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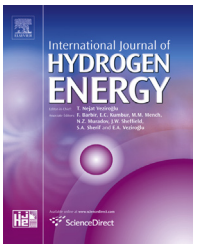

Structure and hydrogen storage properties of mechanically alloyed Ti-V alloys

M. Balcerzak *

Poznań University of Technology, Institute of Materials Science and Engineering, Jana Pawła II No 24, 61-138 Poznań, Poland

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ABSTRACT

Ti-V alloys are potential candidates for hydrogen storage materials. In this study, mechanical alloying under an argon atmosphere was used to produce $Ti_{2-x}V_x$ nanocrystalline alloys (x = 0.5, 0.75, 1, 1.25, 1.5). Shaker type ball mill was used. An objective of the present study was to investigate an influence of chemical composition and method of production on hydrogenation and dehydrogenation properties of Ti-V alloys. X-ray diffraction analyses revealed formation of BCC solid solution after 14 h of milling. It is the first time of obtaining this phase directly from mechanical alloying method. HRTEM images confirmed formation of nanocrystalline materials. Synthesized materials were studied by a conventional Sievert's type apparatus at 303 K. It was observed that the maximum hydrogen storage capacity is increased with increased Ti content in the alloy. $Ti_{1.5}V_{0.5}$ alloy showed high hydrogen storage capacity at room temperature, which reached about 3.67 wt.%. Simultaneously, it was noticed that Ti-rich alloys form more stable hydride phases than V-rich alloys. Observed properties resulted mainly from structure of studied materials.

Introduction

Recently, V-based hydrogen absorbing alloys with body-centered cubic (BCC) structure showed good gravimetric and volumetric capacities compared to rare earth-based storage materials [1]. It is due to the relatively low atomic mass of vanadium. Conventional metal hydrides are characterized by weight capacities less than 1.8 wt.%, while Ti-V based solid solutions exhibit a hydrogen storage capacity close to 4 wt.% [2]. This capacity is connected to the BCC structure which is a coarse packing structure and has more interstitial sites than face-centered cubic (FCC) or hexagonal close-packed structures [3]. For this reason, BCC Ti-V alloys are attractive candidates as possible interstitial hydrogen storage materials.

Conventionally, Ti-V based alloys have been prepared by arc or induction melting – methods producing microcrystalline materials [1,4–6]. However, for some of alloys the desired composition is difficult to obtain by using these techniques. It is due to different melting temperatures of constituting elements. Moreover, poor absorption-desorption kinetics in addition to a complicated activation procedure have limited the practical use of these materials [1].

Substantial improvement of the hydriding–dehydriding properties of metal hydrides could be achieved by the formation of nanocrystalline structure by non-equilibrium processing techniques such as mechanical alloying (MA) [1]. Moreover, in MA there is no limitation on the number and nature of the raw elements used.

* Fax: +48 61 665 3576.
E-mail address: mateusz.balcerzak@put.poznan.pl.

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In the past, TiV alloy was MA in hydrogen and nitrogen atmosphere to form amorphous materials [7]. In recent years, just a few papers were published on Ti-V based materials partially produced by MA method for hydrogen storage applications [8,9]. Ball-milling was also used as a method for surface modification of Ti-V-Cr and Ti-V-Cr-Mn alloys [6,10]. Published results are very promising. However, still little information can be found on Ti-V hydrogen storage alloys produced by MA. Moreover, there is no paper on preparation nanocrystalline Ti-V alloys directly from MA process.

For this reason, in this work, structural and hydrogen storage properties of MA Ti-V alloys were studied.

