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Structure and hydrogenation performances of as-cast $\text{Ti}_{1.1-x}\text{RE}_x\text{Fe}_{0.8}\text{Mn}_{0.2}$ (RE = Pr, Sm and Nd; $x = 0, 0.01$) alloys

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ABSTRACT

The AB-type $\text{Ti}_{1.1-x}\text{RE}_x\text{Fe}_{0.8}\text{Mn}_{0.2}$ (RE = Pr, Sm and Nd; $x = 0, 0.01$) alloys in cast are fabricated. The relationships of phase composition, surface morphology and crystal structure to the hydrogenation performances of the alloys are studied. X-ray diffraction (XRD) results show that the as-cast $\text{Ti}_{1.1}\text{Fe}_{0.8}\text{Mn}_{0.2}$ (TFM for short) alloy includes the base phase of TiFe phase and the second phases of TiFe_2 phase and TiO phase. Backscatter electron (BES) images show that there is Ti segregation phase besides TiFe phase and TiFe_2 phase in the TFM alloy. Substituting Ti with RE partly causes Ti phase to increase and RE phases to generate. The lowest activation temperature decreases from 573 K for the TiFe alloy to 423 K for the $\text{Ti}_{1.1-x}\text{RE}_x\text{Fe}_{0.8}\text{Mn}_{0.2}$ (RE = Pr, Sm and Nd; $x = 0, 0.01$) alloys. Substituting Ti with RE partly makes the incubation time reduce from 5900 s for the TFM alloy to 3850, 3900 and 4050 s for the $\text{Pr}_{0.01}$, $\text{Sm}_{0.01}$ and $\text{Nd}_{0.01}$ alloys, respectively. And it also is able to weaken the stability of the hydrides, while causes variable degrees of the hydrogenation capacity decrease.

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Introduction

The exploitation of clean energy is regarded as the fundamental approach to solve energy crisis and reduce carbon emissions. Wind and solar energy, as two main sources of clean energy, have made remarkable progress in the areas of people's daily life, transportation, industry and agriculture. However, the random variability of the energy sources results in serious inefficiency and waste for the photovoltaic and

wind energy systems [1]. The problem can be resolved by transforming the primary energy source to clean secondary energy, in particular to hydrogen energy [2–4]. As a supplement to the existing renewable energy generation system, redundant power is transformed into hydrogen by water electrolysis for ease of storage and utilization [5–7]. The key links of the energy utilization pattern are sustainable hydrogen production and secure hydrogen storage with high energy density. Compared to hydrogen production, safe and reliable hydrogen storage technology still lags behind, and the

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development of the new energy utilization pattern is therefore affected.

At present, the hydrogen storage technology mainly includes the following types: high-pressure gas tank, liquefying and metal hydride [8–14]. For the high-pressure gas tank, the hydrogen storage density largely depends on the maximum pressure of the tank, reaching to 82 MPa at present, which is fairly difficult to be improved further [15,16]. And the security of the high-pressure gas tank cannot be well supported due to the inflammable and explosive feature of hydrogen gas [17]. For the liquid hydrogen, the cost for liquefaction and storage is too high to be practical in the pattern. Metal hydride is the safest hydrogen storage medium and its volume hydrogen storage density is closer to liquid hydrogen, which make it very suitable for storing hydrogen in the energy utilization pattern.

Unfortunately, although a variety of hydrogen storage alloys have been synthesized, they have the merits and defects of their own. For the AB₅ type alloys, despite the hydrogen storage capacity has been increased notably through alloying with transition metals, it is still difficult to meet demands of socioeconomic development due to the limited theoretical capacity [18]. For the Mg-based alloys, the over 5.5 wt% of mass hydrogen storage density is satisfying, but the decomposition temperature of hydrides is up to 573 K and the dehydrogenation kinetics is very poor [19]. Ouyang et al. [20–22] improve the thermodynamics and kinetics using ball-milling assisted by dielectric-barrier discharge plasma to some extent. Especially the Mg₂In_{0.1}Ni alloy, the dehydrogenation enthalpy is only 38.4 kJ mol⁻¹ H₂, which is far lower than that of MgH₂ (75 kJ mol⁻¹ H₂) [20]. For the AB₃ and AB_{3,5} type alloys, the discharge capacity and high-rate discharge performance have been significantly improved [23,24], while the large-scale preparation has not been well developed. ZrFe₂ alloy is a typical representative of unstable metal hydrides with hydrogenation platform pressure of 69 MPa at room temperature, which is too high to use in practice. Substituting Fe with V is able to reduce the platform pressure to 1.12 MPa at 273 K with 1.51 wt% of reversible hydrogen capacity [17]. By contrast, TiFe-based alloys have advantages of hydrogen storage density as high as 1.86 wt%, moderate pressure, room temperature operation and low cost, which is the best choice for the hydrogen storage system. However, the activation problem (activation temperature: 573 K) has to be solved before its application [25].

