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Hydrogenation and microstructural study of melt-spun $Ti_{0.8}V_{0.2}$

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ABSTRACT

In this work we utilized the melt spinning process to prepare a nanostructured $Ti_{0.8}V_{0.2}$ alloy for hydrogen storage applications. The alloy ribbons were solidified from the melt using two different wheel spinner velocities, 1000 and 3000 rpm. LOM, and SEM were utilized to examine the microstructures of the ribbons and their corresponding hydrides. Hydrogen absorption and desorption experiments were performed using a TDS setup. Arc melted $Ti_{0.8}V_{0.2}$ and rapidly solidified (RS) materials (RS1000 and RS3000) formed FCC dihydrides with lattice parameters ranging from 4.4198 to 4.4338 Å. RS resulted in a dramatic decrease of the grain size, down to smaller than 200 nm for the hydrogenated $Ti_{0.8}V_{0.2}$ RS3000 alloy. The thermal stability of the hydrides was strongly affected by the RS solidification rate. For the hydride of $Ti_{0.8}V_{0.2}$ RS3000, a significant decrease in the thermal stability was observed, so the peak of hydrogen desorption was shifted to much lower temperatures, by ~80 °C, as compared to the hydrogenated as cast alloy.

1. Introduction

Titanium, vanadium and their alloys have high hydrogen gravimetric and volumetric absorption capacities reaching ~4 wt.% H or 150 kg H/m^3. The hydrogenation process is very exothermic. Hence, these alloys are promising candidates for hydrogen and heat storage applications, particularly in stationary systems. Both the H storage capacities and the hydrogenation enthalpies may be modified by changing the content of vanadium, or by adding a third component, including different transition elements, to the binary Ti–V alloys crystallizing with the BCC-type crystal structures with the highest values of hydrogen densities [1–3]. This possibility is very useful when specific operating working temperatures are to be optimized. Further to the modification of the chemical composition, a convenient way to control the properties is by selecting and optimizing the conditions of the synthesis process.

As the chemical element distribution, the crystal structure, and the microstructure of an as cast alloy are all determined by the solidification rate, the rapid solidification (RS) process can be applied to produce optimized microstructures, by effectively controlling this parameter. Rapid solidification/rapid quenching is especially beneficial for the Ti-based alloys because it suppresses the formation of the phases other than the BCC alloy [4,5]. In addition, homogeneous element distribution may be achieved. Thus, better control over the equilibrium pressures of hydrogen absorption–desorption can be obtained [6]. Furthermore, RS has been found to improve cycling properties of the hydrides [7,8]. Melt spinning is one type of the RS technique which has being used for optimizing the microstructures of the Ti–V based alloys [6,9] as well as for producing the nanostructured Mg–Mm–Ni composites [10]. In the present work, we have utilized the melt spinning process to further modify the hydrogen sorption properties of the Ti–V alloys. The aim was in studying the morphology and microstructure of the $Ti_{0.8}V_{0.2}$ alloys and their hydrides and relating them to the hydrogen absorption–desorption behaviour of the alloy, in order to propose the ways of optimizing the preparation route.

2. Experimental procedure

The as cast $Ti_{0.8}V_{0.2}$ used for rapid solidification was prepared by arc melting the individual metals, Ti and V (both having purity of 99.9%), in argon gas. The sample with the mass of 10 g was turned over and remelted several times to achieve a better homogeneity. This button-shaped sample was then cut into pieces for the preparation of the ribbons during the melt spinning performed in argon gas. Two different copper wheel spinner velocities were employed, i.e. 1000 and 3000 rpm. The morphology and microstructure of the ribbons were characterized by light optical microscopy (LOM) and field emission SEM. Hydrogenation and dehydrogenation were done in the Sieverts type TDS setup. The ribbons were activated by heating in vacuum to 600 °C with a dwell time of 30 min, followed by cooling to room temperature. First hydrogenation was performed at initial hydrogen pressure of 6 bar by heating the sample from room temperature to 400 °C with a heating rate of 5 K/min. Thermal Desorption Spectroscopy (TDS) was conducted in dynamic vacuum (with starting pressure of ~1×10^{-5} mbar), using a constant heating rate of 5 K/min in a temperature interval from room temperature to 800 °C. Subsequent rehydrogenation was performed at 30 °C at hydrogen pressure of 6 bar. To achieve higher accuracy, the mass of the sample used in each measurement was

