Optimization of the First Hydrogenation Reaction Via Introducing Active Sites Through Y-Doping

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Abstract: Mg-based hydrogen storage alloys are considered as hydrogen storage materials with great development potential, but their sluggish kinetics restrict their applications. Activation property is also considered to be one of the important indicators for evaluating the performance of hydrogen storage alloys. In this study, as the doping amount of Y element increases, the grain size decreases and the initial hydrogenation performance gradually improves. The first hydrogenation time of Y1 sample is only 8554 s. Due to the strong affinity between Y and H atoms, the number of active sites increases, which shortens the "incubation period" and accelerates the adsorption and dissociation process of H molecules.

Keywords: Hydrogen storage, Mg-based alloy, Activation performance

1 Introduction

Mg-based alloys are considered to be one of the most promising hydrogen storage materials with important practical value and application prospects due to their widespread source, low price and high capacity(7.6 wt.% and 110 g/L) [1]. Nevertheless, the practical application of MgH_2 is limited by its poor thermodynamic and kinetic properties, which are attributed to the difficult dissociation of H molecules, the slow diffusion rate of H atoms and the high energy of Mg-H bonds [2]. Alloying is an effective method to improve the performance of Mg-based hydrogen storage alloys [3].It is found that the addition of transition metal (TM) elements and rare earth (RE) elements can effectively weaken the bond energy between Mg and H atoms and accelerate the recombination and dissociation of H molecules [4].

2 Experimental procedure

Materials preparation

The $Mg_{97}Ni_{2-x}Y_x$ (x=0, 0.25, 0.5, 1) as-cast alloys were prepared in an electric resistance-heated furnace under the protection of SF_6 shielding gas atmosphere.The as-cast alloys were synthesized by the industrial pure magnesium (99.9%), Mg-70wt.%Ni and Mg-20wt.%Y intermediate alloys. An excess of 3 wt.% Mg was added in order to compensate for Mg evaporation losses from the melting process. To simplify the description, $Mg_{97}Ni_{2-x}Y_x$ (x=0, 0.25, 0.5, 1) samples are abbreviated as Y_0, $Y_{0.25}$, $Y_{0.5}$ and Y_1, respectively.

The microstructures of the as-cast alloys were characterized by scanning electron microscopy (SEM). Hydrogen storage properties of the as-cast alloy powder samples were measured with a precision Sieverts-type apparatus.

3 Result and discussion

Microstructure characteristics

The microstructures of the as-cast alloys are exhibited in Fig. 1. Two phases are distinguished in Y_0 alloy, the primary phase is a blossom-shaped Mg phase, and the eutectic is Mg+Mg_2Ni. Doping with Y element in $Y_{0.25}$, $Y_{0.5}$ and Y_1 alloys, blocky NiY_3 phases are preferentially precipitated, which act as nucleation sites for Mg phases and hinder the growth of Mg grains. As the amount of Y doping increases, the sizes of the Mg and NiY_3 phases decrease, and the distribution of NiY_3 phases becomes more diffuse.

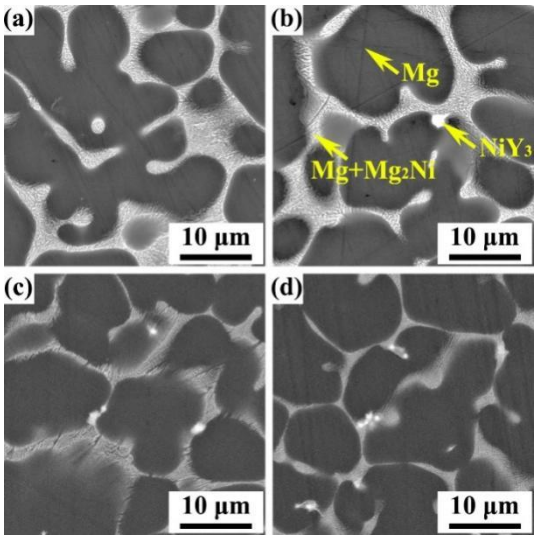

Fig.1 Microstructures of the as-cast alloys: (a)Y_0, (b)$Y_{0.25}$, (c)$Y_{0.5}$, (d) Y_1.

4 Activation performance

Due to the active chemical properties of Mg, a dense MgO film is easily formed in oxygen-containing environments, which hinders the reaction between Mg and H atoms. During the activation process, cracks gradually appear on the oxide film and expose the fresh surface owing to the expansion or contraction of lattice volume. Therefore,

activation property is considered to be one of the important indicators for evaluating the performance of hydrogen storage alloys.

In this experiment, each sample is carried out three cycles of hydrogen absorption and desorption activation at 400 ℃ under 3 MPa and 0.1 MPa). Fig.2 (a-d) shows the hydrogen absorption curves, revealing a great difference in the first cycle. The first hydrogenation process of the Y_1 sample is only 8554 s. However, the first hydrogenation process of Y_0 sample is 13581s, which is 1.5 times that of the Y_1 sample.The initial stage of activation with almost no hydrogen absorption is called the "incubation period". There is no "incubation period" in Y_1 alloy, but there is a brief incubation period in $Y_{0.25}$, $Y_{0.5}$ and Y_1 alloys.

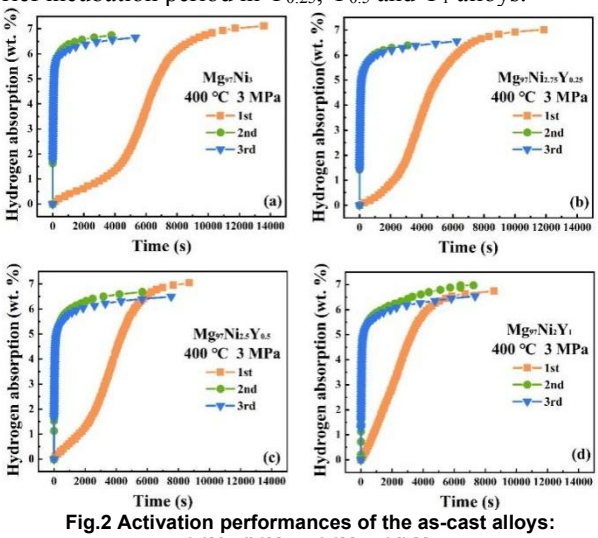

Fig.2 Activation performances of the as-cast alloys: (a)Y_0, (b)$Y_{0.25}$, (c)$Y_{0.5}$, (d) Y_1.

The hydrogen absorption process can be summarized as follows: (1) Adsorption and dissociation of H_2 molecules on the surface, (2) diffusion of H atoms, (3) formation of α-solid solution, (4) formation of β-metal hydrides. Due to the strong affinity between Y and H atoms, NiY_3 phase first attracts H molecules and acts as an active site, which accelerates the adsorption and dissociation process of H molecules. The decrease in grain size after doping with element Y accelerates the diffusion process of hydrogen atoms, which is because grain boundaries are fast diffusion channels for H atoms. Therefore, doping with Y element can significantly improve the initial hydrogenation performance.

5 Conclusion

(1) As the amount of Y doping increases, the sizes of the Mg and NiY_3 phases decrease.
(2) The first hydrogenation process of the Y_1 sample is only 8554 s, which is 0.63 times that of the Y_0 sample.
(3) The number of active sites increases with increasing Y element content, which shortens the "incubation period" and accelerates the adsorption and dissociation process of H molecules.

6 Acknowledgments

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