Preparation and Hydrogen Absorption/Desorption Mechanism of High-Performance and Low-Cost BCC Type Hydrogen Storage Alloys

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Abstract: Efficient, safe and economical hydrogen storage technologies are essential for the widespread application of hydrogen as an energy carrier, and Vanadium (V)-based BCC alloys stand out due to their high theoretical hydrogen storage capacity. However, the high cost of V limits their practical application. In this work, three types of BCC hydrogen storage materials were developed. Firstly, a novel high entropy BCC hydrogen storage alloy was constructed by co-doping Mo and Ce; secondly, the BCC structure of low-V alloy was maintained based on melt-spining; finally, V-free BCC hydrogen storage alloy was constructed by completely replacing V with Mo. The effective hydrogen desorption capacity of the alloys reaches 2.4 wt% above 0.1 MPa, which provides guidance for the application of BCC-type alloys in gas-solid hydrogen storage. The hydrogen absorption/desorption mechanism of the BCC alloys were studied.

Keywords: Hydrogen storage alloys; BCC phase; High entropy alloys; Low-V; V-free.

1 Introduction

Hydrogen energy vital for energy security and dual-carbon goals faces storage/transportation challenges due to its physicochemical properties. Solid-state storage, offering safety, and low pressure, is a promising alternative attracting research focus. Alloy-based hydrogen storage materials are mature, used in gas-solid storage, compression, recovery, and purification. Rare earth alloys have rapid kinetics but Ni cost limits gas-solid use [1]. Ti-based alloys, low-cost and stable, favor large-scale systems but have low capacity and production issues [2]. Mg-based materials, high-capacity and cost-effective, need advancements in material prep, tank design, and heat integration for industrialization [3]. V-based BCC alloys [4-6], like V-Ti-Cr, show impressive hydrogen storage capacities, outperforming rare earth and Ti-based alloys. However, high V costs and impurity issues hinder their use. Researchers aim to reduce costs, enhance stability, and improve performance through element substitution, innovative preparation methods, and seeking cheaper V sources, to develop cost-effective BCC alloys for practical hydrogen storage.

Inspired by the research described above, three distinct categories of BCC-type hydrogen storage alloys (high-entropy, low-V, V-free alloys) were prepared in this work. This comprehensive research endeavor underpins the foundation for the practical application of cost-effective and efficient hydrogen storage solutions.

2 Experimental procedure

The alloy was prepared by arc melting Ti, Cr, V, Mn, Mo, and Ce in a vacuum furnace. The alloys were crushed, sieved, and analyzed via XRD, SEM-EDS, TEM, and XPS. After vacuum activation, their hydrogen storage performance was tested, including kinetics, PCT curves, cycling performance. Effective hydrogen desorption capacity was measured at pressures above 0.1 MPa.

3 Result and discussion

1 High entropy BCC type alloy

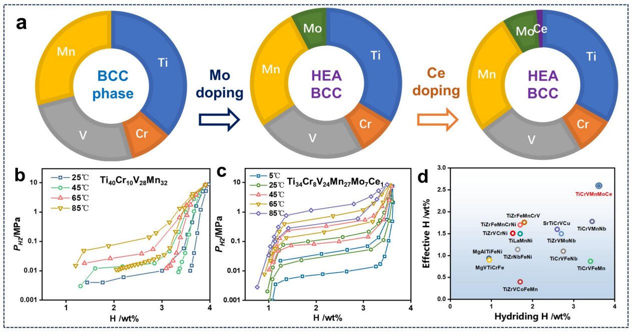

Fig. 1 (a) Diagram of preparation of high entropy alloy, PCT curves of HEA (b) before and (c) after doping, (d) Comparison of hydrogen storage capacity with HEA.

To overcome these challenges, a BCC-type TiVCrMnMoCe HEA with an effectively dehydriding capacity of 2.5 wt% above 0.1 MPa was prepared (Fig. 1). By introduction of Mo and conducting heat treatment, the precipitation of Ti-rich phase in HEA was successfully suppressed, resulting in improved compositional uniformity and dehydriding capacity. Consequently, the effective dehydriding capacity increased significantly from 0.60 wt% to 2.50 wt% at 65 °C, surpassing that of other types of hydrogen storage alloys under the same conditions. Moreover, the addition of 1 wt% Ce enabled initial hydrogen absorption at 25 °C without the need for activation at 400 °C. Furthermore, Ce doping reduced the dehydriding activation energy of the HEA from 52.71 to 42.82 $kJ\cdot mol^{-1}$. Additionally, the enthalpy value of dehydrogenation decreased from 46.89 to 17.96 $kJ\cdot mol^{-1}$, attributed to a decrease in the hysteresis factor from 0.68 to 0.52.

