Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Effect of processing parameter on hydrogen storage characteristics of as quenched $Ti_{45}Zr_{38}Ni_{17}$ quasicrystalline alloys

Rohit R. Shahi [a], T.P. Yadav [a], M.A. Shaz [a], O.N. Srivastava [a,*], S. van Smaalen [b]

[a] Hydrogen Energy Centre and Unit of Nano Science and Technology, Department of Physics, Banaras Hindu University, Varanasi, Uttar Pradesh-221005, India

[b] Laboratory of crystallography, University Of Bayreuth, Bayreuth 95440, Germany

ARTICLE INFO

Article history:
Received 22 July 2010
Received in revised form
9 October 2010
Accepted 11 October 2010
Available online 20 November 2010

Keywords:
Hydrogen storage materials
Rapid solidification
Nano-quasicrystalline

ABSTRACT

The present study deals with the microstructural changes with respect to the processing parameter (quenching rate) and their correlation with hydrogen storage characteristics of $Ti_{45}Zr_{38}Ni_{17}$ quasicrystalline alloys. The ribbons of the alloy have been synthesized at different quenching rates obtained through different wheel speeds (35, 40, 45 and 50 m/s) and investigated for their hydrogen storage characteristics. The lower cooling rate obtained through low wheel speed (35 m/s) produces, i-phase grains whose size ranges from 300-350 nm, whereas higher cooling rates obtained through high wheel speed (45 and 50 m/s) promote the formation of grains with size ranges from 100-150 nm in $Ti_{45}Zr_{38}Ni_{17}$ ribbons. It has been found that the ribbons synthesized at 35 m/s absorbed ~2.0 wt%, whereas ribbons synthesized at 50 m/s absorbed ~2.84 wt. % of hydrogen. Thus the hydrogen storage capacity of ribbon increases for the ribbons produced at higher quenching rate. One of the salient features of the present study is that the improvement of hydrogen storage capacity obtained through higher quenching rates (~45 to 50 m/s wheel speed) leading to the formation of lower grain size.

1. Introduction

Quasicrystals have been found to exhibit certain important characteristics like, high hardness, low surface energy, high oxidation resistance and low thermal conductivity. These properties make these materials attractive for technological applications [1]. After the discovery of thermodynamically stable icosahedral quasicrystalline (IQC) phase in Ti-based alloys by Kelton et al. [2,3], these materials have received attention as hydrogen storage materials, specifically for fuel cell and battery applications. Quasicrytalline alloys have lately been shown to reversibly store a large amount of hydrogen this may occur due to higher density of interstitial voids available in QC alloys. The storage capacity can reach up to 3 wt. % of hydrogen [4]. This may be better than that of the crystalline La-based, V-based and FeTi hydrogen storage alloys [5–7]. In Ti/Zr based IQC alloys the presence of Ti and Zr (which has higher affinities for hydrogen and has the tetrahedral coordinated sites) makes them a promising material for the hydrogen storage applications. Particular attention has been recently focused on Ti-Zr-Ni alloys [2,8–14]. In the case of Ti-Zr-Ni IQC alloy, the catalytic activity of Ni enhances the dissociation of the hydrogen molecules into hydrogen atoms at the surface of IQC alloy. The Ti/Zr based IQC alloys can be

* *Corresponding author*. Tel.: +91 5422368468; fax: +91 5422369889.
E-mail address: hepons@yahoo.com (O.N. Srivastava).

0360-3199/$ – see front matter © 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijhydene.2010.10.031

synthesized by rapid quenching [15–17], mechanical alloying followed by annealing [4,18,19] and solid state transformation [2]. The hydrogenation studies on these alloys reveal that the maximum hydrogen uptake capacity is ~2.2 wt.% (which corresponds to~1.5 H/M) for the $Ti_{45}Zr_{38}Ni_{17}$ IQC alloys [4,8–11].

The structure and phase formation of Ti-Zr-Ni alloy system is strongly affected by processing parameters [20,21] and chemical compositions [22]. Several studies [14,23,24] reveal that the compositional changes may influence the hydrogen storage capacity of Ti/Zr alloys. The present investigation is focused on the effect of quenching rate on phase formation and the hydrogen storage characteristics of synthesized $Ti_{45}Zr_{38}Ni_{17}$ ribbons. It has been found that the ribbons synthesized at 35 m/s produces i-phase grains with size ranges from 300-350 nm whereas ribbons synthesized at high quenching rate (45 m/s) promotes the formation of grains with size ranges from 150-100 nm. Further increase in the wheel speed (50 m/s) promotes the formation of finer grain sizes (100-30 nm) in $Ti_{45}Zr_{38}Ni_{17}$ ribbons. The present report deals with the synthesis, phase formation, change in the microstructure with respect to change in quenching rate and their correlation with hydrogen storage characteristics of quasicrystalline $Ti_{45}Zr_{38}Ni_{17}$ ribbons. It has been found that the hydrogen storage characteristic is enhanced by increasing quenching rate from 35 m/s to 50 m/s.