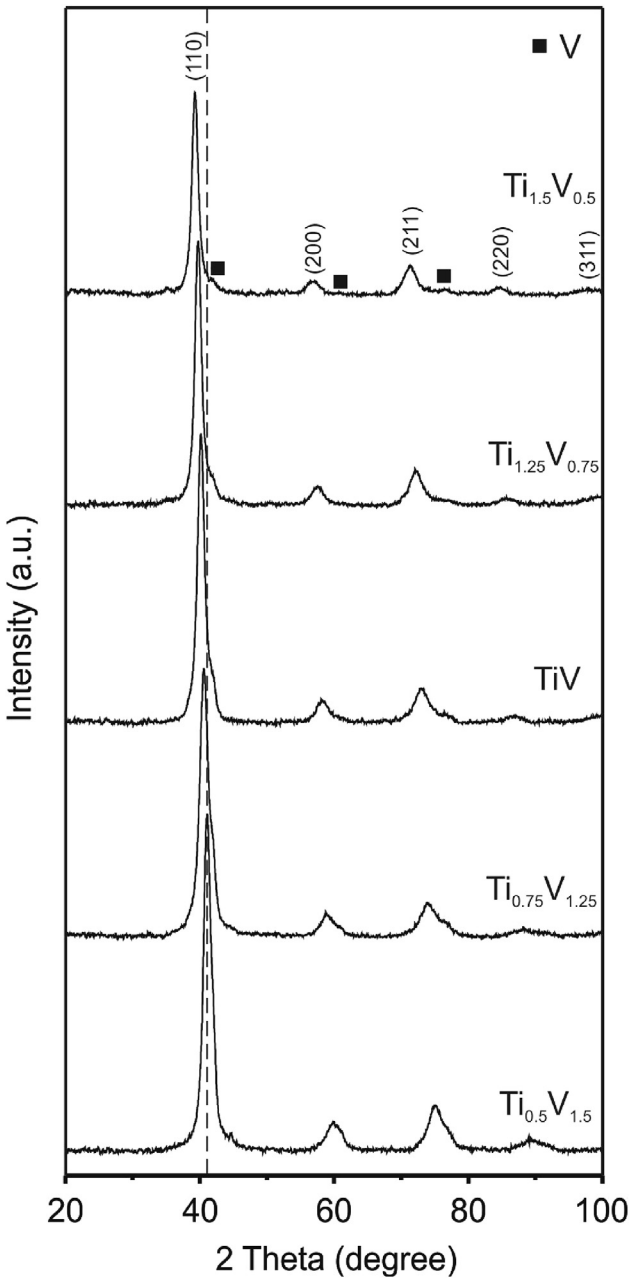

Fig. 1 – XRD spectra of Ti-V alloys after 14 h of mechanical alloying.

Experimental details

Chemicals

Used commercial powders: Titanium powder (Alfa Aesar, −325 mesh, 99.5%), Vanadium powder (Alfa Aesar, −325 mesh, 99.5%).

Preparation of experimental materials

$Ti_{2-x}V_x$ alloys powders (x = 0.5, 0.75, 1, 1.25, 1.5) were prepared by MA process. A shaker type ball mill (SPEX 8000 Mixer Mill) was used. A composition of a starting materials mixture was corresponding to a stoichiometry of an "ideal" reaction. The ball to powder weight ratio was around 6.5:1. Stainless steel balls were used. MA process lasted 14 h and was carried out in argon atmosphere. MA was stopped every 1 h to dissipate a heat and to reduce an excessive rise in temperature. These breaks in MA process were done also to crush bulk materials in vials as well as to scrape powder adhered to balls and walls.

Table 1 – Structural parameters obtained from the Rietveld refinement of Ti-V X-ray diffraction data.

Sample	Phase	Fraction (%)	a (Å)	V (Å^3)	R_{wp}	Final reduced chi^2
$Ti_{1.5}V_{0.5}$	Ti-V	92.6	3.239	33.98	5.7	1.8
	V	7.4				
$Ti_{1.25}V_{0.75}$	Ti-V	90.8	3.207	32.98	5.2	2.1
	V	9.2				
TiV	Ti-V	97.6	3.156	31.43	5.0	2.2
	V	2.4				
$Ti_{0.75}V_{1.25}$	Ti-V	90.7	3.135	30,81	7.9	2.0
	V	9.3				
$Ti_{0.5}V_{1.5}$	Ti-V	93.8	3.101	29.82	5.8	1.3
	V	6.2				

R_{wp}-final weighted average Bragg R-factor.

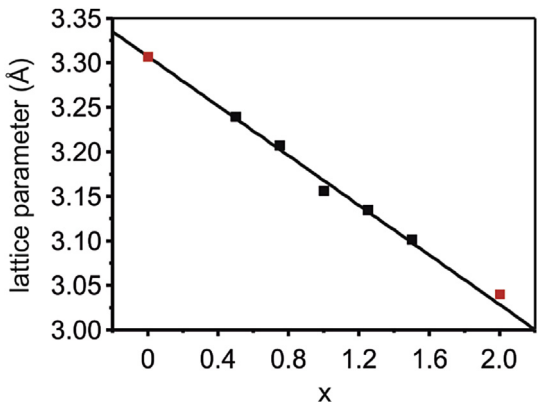

Fig. 2 – Lattice parameter as a function of x in $Ti_{2-x}V_x$. Ti and V lattice parameters are marked by red squares (values from literature) [17,18]. The x values are calculated from EDS data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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