

Effects of Cu on the microstructure and hydrogen storage properties of Mg-20Ni alloy

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Abstract. In order to improve the hydrogen storage capacity of hypereutectic Mg-Ni alloy, the Mg₄₀Ni₁₀ and Mg₄₀Ni₈Cu₂ alloys were prepared by metallurgy method. The effects of Cu on the alloys' phase composition, microstructure were studied systematically. The volumetric Sieverts' method was used to test and analyze the activation performance and hydrogen absorption and desorption kinetic performance of the alloys. It was found that the partial substitution of Ni in the Mg₂Ni-riched matrix alloy with Cu can change the primary Mg₂Ni and eutectic Mg-Mg₂Ni morphology of the alloy. With the doping of Cu content, although the activation property of the alloy decreases, the hydrogen storage capacity as well as the kinetic of hydrogen absorption and desorption are improved significantly.

1 Introduction

Mg-based hydrogen storage alloys have higher hydrogen storage capacity than other alloys, and their theoretical hydrogen storage capacity can reach 7.62 wt.%[1]. However, the strong ionic bond between Mg and H makes MgH₂ more stable, so the pure Mg alloy has a higher hydrogen desorption temperature. Many measures have been taken to improve the thermodynamic and kinetic properties. Such as reducing the stability of hydride[2,3], refining grain size or forming amorphous grains[4,5], catalyzing and surface modification by catalyst[6–8]. The compound Mg₂Ni has a strict stoichiometric ratio, which has a strict stoichiometric ratio of Mg and Ni, can absorb hydrogen under the reaction conditions of 250°C and 2 MPa hydrogen pressure, and its theoretical hydrogen storage can reach 3.62 wt%. However, there is still a long way to go before it can be used as a mobile energy storage carrier due to the drawback of hydrogen storage capacity. Chen et al. [9] prepared Mg-rich alloys(Mg-Ni-Cu) and found that Mg-6Ni-3Cu alloys had good activation properties and a fast hydrogen absorption rate. Zhang et al. [10] reported that the substitution of Cu for Ni in Mg₂Ni can improve the alloys' hydrogen absorption and desorption capacity by the method of melt-spinning. Li et al. [11] studied the Mg-Ni-Y alloys, found that the addition of yttrium (Y) can decrease the entropy and enthalpy for the de-/hydrogenation of Mg and Mg₂Ni.

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At present, there are few studies on the effect of Cu on the microstructure of hypereutectic Mg-Ni alloy and its relationship between the microstructure and isothermal de-/hydrogenation properties. In this paper, hypereutectic Mg-Ni alloy $Mg_{40}Ni_{10}$ is selected as the matrix, and the ternary hydrogen storage alloys are obtained by adjusting the ratio of Cu. The change of Cu content results in the change of morphology of primary Mg, especially Mg-Ni eutectic. The change of the structure and the phase caused by Cu affect the hydrogen storage performance together.

2 Experiment material and setup

The $Mg_{40}Ni_{10}$ and $Mg_{40}Ni_8Cu_2$ ingots were prepared by electronic-resistance furnace with pure magnesium, shot copper and intermediate alloy at $750^{\circ}C$ and then cooled with furnace to get the nearly equilibrium structure. In order to get the better de-/hydrogenation properties, the as-cast ingots were pulverized by a planetary high energy ball-milling (HEBM) machine in a stainless-steel container. And the samples were milled under the protection of argon at the rotate speed of 200 rpm for 2 h and alternated rotate direction every 20 min.

The morphology of the hypereutectic Mg-Ni alloy and the particle were examined by scanning electron microscopy (SEM). The X-ray diffraction (XRD) worked with $CuK\alpha 1$ radiation was used to determine phase composition of the alloys, which experimental parameters are 40 kV, 40 mA and a scanning rate of $10^{\circ}/min$. The hydrogen absorption behaviors were measured by volumetric Sieverts-type apparatus with the ~ 0.6 g of powder samples. The hydrogen absorption kinetics of $Mg_{40}Ni_{10-x}Cu_x$ alloys were carried at the temperature of $275^{\circ}C$ and the pressure of 2.0 MPa.