2. Experimental details

2.1. *Material synthesis*

An alloy ingot of $Ti_{45}Zr_{38}Ni_{17}$ was prepared by RF-induction melting of a corresponding stoichiometric mixture of pure Ti (99.9%), Zr (99.9%) and Ni (99.9%) metal in a pure graphite crucible under argon gas atmosphere. About 20 gm as cast ingot was taken out and melted three times to achieve chemical homogeneity. The alloy ingot was subjected to rapid solidification by employing melt spinning using a copper wheel (diameter ~14 cm) at various tangential velocities: 35, 40, 45 and 50 m/s. The ribbons so formed have the thickness of ~40 to 50 μm and lengths of ~25 to 40 cm.

2.2. *Characterizations and hydrogen storage behavior*

The structural and microstructural features of the quenched ribbons have been characterized by using powder X-ray diffraction (XRD) (X'Pert PRO manufactured by PAN alytical) employing Cu-Kα radiation and transmission electron microscopy (TEM) (FEI, TECNAI (20 G^2)). To investigate the effect of strain and grain refinement, the slow scan XRD (0.008 step size and 50 s/step) was done with monochromatic Cu-$K\alpha_1$ ($\lambda = 1.5405980$ Å) radiation. The peak fitting was performed with the Pseudo-Voigt profile function using the program Jana 2006 [25]. The TEM samples were prepared by thinning the ribbons through an electro-polishing unit (Tenupol-5) using an electrolyte prepared by 1:4 ratios of $HClO_4$ and methanol at −30 °C. The surface morphology and composition of the synthesized as well as hydrogenated ribbons were characterized by employing scanning electron microscopy (SEM) (Quanta-200) equipped with X-ray energy dispersive spectrometer (EDAX) secondary electrons were used for image formation. The hydrogen sorption characteristics, each having 200 mg of the synthesized ribbon were examined by using the computerized Pressure-Concentration-Temperature (PCT) apparatus. The details of the apparatus have already been published elsewhere [26].

3. Results and discussion

3.1. *Effect of the quenching rate on the structure and microstructure of quenched ribbons*

We first investigated the effect of solidification rate on the phase formation and the microstructure of the $Ti_{45}Zr_{38}Ni_{17}$ as quenched ribbons and their correlation with hydrogen storage characteristics. Fig. 1 represents XRD patterns of $Ti_{45}Zr_{38}Ni_{17}$ ribbon synthesized at different wheel speeds. The XRD pattern of the alloy melt spun at 35 m/s (Fig. 1 (a)) reveals the presence of icosahedral quasicrystalline phase (IQC). Fig. 1 (b) represents typical XRD pattern of the ribbon synthesized at copper wheel speed of 40 m/s, revealing the presence of IQC phase. To investigate the structural modification regarding quenching rate, we further increased the wheel speed from 40 m/s to 45 and 50 m/s Fig. 1 (c) shows the XRD pattern of as quenched ribbon synthesized at 45 m/s revealing the presence of i-phase with greater peak broadening as compared to ribbons synthesized at 40 m/s. The XRD pattern of synthesized ribbons at 50 m/s is shown in Fig. 1(d). The peak broadening occurs due to the formation of finer grains and strain developed at higher wheel speeds.

Fig. 2 represents the TEM micrograph of ribbon synthesized at 35 m/s. The SAED pattern from the microstructure (Fig. 2 (a)) shows the characteristic fivefold icosahedral symmetry. Fig. 2 (c)and (d) represent the SAED patterns obtained through different tilt of the region (shown in Fig. 2 (a)) shows the characteristic threefold and twofold icosahedral symmetries respectively. It has been found that the grain size of the

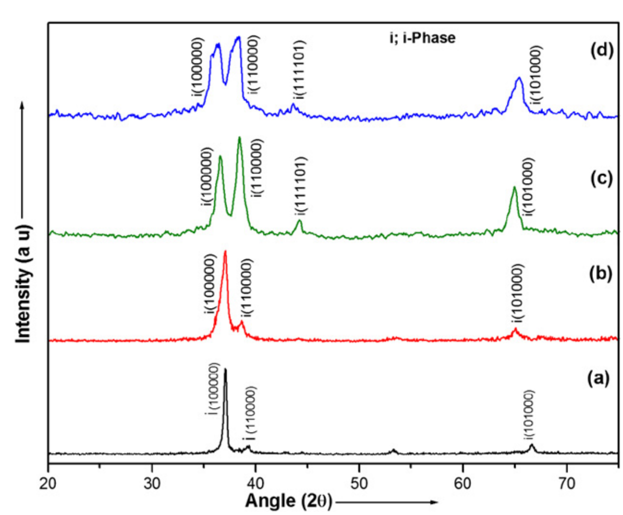

Fig. 1 – XRD patterns of as synthesized ribbon at wheel speed of (a) 35 m/s, (b) 40 m/s, (c) 45 m/s and (d) 50 m/s.