2 Low-V BCC type alloy

Herein, a low-V BCC alloy ($Ti_{41}Cr_{50}V_5Mo_4$) with an excellent dehydriding capacity (2.4 wt%) is developed via Mo partial substitution and coupling with the melt-spin process (Fig. 2). The alloys' crystal structures, micromorphology, and de-/hydrogenation mechanisms are investigated systematically. It is found that the Mo-substitution and the melt-spin process can keep and extend the BCC zone in the low-V portion of Ti-Cr-V phase diagram, and Mo atom is uniformly distributed in the BCC alloy. The dehydrogenation mechanism of the low-V BCC alloy was determined to follow a diffusion-controlled model with an activation energy of 52.38 kJ/mol. The cycle test also proves that the synergistic effect of Mo substitution and melt spin improved the durability of the low-V alloy. The retention rate of hydrogen capacity can achieve 94 % after 15 cycles.

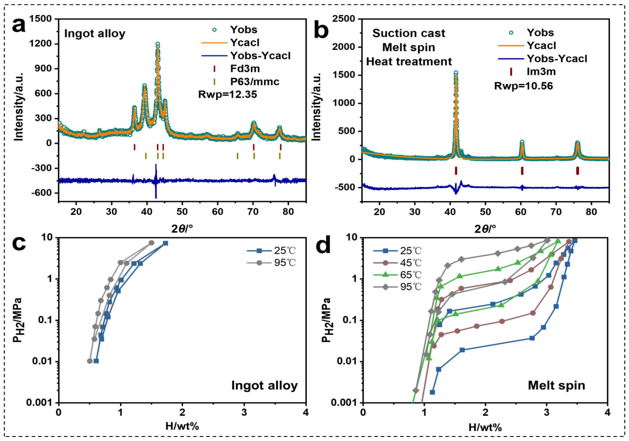

Fig. 2 Crystal structure of low-V alloy (a) before and (b) after melt spin, PCT curves of low-V alloy (c) before and (d) after melt spin.

3 V-free BCC type alloy

An easily activated and high-performance V-free BCC type alloy ($Ti_{40}Cr_{50}Mo_{10}Ce_1$) was successfully synthesized by heat treatment and Ce doping (Fig. 3). The heat treatment significantly increased its dehydriding capacity to 2.5 wt%, attributed to a reduced slope factor (0.76−0.17), making it comparable to V-based BCC-type alloys. And after Ce doping, enabled room temperature hydrogen absorption without high-temperature activation. Ce doping did not significantly affect the activation energy, enthalpy change, or hysteresis factor of the alloy during de/hydrogenation. Additionally, the V-free BCC-type alloy, after heat treatment and Ce doping, exhibited excellent cyclic stability, with a capacity retention rate of 90% after 100 cycles.

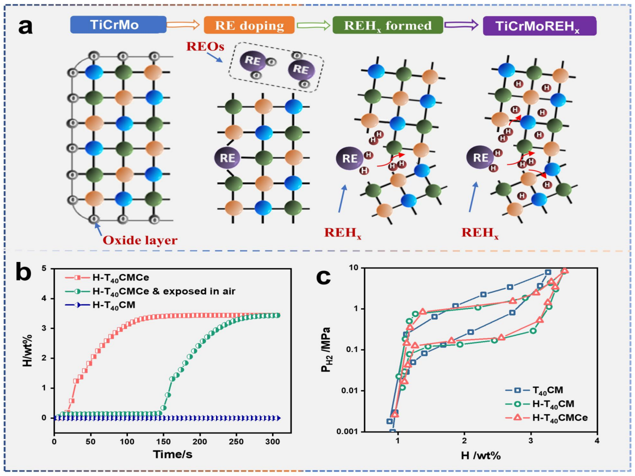

Fig. 3 (a) Activation diagram, (b) activation properties of rare earth-doped alloys and (c) PCT curves of V-free alloys before and after Ce doping and heat treatment.

Conclusion

In this work, three high-performance BCC type hydrogen storage alloys were successfully synthesized. A BCC-type Ti–V–Cr–Mn–Mo–Ce HEA with an effectively dehydriding capacity of 2.5 wt% above 0.1 MPa was prepared. a low-V BCC alloy ($Ti_{41}Cr_{50}V_5Mo_4$) with an excellent dehydriding capacity (2.4 wt%) is successfully developed via Mo partial substitution and melt-spin process. An easily activated and high-performance V-free BCC-type alloy ($Ti_{40}Cr_{50}Mo_{10}Ce_1$) was successfully synthesized by heat treatment and Ce doping.

Acknowledgments

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