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Synthesis, characterization and hydrogen storage behaviour of AB_2 ($ZrFe_2$, $Zr(Fe_{0.75}V_{0.25})_2$, $Zr(Fe_{0.5}V_{0.5})_2$) type materials

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ABSTRACT

In this paper, we describe and discuss the synthesis, structural-microstructural and hydrogen storage behaviour of three AB_2 type storage materials namely (a) $ZrFe_2$, (b) $Zr(Fe_{0.75}V_{0.25})_2$ and (c) $Zr(Fe_{0.5}V_{0.5})_2$. These alloys were synthesised by radio frequency induction melting in argon atmosphere. X-ray diffraction and transmission electron microscope have been employed for structural and microstructural characterizations. The XRD study reveals that the lattice constants and the unit cell volume of $ZrFe_2$, $Zr(Fe_{0.75}V_{0.25})_2$, $Zr(Fe_{0.5}V_{0.5})_2$ alloys, which has C14 type hexagonal Laves phase. The Surface morphology and elemental composition of these alloys were investigated by scanning electron microscope and energy dispersive X-ray analysis. The pressure composition isotherms of these alloys were investigated at room temperature and pressure ranges of 0–100 atm respectively, measured through a fully computerized PCI apparatus. As we increase the concentration of V (substituted for Fe), the total hydrogen storage capacities increased up to 1.45 wt%. This capacity is achieved in $Zr(Fe_{0.5}V_{0.5})_2$ alloy, while the reversible hydrogen storage capacity decreases due to the formation of a stable hydride phase. It has been found that the lattice constants increase with higher vanadium concentration. This is indicating that the majority of vanadium atoms reside in the B-site. The broader X-ray diffraction peaks observed in $Zr(Fe_{0.5}V_{0.5})_2$ alloy indicates a higher degree of disorder for alloys with the higher V-content. The yet another interesting feature observed in our present study is that the plateau pressure remains well below 1 atm for all the compositions.

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1. Introduction

The emission of green house gases from industries and automobile exhaust makes serious impact on the climate change [1]. Unlike petroleum fuels, hydrogen is clean (pollution-free), renewable and environmental/climate friendly. Hydrogen is promising alternative energy carrier and it is the only fuel which is indigenous, pollution-free and completely renewable. Development of sustainable energy and a policy such as

hydrogen economy is the key for fulfilling the growing energy requirements without compromising the environmental cleanliness. Hydrogen economy cuts across hydrogen production, storage and distribution/application etc; among these, storage is the most critical area at present [2]. It is known that hydrogen storage in metal hydrides is one of the attractive and softer modes for storing gaseous hydrogen [3]. One attractive class of metal hydride system, the Zr-based AB_2 system usually shows higher hydrogen storage capacity,

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rapid kinetics and relatively longer electrochemical charge–discharge cycle life than the well known AB₅ type storage materials [4]. The excellent properties of AB₂ type alloys make them promising hydrogen storage materials and these characteristics make Zr-based AB₂ type alloys potential material for hydrogen storage applications [5].

In addition to their technological potential, such materials raise questions of fundamental interest concerning the effect of hydrogen absorption on their structural, electrical, and magnetic properties [6]. The stoichiometric Zr-based AB₂ compound can be stabilized either as C14 or C15 type phase [7]. Many geometrical, theoretical, experimental investigations have been made in order to explain the storage mechanism in Zr-based AB₂ type alloys [8–12]. The effect of the Co substitution has been reported the suitability of the intermetallic compound of zirconium for hydrogen storage and recovery applications for hydrogen isotopes, including tritium [6]. The study on partial replacement of Fe by Al has also been performed regarding thermodynamical and structural aspects [9]. Shaltiel et al. has reported that the formation of the hydrides, hydrogen absorption and desorption properties of AB₂ laves phase of pseudobinary compounds Zr(Co_xM_{1-x})₂ and Zr(Fe_xM_{1-x})₂ (M = V, Cr, Mn) [13].

The substitution of Ni at Fe site in ZrFe_{2-x}Ni_x (x = 0.2, 0.4, 0.6, 0.8) has been investigated and in this case the enthalpy of dissolved hydrogen in ZrFe_{2-x}Ni_xH (x = 0.2, 0.4, 0.6, 0.8) decreases with increasing the content of Ni [14]. Jain et al. has reported the thermodynamics and structural aspects of hydrogen absorption in Zr_{1-x}Cr_xFe₂ alloys [15]. Recently, two plateaus have been observed in ZrFe_{2-x}Ni_x (x = 0.2, 0.4, 0.6, 0.8) alloys on the desorption isotherms of the samples with x = 0.2 and 0.4 [16]. The stability and phase composition has been observed from X-ray diffraction and Mössbauer spectroscopy studies in Zr–Fe–V alloy after hydriding and vacuum dehydriding cycles recently [17]. The increase in Fe content in ZrFe_x alloys (1.9 ≤ x ≤ 2.5) leads to increase in hydrogen absorption and desorption pressures of hydrides and reduction of the β – α phase transition Enthalpy [18].