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0.5–1 g. The crystal structure data were evaluated using Synchrotron X-ray diffraction performed at the beam station BM1A accommodated at the Swiss-Norwegian Beam Lines, European Synchrotron Research Facility, Grenoble, France with the wavelength of $\lambda = 0.72085$ Å. The samples were placed into quartz glass capillaries (0.5 mm in diameter and 0.1 mm wall thickness).

3. Results and discussion

An arc melted $Ti_{0.8}V_{0.2}$ was found to crystallize with a BCC crystal structure (space group $Im\bar{3}m$), with a unit cell parameter of 3.2298 Å. The melt spinning produced ribbons of different thickness, which decreased with increasing the wheel spinner velocity, being approximately 53.4 μm for RS1000 and 20.3 μm for RS3000. Changes in the thickness of the ribbons are because of an inverse proportional dependence of the thickness and the solidification rate. The microstructures of the ribbons were studied by LOM and SEM. An average grain size of the BCC phase in the $Ti_{0.8}V_{0.2}$ ribbons was 20.1 μm for RS1000 and 5.3 μm for RS3000. A decrease in the grain size with increasing solidification rate was expected and was observed earlier [11,12].

Hydrogenation of the ribbons was performed after degassing of the sample by heating it from room temperature to 600 °C in vacuum. During the hydrogen absorption experiment, the sample was heated from RT to 400 °C with a rate of 5 K/min at a starting H_2 pressure of 6 bar. We note that crushed into the pieces as cast alloy was not able to absorb reasonable amount of hydrogen at such experimental conditions. In order to obtain completely saturated by hydrogen samples, as cast alloy must be hydrogenated and dehydrogenated at least one cycle. Fig. 1 presents kinetic curves of the first hydrogenation of the RS1000 and RS3000 ribbons. Both samples exhibit an incubation period preceding the onset of hydrogen absorption, when the surface oxide layers present on the ribbons were penetrated by hydrogen gas. The incubation time was around 7 min for the RS1000 ribbons and 12 min for the RS3000 ribbons. The reason for such a difference is in a fact that the surface to volume ratio for the RS3000 ribbons is higher than that for the RS1000 sample. During the active hydrogen absorption, both samples were saturated with hydrogen before reaching 150 °C. The hydrogen absorption capacity of the Ti–V ribbons was lower than that of the arc melted pre-alloy. Indeed, the as cast alloy absorbed 3.95 wt.% H, while $Ti_{0.8}V_{0.2}$ RS1000 and $Ti_{0.8}V_{0.2}$ RS3000 absorbed 3.75 wt.%

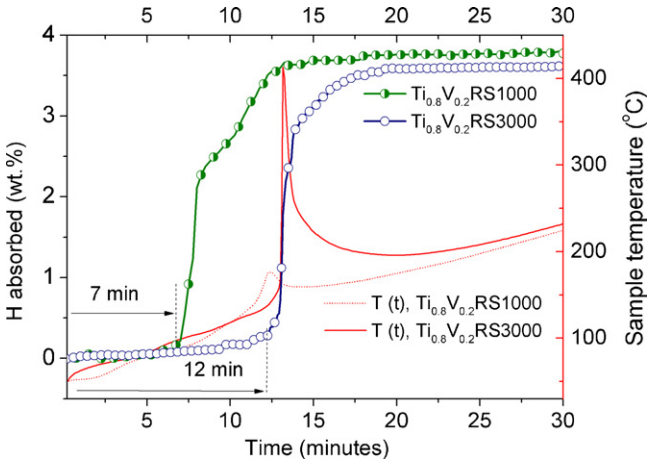

Fig. 1. First hydrogenation of the melt-spun $Ti_{0.8}V_{0.2}$ ribbons. Ribbons were heated from RT to 400 °C at the initial hydrogen pressure of 6 bar. Sample temperature $T(t)$ during hydrogen absorption shows a significant exothermic effect of hydrogenation.

