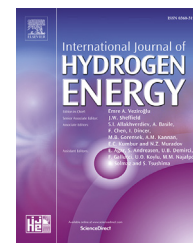


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Effects of microstructure and phase composition on the electrochemical activation properties of $Ti_{1.8}(VFe)CrNi_{0.2} + x\text{wt.}\%LaNi_5$ ($x=0, 2.5, 4, 5, 6, 10, 20$) metal hydride alloys

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ABSTRACT

Ti-V-based alloys possess the tremendous hydrogen storage capacity, but low electrochemical activity. In order to improve the electrochemical properties of this kind of alloys, a commercial hydrogen storage alloy, LaNi₅, with higher electrochemical activity were introduced and re-melted with Ti_{1.8}(VFe)CrNi_{0.2} as master alloy. The new metal hydride composite alloys, Ti_{1.8}(VFe)CrNi_{0.2} + x wt.% LaNi₅ ($x = 0, 2.5, 4, 5, 6, 10, 20$), were prepared and their solidification microstructure and electrochemical characteristics were investigated in this work. It was found that the structural features of the composite alloys varied regularly with increase of amount of LaNi₅. Meanwhile, the microstrain and dislocation, respectively, formed in the major phase and minor phase of the composites. The changes of structural features, especially, the microstrain and dislocation, provided more active sites for hydrogen adsorption, and the symbiosis relation between the phases from the master and the new phases from LaNi₅ brought about more crystal interfaces as diffusion path for hydrogen atoms. As a result, hydrogen atoms can be diffused easily from the major phase to minor phase. The results indicated that the composite Ti_{1.8}(VFe)CrNi_{0.2} + 5 wt.% LaNi₅ exhibits the best maximum discharge capacity of 360 mAh/g after 9 cycles. It is found that there are parallel zone axes and similar Kikuchi poles in major phases, and TiNi minor phase of the composite with 5 wt.%LaNi₅. It is evident that there exists a symbiosis relation between the major phases and TiNi minor phase.

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Introduction

Single-phase Ti-V-based hydrogen storage alloys with BCC structure were paid more attention due to their tremendous hydrogen storage capacity [1–5]. However, there exist still

many urgent problems to be solved for this kind of alloys, such as high price due to metal vanadium, high rate of degradation, and low electro-catalytic activity, so that they cannot go into commercial service successfully. As so, the replacement of V element in Ti-V-based hydrogen storage alloys by introducing Fe was investigated in order to cut the cost [6] and it achieved

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the better effect. But the more important problem for Ti-V-based alloys as Ni/MH cathode materials is low electrocatalytic activity. Many researchers have carried out the work on this subject. For example, several investigations have been conducted to improve the electrochemical activation properties of Ti-V-based alloys electrode, especially, on addition of other elements, such as rare earths [7–9], Fe [10], Ni [11], etc., and/or rapid solidification of alloy melt by which the structure of dendrite crystal, TiNi phase and Ti₂Ni phase formed in the alloys [12]. Nevertheless, these results of the experiment were still unsatisfactory.

Recently, some reports on the improvement of activation properties of Ti-V-based alloys have brought some interesting responses from researches in this field all over the world. LaNi₅ has the advantages of easy activation, long cycle life and low cost. In order to obtain excellent comprehensive performance, some novel composites of Ti-V-based alloys with a different amount of alloy LaNi₅ are manufactured and investigated [13]. For instance, the composite alloy of Ti_{0.9}Zr_{0.2}Mn_{1.5}Cr_{0.3}V_{0.3} and 5 wt% or 10 wt% La_{0.7}Mg_{0.25}Zr_{0.05}Ni_{2.975}Co_{0.525} were synthesized by ball-milling. The results showed that the activation and maximum discharge capacity were remarkably improved due to the presence of LaNi₅ phase [14,15]. But unfortunately, the alloys were oxidized temporarily at high temperatures caused by high speed friction during the ball-milling process, and poor interface bonding formed at the interfaces between the different phases, at which there were large scale oxide film covered and/or amount of oxide inclusion.