3 Results and discussion

3.1 Microstructure and phase composition

It can be seen from Fig. 1 that there are mainly two types of structure in the as-cast alloys. Due to differences in atomic mass, it is obvious that the bright region is the primary Mg_2Ni phase, and the dark region is the eutectic region of Mg_2Ni -Mg. With the doping of Cu element, eutectic structure changes from lamellar to lath and then to rod bar. In $Mg_{40}Ni_8Cu_2$ alloy, the primary phase gradually aggregates and grows up, changing from continuous blocks with banded distribution to long and thick strips. In the hypereutectic Mg-Ni alloys, Mg_2Ni is the dominant phase because it has the highest diffraction peak strength. The addition of Cu only introduces a small amount of Mg_2Cu phase (Fig. 2), so when the substitution amount of Cu in $Mg_{40}Ni_{10-x}Cu_x$ equals to 2 at.%, the diffraction peak of Mg_2Cu phase does not appear in the diffraction pattern due to the dissolution of Cu atoms in the lattice sites of Mg_2Ni . Combined with SEM results, it can be concluded that the alloys' phases are primary Mg_2Ni and the eutectic structure of Mg- Mg_2Ni - Mg_2Cu .

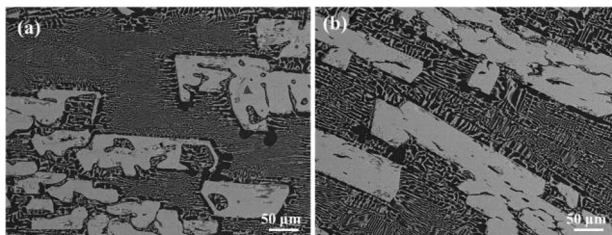


Fig. 1. SEM/BSE micrograph of (a) $Mg_{40}Ni_{10}$ and (b) $Mg_{40}Ni_8Cu_2$ alloys.

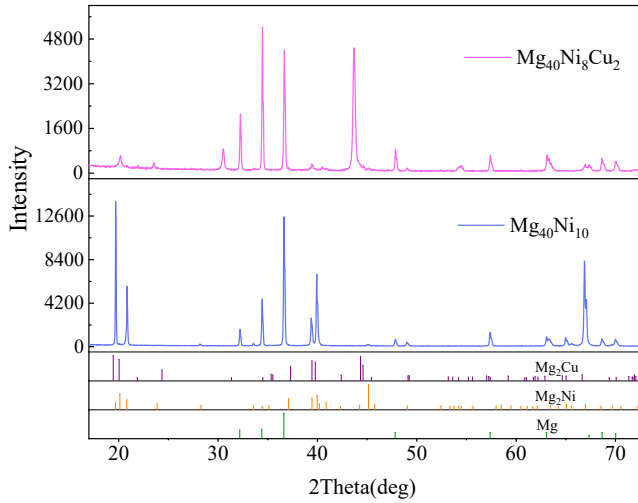


Fig. 2. XRD results of $Mg_{40}Ni_{10}$ and $Mg_{40}Ni_8Cu_2$ alloys.

3.2 Activation Properties

It can be seen from the hydrogenate activation curve of $Mg_{40}Ni_{10}$ that the curves of the alloy hardly change after the third hydrogen release, and the single hydrogen absorption value can reach 4.2 wt.%. The hydrogen absorption rate of the $Mg_{40}Ni_{10}$ alloy is relatively fast within 1.2 minutes at the beginning of hydrogen absorption, which is the first stage of the hydrogen absorption reaction, and then to the 5th minute is the second stage of the hydrogen absorption reaction. The hydrogen absorption rate of the alloy begins to gradually decrease. With the extension of time, the reaction continues to go on and its rate gradually slows down, and finally basically no longer changes. As a result, the hydrogen storage capacity of the alloy is reached.

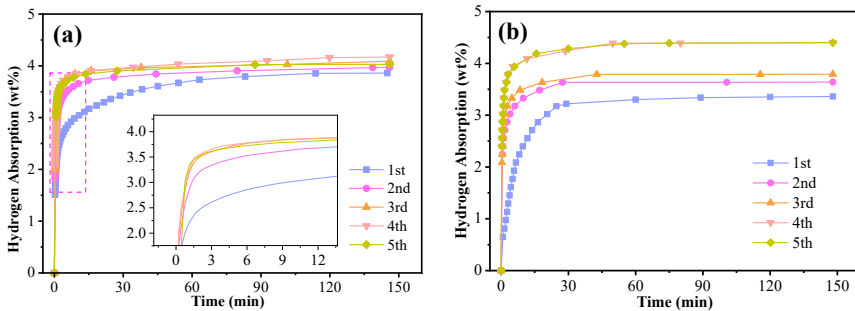


Fig. 3. Activation properties of (a) $Mg_{40}Ni_{10}$ and (b) $Mg_{40}Ni_8Cu_2$ alloys.