Large numbers of studies have been concentrated on lowering the activation temperature and shorting the incubation time of TiFe-based alloys, including over-stoichiometrical method [26,27], element substitution [28–34], surface modification [35,36] and new manufacturing technology [37–40]. In our previous study, it has been proved that mechanical milling the Ti_{1.1}Fe_{0.9}Ni_{0.1} and Ti_{1.09}Mg_{0.01}Fe_{0.9}Ni_{0.1} alloys with carbonyl Ni contributes to the enhancement of the electrochemical capacity, while has no significant effect on the activation performance [41]. Element substitution is the most suitable to industrial production. Lee et al. [28] reported that the TiFe_{0.8}Mn_{0.2} alloy is able to be activated at room temperature, but it takes longer than 1 day for the first hydrogen absorption process. Adding rare earth element La or Ce into the TiFe-based alloys is beneficial to reduce the

activation condition, while it causes the hydrogenation capacity to decrease because the decomposition temperature of the rare earth hydrides is far higher than 573 K [26,42]. At present, there is no satisfactory solution for the activation problem and the activation mechanism is still not clear. Therefore, in this paper, the over-stoichiometrical Ti was added into the TiFe_{0.8}Mn_{0.2} alloy for reducing the activation condition and shorting the activation cycle. The trace amounts of rare earth elements were added into the as-cast Ti_{1.1-x}Fe_{0.8}Mn_{0.2} alloy for further reducing the activation condition while avoiding excessive capacity loss. The alloy composition is Ti_{1.1-x}RE_xFe_{0.8}Mn_{0.2} (RE = Pr, Sm and Nd; x = 0, 0.01). The activation performance, hydrogen storage capacity and thermodynamics are studied in detail.

Experimental

In this research, the as-cast Ti_{1.1-x}RE_xFe_{0.8}Mn_{0.2} (RE = Pr, Sm and Nd; x = 0, 0.01) alloys were prepared through melting titanium sponge, pure iron, electrolytic manganese and rare earth ingots (RE = Pr, Sm and Nd) using a vacuum induction melting furnace with a medium-frequency power supply. Considering the volatilization loss, 5 wt% of additional manganese and rare earth elements was added into the furnace in the charging due to the fact that the melting point and boiling point of manganese and rare earth elements are far below that of Ti and Fe. Before melting the metal materials, the air in the furnace was removed firstly using a vacuum air-removed system, which is equipped with a mechanical pump, a roots pump and an oil diffusion pump. Until the vacuum reached 5 × 10⁻⁶ MPa, the medium-frequency power supply was activated. And the vacuum air-removed system operates continuously during the period. After preheating the metal materials for 20 min, closing the vacuum pumps and breaking the vacuum with 0.04 MPa of helium gas to restrain volatilization of manganese and rare earth elements. Increasing the power to ensure the metal materials were completely melted, and the liquid alloy was cast into six cylindrical ingots with 8 cm height and 3 cm diameter before being cooled inside the furnace to room temperature. The obtained cylindrical ingots were crushed and screened in the air. And the alloy particles (average particle size: 48–72 μm) were chosen as test samples. For ease of description, the as-cast Ti_{1.1-x}RE_xFe_{0.8}Mn_{0.2} (RE = Pr, Sm and Nd; x = 0, 0.01) alloys were represented by TFM, Pr_{0.01}, Sm_{0.01} and Nd_{0.01}, respectively.

The data of X-ray diffraction (XRD), 2θ ranging from 10 to 90°, was recorded using D/max/2400 model diffractometer with an operating voltage of 40 kV and a current of 160 mA, using CuKα₁ radiation. The morphology of the cross section of the cylindrical ingots and the alloy powders was carried out in a Quanta 400 model Scanning electron microscope (SEM). Analysis of the crystal type and crystalline interplanar spacing was performed by TecnaiG2 F30 model Field emission transmission electron microscopy (FETEM). Oxygen–Nitrogen analyzer (ON-3000) was used to measure the oxygen content of the alloy powders.

1 g of the alloy powders, placed in the steel reactor of an automatically controlled Sieverts measuring system, reacts with hydrogen and reaches the activation state through three

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