INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 37 (2012) 3283–3291

Available online at www.sciencedirect.com

SciVerse ScienceDirect

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

Hydrogen absorption kinetics of V4Cr4Ti alloy prepared by aluminothermy

Sanjay Kumar, Manju Taxak, Nagaiyar Krishnamurthy*

Fusion Reactor Materials Section, Bhabha Atomic Research Centre, Mumbai 400 085, India

ARTICLE INFO

Article history:
Received 18 September 2011
Received in revised form
4 November 2011
Accepted 7 November 2011
Available online 9 December 2011

Keywords:
Aluminothermy
H absorption
Absorption kinetics

ABSTRACT

The hydrogen absorption kinetics of V4Cr4Ti alloy, synthesized by aluminothermy process has been investigated in the temperature range of 373–773 K. The obtained hydrogen absorption kinetic curves were linearly fitted using a series of mechanism function to reveal the kinetics parameter and reaction mechanism. Nucleation and growth, one dimensional diffusion and three-dimensional diffusion processes are the intrinsic rate limiting steps of hydrogen absorption at 373 K. It was found that nucleation and growth processes disappear between 413 K–473 K. However at higher temperatures (>473 K), nucleation and growth as well as one dimensional diffusion process disappear. In the temperature ranges investigated (473 K–773 K), three-dimensional diffusion process was the intrinsic rate limiting step. The apparent activation energy was calculated using Arrhenius equation and found to be 6.1 kJ/mol. This value appears to be relatively higher which can be attributed to the presence of aluminium, which has blocked the absorption sites and increased the activation energy.

1. Introduction

In the search of alternative fuels, hydrogen looks promising, renewable and eco-friendly for transportation and domestic applications [1]. The key issues related to the application of hydrogen as portable fuel and to develop hydrogen based economy are safe and portable hydrogen storage system. The storage of hydrogen in the form of metal hydride looks promising and safe source of energy because it absorbs high volumetric hydrogen with good absorption–desorption kinetics and cyclic properties [2–13]. Hydrogen absorption capacity of metallic vanadium is excellent [14] and hence vanadium based alloys particularly with titanium and chromium is being actively developed as hydrogen storage media. The presence of titanium and chromium could modify the stability of β phase and as a consequence increases the usable volumetric hydrogen [15–17]. Moreover, the alloys showed very good combination of absorption–desorption kinetics and cyclic properties [18,19]. Eventually these alloys showed high volumetric hydrogen absorption capacity compared to the existing hydrogen storage materials [20–24]. Furthermore alloy of vanadium, V4Cr4Ti, offers a potential for high performance, environmentally attractive blanket module system in thermonuclear (fusion) reactor [25,26]. Thermonuclear reactor's concept is based on magnetic confinement of deuterium–tritium fuel cycle with self cooled $Pb_{83}Li_{17}$ eutectic as a coolant and tritium breeder. Since tritium production in $Pb_{83}Li_{17}$ coolant is essential to sustain the fuel cycle, consequently, hydrogen transmutations will occur and extensively interact with the structural materials. Hydrogen is mobile in most of the materials at elevated temperature including vanadium based alloys, which inherently show high hydrogen

* *Corresponding author*. Tel.: +91 22 2559 0489; fax: +91 22 2559 5151.
E-mail address: sanjay.barc@gmail.com (S. Kumar).

doi:10.1016/j.ijhydene.2011.11.057

solubility [27]. Besides good thermo-mechanical and radiation resistance properties, the candidature of fusion reactor structural materials will be qualified by considering its hydrogen embrittlement and hydrogen absorption–desorption kinetics behaviors.

In this context, kinetics data of hydrogen absorption in V–Ti–Cr alloy will be useful to design and develop a range of V–Ti–Cr alloys for the specific applications like, materials for hydrogen storage media where not only good volumetric absorption of hydrogen but good absorption–desorption kinetics is an essential parameter, or, as a fusion reactor blanket module material, where materials immune to hydrogen embrittlement, low hydrogen solubility and slow absorption kinetics are desired properties.