These Zr-based AB₂ type materials such as ZrFe₂ have been chosen since they usually exhibit low plateau pressure ~ 1 atm. This is greatly advantageous when low pressure hydrogen is present, for example extraction of hydrogen (through absorption) from a mixture of gases. Most of the work has concentrated on the alloy preparation and hydrogen absorption behaviour determination [17]. However, few attempts have been made on the characterization by electron microscope to understand the microstructure of AB₂ type alloy [19]. In the present work, we are trying to reduce the stability as well as plateau pressure even well below 1 atm of ZrFe₂ based alloys by substituting Fe by V and also investigating the structural and hydrogenation properties of ZrFe₂, Zr(Fe_{0.75}V_{0.25})₂, Zr(Fe_{0.5}V_{0.5})₂ alloys in detail.

2. Experimental details

The ZrFe₂, Zr(Fe_{0.75}V_{0.25})₂, Zr(Fe_{0.5}V_{0.5})₂ alloys have been synthesized by melting stoichiometric mixture of Zr (99.6%), Fe (99.9%) and V (99.5%) in radio frequency induction furnace (18 kW). The individual elements were at first mixed in correct

stoichiometric proportions and pressed into a cylindrical pellet of 1.5 cm diameter, 1 cm thickness by applying a pressure of ~ 3 × 10⁴ N/m². The pellet (10 g by weight) was then placed in a silica tube surrounded by an outer Pyrex glass jacket. Under continuous flow of argon gas into the silica tube, the pellet was melted using radio frequency induction furnace (18 kW). During melting process, water is circulated in the outer jacket around the silica tube to reduce the contamination of the alloy. For each prepared composition, the melting atmosphere was further purified by previously melting Ti buttons taking advantage of its getter properties with respect to O₂. The alloys were melted repeatedly two to three times to achieve homogeneity. The gross structural characterization to identify the crystal structure of the alloy was performed by employing X-ray diffraction technique. The XRD measurements were performed at room temperature using a Powder diffractometer between 10° and 80° in 2θ and a step of 0.05. The ingots were crushed, mechanically grind and the powder sample was subjected to X-ray diffraction studies employing a Philips X-ray powder diffractometer PW-1710 equipped with a graphite monochromator and CuKα radiation, α = 1.5406° Å. XRD patterns of the as-cast and dehydrogenated samples were taken. The surface microstructural characteristics of the as-cast and dehydrogenated samples were monitored by employing scanning electron microscope (SEM) in secondary electron imaging mode (Philips XL-20 series SEM) Transmission electron microscopy (TEM) was carried out in a Philips CM-12 and Tecnai 20 G² electron microscope at 200 kV employing imaging and diffraction modes. A chemical analysis, using an EDX attached to a Tecnai 20 G² exhibited that oxidation and contamination in the alloy are within acceptable limits. The grain size and the lattice strain of the sample can be calculated from the integral width of the physical broadening profile. Cauchy and Gaussian components can be obtained from the ratio of full width at half maximum intensity (2ω) and integral breadth (β) [20]. In a single line analysis the apparent crystallite size 'D' and strain 'e' can be related to Cauchy (β_c) and Gaussian (β_G) widths of the diffraction peak at the Bragg angle θ;

$$D = k\lambda/\beta_c \cos \theta \quad (1)$$

and

$$e = \beta_G/4\tan \theta \quad (2)$$

The constituent Cauchy and Gaussian components can be given as

$$\beta_c = (a_0 + a_1\psi + a_2\psi^2)\beta$$

$$\beta_G = (b_0 + b_{1/2}(\psi - 2/\pi)^{1/2} + b_1\psi + b_2\psi^2)\beta$$

Where a₀, a₁ and a₂ are Cauchy constants, b₀, b_{1/2}, b₁ and b₂ are Gaussian constants and ψ = 2ω/β where β is the integral breadth obtained from XRD peak. The values of Cauchy and Gaussian constant have been taken from the table of Th. H. de Keijser et al. [21]: a₀ = 2.0207, a₁ = 0.4803, a₂ = 1.7756; b₀ = 0.6420, b_{1/2} = 1.4187, b₁ = 2.2043, b₂ = 1.8706. From these, we have calculated the crystallite size D and the lattice strain 'e' for the dehydrogenated alloys.

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