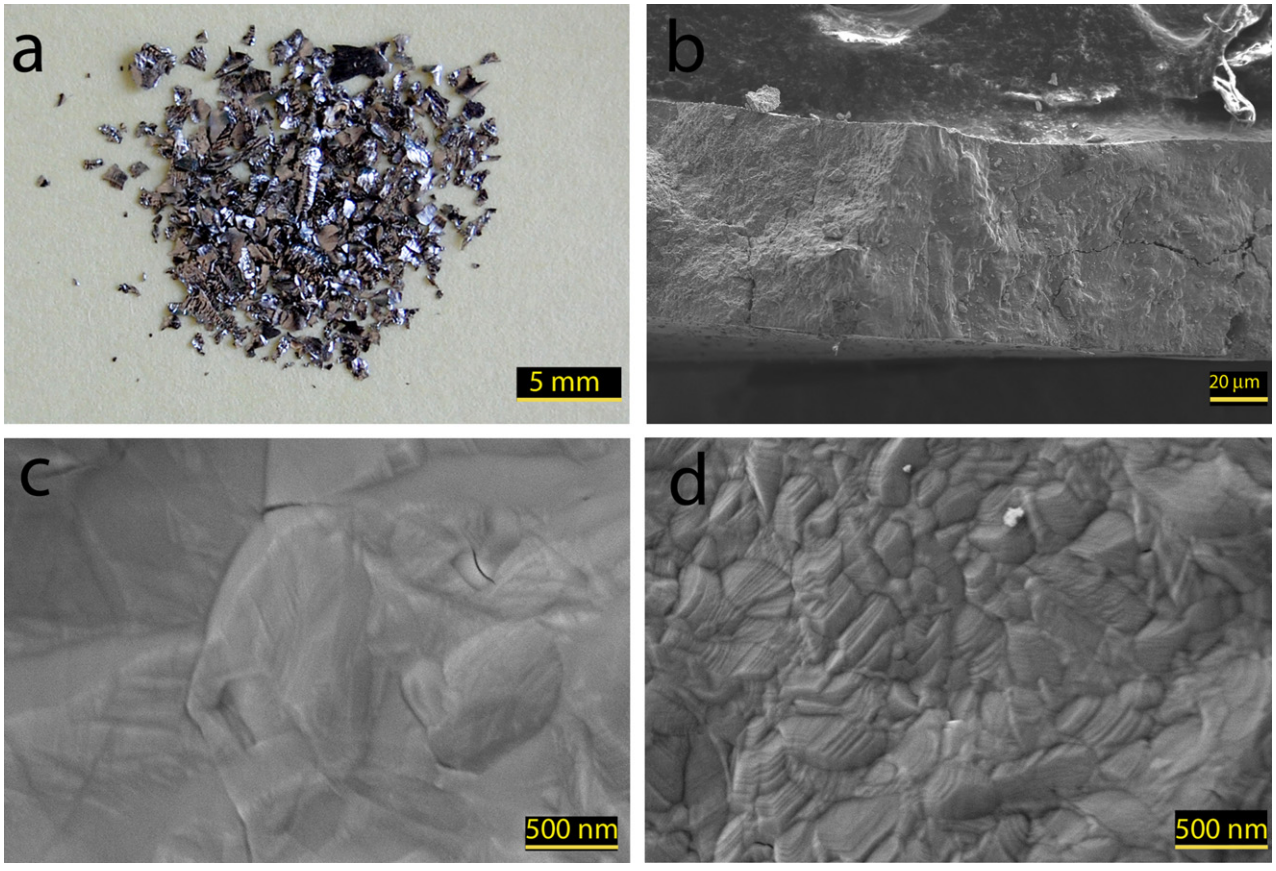

Fig. 2. (a) General view of the hydrogenated ribbons. (b) Morphology of a hydrogenated ribbon (cross-section view). (c) Microstructure of the hydrogenated $Ti_{0.8}V_{0.2}$ RS1000. (d) Microstructure of the hydrogenated $Ti_{0.8}V_{0.2}$ RS3000.