The available literature data revealed that the kinetics of gas–solid reaction depends upon various parameters [28–30]. One of the essential parameter is the materials synthesis routes [31,32]. Vacuum arc melting of the constituent alloying components in high pure metallic form is the most conventional route for the synthesis of alloys and intermetallics including V–Ti–Cr alloy [33,34]. Key issues in this synthesis process are the production cost, because, it uses expensive high pure metals, and inhomogeneity due to the insufficient mixing during arc melting. Another synthesis process of V–Ti–Cr alloy reported earlier was from oxide mixture in $CaCl_2$, similar to FFC Cambridge process [35]. This synthesis process uses chlorides at elevated temperature and hence considered as less eco-friendly and costly. Vanadium and most of its alloys are generally produced via aluminothermy reduction of appropriate mixture of oxides [36]. The process is highly cost-effective. However, the product retains several atom percent of aluminum even after purification by evaporating aluminum using electron beam melting [37,38]. The kinetics study on V–Ti–Cr alloys prepared by aluminothermy process will be useful to implement aluminothermy process to produce V–Ti–Cr alloys for various applications where hydrogen solubility and kinetics are the key concerns. This would lower the cost of producing such alloys and promote their practical uses. In the present investigation, the hydrogen absorption kinetics in V4Cr4Ti alloy, prepared by aluminothermy process, were studied at constant pressure employing variable weight technique. The kinetics data (activation energy) is not available for this alloy as per the author's knowledge, but it is appears to be high [39,40], however, this value is very much comparable with respect to the other intermetallics hydrogen storage system [4,41]. Relatively higher kinetic energy could be attributed to the presence of aluminium. In the whole text V4Cr4Ti is designated as alloy.

2. Experimental

2.1. *Sample preparation and characterization*

The alloy was prepared by aluminothermy process. As reported by Kumar et al. [42] loading pattern of Ti in the thermite process was highly unpredictable and hence only close to desired composition could be achieved by this process. In present investigation, alloy was synthesized by aluminothermy process and purified by electron beam (EB) melting. EB melted alloy was used in the present investigation without addition or dilution of the component. The purpose of the work was to present the absorption kinetics behaviour of the alloy synthesized by thermite process without any modification. The resulting alloy button was consolidated by vacuum arc melting followed by hot rolling into 0.3 mm thick strip. The hot rolled strip was cut into small pieces of an average weight of 400–500 mg and annealed at 1473 K temperature under high vacuum condition ($\sim 10^{-6}$ torr pressure) to release the residual stress developed during the hot rolling. The detailed chemical composition of the specimen is presented in Table 1. The structure and composition of specimen was analyzed by XRD (M/s Philips PW 1830 difractometer) and SEM-EDAX (AIS-2100 CERON), and results are presented in Fig. 1 and Fig. 2, respectively. From the figures it is clear that alloy is a single phase solid solution of vanadium with a bcc crystal structure. A slight positive shift of 2θ value compared to pure vanadium was observed that could be attributed to the presence of chromium. SEM analysis revealed the homogeneity in the sample. Before hydrogenation, the alloy samples were metallographically polished up to three delta finish using high grade emery papers and diamond paste. The mirror finished specimens were preserved in argon gas flushed vacuum desiccators to avoid any oxide layer formation. These samples were used for all the hydrogen absorption kinetics experiments using 99.999% pure hydrogen gas.

2.2. *Method*

A schematic diagram of the apparatus used in the present investigation is shown in the Fig. 3. The apparatus consists of a reaction chamber made of quartz, vacuum system and sample holder connected to the modified thermobalance through quartz hanger. Reaction chamber could be placed inside the control resistance heating furnace directly as and when required. Along with furnace temperature, sample temperature was separately measured by placing a K-type thermocouple adjacent to the sample holder. Electronic pressure controller [EPC] was used to introduce hydrogen gas in the reaction chamber and maintained the constant pressure. A display unit was used to read the instantaneous weight gain (TG) as well as instantaneous rate of weight gain (DTG). Two types of hydrogen absorption experiments were conducted in the present investigation: continuous heating and isothermal heating. The continuous heating experiments were performed to determine the starting temperature of hydrogen absorption, while the isothermal experiments were carried out to determine the kinetics parameters of hydrogen absorption. In the continuous heating experiment, the sample was kept in the sample holder in the reaction chamber followed by evacuation to $\sim 10^{-6}$ torr. The vacuum system was disconnected and hydrogen gas was slowly introduced in the

Table 1 – The chemical composition of V4Cr4Ti alloys.

V	Ti	Cr	O	N	Al	Fe
Balance	3.979	4.010	0.013	0.101	0.859	0.052