In this case, a method of preparation of composite by re-melting comes into researchers' sight and some useful and beneficial results have been obtained. The results indicate that the activate characteristics and maximum discharge capacity of Ti-V-based alloys have been improved by adding LaNi₅ with the melting method [13,16,17,25] due to the synergistic effect between major phase and minor phase, which are joined closely, provided many active sites, as the major phase in the dendrite. Despite all these, it's probably worth pointing out, however, that the mechanism of influence of dendrite crystal on the activation of composites is not exactly known.

The hydrogen diffusion is an important controlling procedure in an electrochemical reaction of hydrogen storage alloys. It has been proved that hydrogen diffusion would be occurred with the interface effect and strain [18,26]. It is also considered that interface effect, i.e., coherent boundary, exists between catalytic phases and storage phases [17,19]. In addition, the activate characteristics of alloy change with supersaturated solid solution of additive other atoms in the alloys, or the plastic deformation of the alloys based on the Williamson-Hall method [13,20]. It must be particularly pointed out that hydrogen atoms can be trapped by the dislocations in the grain [21–23]. Therefore, the activate characteristics of alloys are strongly depended on their phase compositions, as well as microstructure feature, such as grain size, strain, dislocations, and so on.

In the previous work of our group, Mg₂Ni/Mm_{0.3}Ml_{0.7}Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3} composite hydrogen storage alloys prepared by two-step re-melting and their activation characteristics and microstructure were investigated [24]. It

was found that composite hydrogen storage alloys prepared by re-melting possess more perfect electrochemical characteristics than the matrix and the other one as additive. In view of the above mentioned facts, in the present work, the composite alloys of Ti_{1.8}(VFe)CrNi_{0.2} as matrix alloy, with x wt.% LaNi₅ (x = 0, 2.5, 4, 5, 6, 10, 20) as additive were prepared by re-melting, and their activation characteristic and microstructure were investigated. And furthermore, it is also expected that relationship between the electrochemical activities of hydrogen storage alloys with their microstructure feature can be revealed.

Experimental materials and procedures

As-cast LaNi₅ and Ti_{1.8}(VFe)CrNi_{0.2}, were prepared separately, and then they were mixed in the designed proportion to be re-melted for fabrication of the composite alloys, in a high frequency induction furnace with a water-cooled cooper crucible under an argon atmosphere. The microstructure of these alloys was observed using a metallographic microscope with a beam wave of full spectrum within a wavelength range of 312 nm–1050 nm (Zeiss, Axio Imager A1M) and the grain size D_{size} was calculated by a line intercept method. The microstructure feature of the alloys and their compositions as well as element distribution of the composite containing 5 wt% LaNi₅ were observed and analyzed by using field emission scanning electron microscopy–energy dispersive spectroscopy (FESEM–EDS, Sigma500), respectively. The solid solubility of each kind of atoms in the alloys and the phase structure of composites were analyzed quantitatively by electron backscattered diffraction (EBSD), at 20 kV of acceleration voltage, 70° of gradient of sample, 92.96% of hit ratio, and 22.27 Hz of picking rate.

The analysis of phase compositions of the composite or alloys (crushed into powders with a size less than 50 μm), was conducted with a X-ray diffractometer (D/MAX-YB, Rigaku, Japan) using Cu K α radiation with a wavelength 0.1541 nm, in the 2-theta/° range from 30 to 85°, and at a 5°/min of scanning rate at room temperature. Full width of XRD peak at half maximum (FWHM) β was obtained from XRD patterns.

Electrochemical activities and discharge capacity tests were carried out in a standard three electrode cell system consisting of the metal hydride electrode, Ni(OH)₂/NiOOH electrode and a reference electrode (Hg/HgO), in 6 mol/L KOH aqueous solution as electrolyte, with a LAND BT1-10 battery testing instrument under computer control. The composite or alloys powders were prepared by mechanical pulverization to a particle size that less than 48 μm, mixed with nickel powder in a mass ratio of 1:4, and pressed under a pressure of 15 MPa for 20 min to form pellets in diameter 10 mm and about 1 mm in thickness. Each test cell comprised of a working electrode (MH electrode), a sintered Ni(OH)₂/NiOOH-counter electrode and a reference electrode (Hg/HgO electrode). A non-woven nylon-cloth separator was inserted between two counter electrodes. The metal hydride electrodes were fully charged (the over-charged ratio is approximately 40%) at a current density of 300 mA/g, and then discharged to –0.6 V versus Hg/HgO at 60 mA/g during the charge/discharge cycles at 323 K.

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