HPT) method (see the background and the principles of the method in Refs. [38,39]), in which the lattice defects and ultrafine grains are generated on the overall bulk material, several techniques have been developed to generate lattice defects and fine microstructure on the surface by mechanical processes [40,41] or by beam-assisted treatments [42,43]. Among these techniques, the surface mechanical attrition technique (SMAT) [44,45], which is also referred to as ultrasonic shot peening (USP/USSP) [46] or severe shot peening (SSP) [47], is rather versatile because it can produce controllable gradient-structures (i.e. graded microstructure) consisting of different successive zones towards the extreme surface [48]: (i) an undeformed zone with coarse grains in the bulk, (ii) a “deformation zone” containing plastically induced defects (dislocations, twins …), (iii) a “transition zone” within which the formation of dislocation cells and subgrains initiate the microstructure refinement process, and finally (iv) a “nanostructured zone” where the formation of ultrafine grains is completed. Although the Ti-V-Cr alloys are rather brittle when compared to the metals that were processed by SMAT so far [44–48], it is still possible to achieve a kind of gradient-structure in these alloys with a simple goal of easy hydrogenation activation without destroying the hydrogen storage reversibility.

In this study, and for the first time, ultrasonic SMAT processing has been applied on Ti-V-Cr hydrogen storage materials to create gradient-structures with higher densities of structural defects at the surface and determine the hydrogen storage behavior. The behavior of these SMAT-processed samples has been compared with those processed by HPT which contain a more uniform distribution of ultrafine grains and lattice defects all through the samples. Since the SMAT process has a high potential for commercialization when compared to the HPT process, the aim of this study is not only to give more insights into the understanding of the critical role of structural defects in hydrogen storage behavior of Ti-V-Cr alloys but also to introduce the SMAT process as a new route for processing hydrogen storage materials.

2. Experimental materials and procedures

Two Ti-V-Cr alloys with the compositions of $Ti_{10}V_{75}Cr_{15}$ and $Ti_{25}V_{50}Cr_{25}$ and grain sizes in the range of 50 μm–500 μm were prepared by arc melting under argon in a water-cooled copper mold (the samples were used without further heat treatment). Examination of arc-melted samples by X-ray diffraction (XRD) analysis confirmed that the BCC phases with the lattice parameters of 0.303 nm for the $Ti_{10}V_{75}Cr_{15}$ alloy and 0.306 nm for the $Ti_{25}V_{50}Cr_{25}$ alloy are formed. The $Ti_{25}V_{50}Cr_{25}$ alloy was harder (hardness: 421 ± 13 Hv) and more brittle than the $Ti_{10}V_{75}Cr_{15}$ alloy (hardness: 298 ± 11 Hv) due to its larger fraction of Cr. Following the arc melting, discs with 10 mm diameter and 0.85 mm thickness were cut from the ingots using an electric discharge machine and mechanically polished to a thickness of 0.8 mm.

For SMAT processing, the discs were peened at room temperature with 2 mm diameter steel shots (100 C6 steel in the French AFNOR standard) for a period of 480 s under a sonotrode vibrating amplitude of 60 μm and a frequency of 20 kHz using an ultrasonic device (stressonic) developed by the SONATS company [49]. It should be noted that the SMAT processing at cryogenic temperature was also attempted as conducted earlier [50], but the process was unsuccessful because of the brittleness of the TiVCr alloys at the low temperature and the associated significant crushing of the discs. For HPT processing, the discs were compressed between two anvils (made of a martensitic tool steel with the exact dimensions given in Ref. [51]) under $P = 6$ GPa and concurrently processed for $N = 100$ turns at room temperature with a rotation speed of 1 rpm (one turn per minute). Note that no phase transformation was detected using the XRD analysis after SMAT and HPT processing.

The microstructures of SMAT-processed samples were investigated on the cross section of discs by scanning electron microscopy (SEM) and electron back-scattering diffraction (EBSD) analysis. Two types of EBSD analysis were carried out: (i) low-magnification observation using a step size of 500 nm and (ii) high-magnification observation using a step size of 60 nm. The EBSD data were treated in terms of orientation mapping, grain boundary distribution and local misorientation analysis using the ATOM software developed in the LEM3 laboratory, Metz, France [52].

The microstructures after HPT processing were investigated by transmission electron microscopy (TEM) under an acceleration voltage of 200 kV or 300 kV by selected area electron diffraction (SAED), by bright-field and dark-field imaging conditions as well as by high-resolution imaging. For TEM examinations, discs with 3 mm diameter were cut from 3.5 to 5.0 mm away from the center of HPT-processed discs, ground mechanically to a thickness of 0.15 mm and further thinned for electron transparency with an electrochemical polishing system in a solution of 5% $HClO_4$, 25% $C_3H_3(CH_2)_2CH_2OH$ and 70% CH_3OH at 263 K under a voltage of 15 V, as attempted earlier in Ref. [36]. The SAED analyses were conducted on areas with 1.9 μm diameter and the average grain sizes were estimated by measuring the size of bright-contrast regions in the dark-field images.

The hydrogen storage in the samples processed by SMAT and HPT was examined in a Sieverts-type gas absorption apparatus. One disc sample was broken to pieces and subjected to evacuation at room temperature for 2 h to remove the moisture because the samples were in air atmosphere for about one month. The pressure-composition-temperature (PCT) isotherms were measured right after the evacuation for two hydrogenation/dehydrogenation cycles at 303 K followed by a third cycles at 353 K. The samples were evacuated for 2 h at 303 K between the cycles. The samples before and after PCT measurement were examined by XRD analysis using the Cu Kα radiation.

3. Results

3.1. Microstructure after SMAT

Fig. 1 shows the appearance of disc samples as well as the SEM