From the isothermal activation hydrogen absorption curve of $Mg_{40}Ni_8Cu_2$ alloy shown in Fig.3, it can be seen that the substitution of Cu for the B-side element Ni in the Mg_2Ni -rich alloy does not have a considerable positive effect on its activation properties, and the activation property of $Mg_{40}Ni_8Cu_2$ is significantly worse. It can be fully activated after at least 4 times of hydrogen absorption and desorption process. Besides, the hydrogen absorption capacity in the first cycle is small. It can be speculated that at the same time, Mg_2Cu phase also appeared aggregation[12], which would be harmful to hydrogen storage properties. It is worth noting that the $Mg_{40}Ni_8Cu_2$ alloy has the largest hydrogen absorption

during the hydrogen absorption process, reaching 4.5 wt.%. While the maximum hydrogen absorption of $Mg_{40}Ni_{10}$ alloy is only 4.3 wt.%. The first cycle possesses the lowest hydrogen storage capacity as a result of the hydrogen absorbing alloy has not been activated, A layer of oxide/hydroxide covering on the particles surface restricts the reaction of hydrogenation, so the initial hydrogen absorption curve slope is still the youngest, the reaction rate is slow.

3.3 Hydrogen de-/absorption properties

Fig. 4 shows the hydrogen absorption and desorption capacities of $Mg_{40}Ni_{10}$ and $Mg_{40}Ni_8Cu_2$ alloys within 120 min and 60 min respectively. When the temperature is lower than 250°C, the influence of temperature on the single hydrogen absorption of $Mg_{40}Ni_{10}$ alloy is not obvious, and when the temperature reaches 275°C, the once hydrogen absorption amount can reach 4.16 wt%, which is higher than the absorption amount under the reaction conditions below this temperature. Compared with the influence of hydrogen absorption, the influence of temperature on the hydrogen release is more obvious. When the hydrogen release temperature is from 200°C gradually increasing to 275°C, the hydrogen desorption amount of $Mg_{40}Ni_{10-x}Cu_x$ alloy shows an overall increasing trend. At the temperature of 275°C, when the substitution amount equals to 2 at.%, the hydrogen desorption rate and the dehydrogenate amount of the hypereutectic Mg-Ni alloy by Cu have a significant increase. Cu forms a large amount of eutectic structure in Mg-Ni alloy, and the grain boundary and phase boundary are equivalent to the diffusion channel of hydrogen in the process of absorbing and releasing hydrogen, which has a beneficial effect on hydrogen absorption [10,13]. In addition, the substitution of Cu for Ni can shift the platform of the dehydrogenate reaction upward, that is, increase the driving force of the hydride desorption, so it significantly promotes the dehydrogenation reaction.

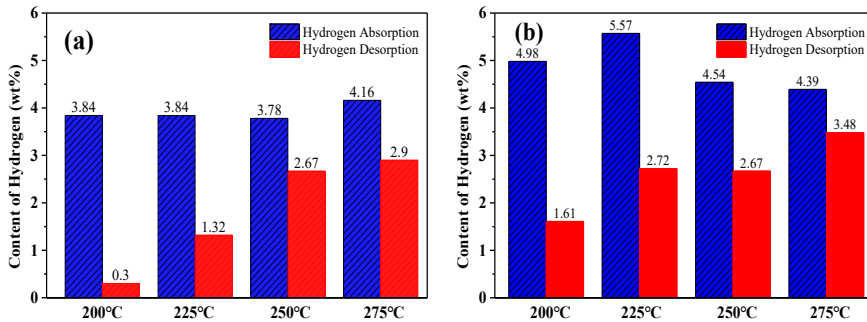


Fig. 4. Capacity of hydrogen de-/absorption of (a) $Mg_{40}Ni_{10}$ and (b) $Mg_{40}Ni_8Cu_2$ alloys.

From Fig. 4, it can be seen that $Mg_{40}Ni_{10}$ alloy exhibits good hydrogen absorption kinetics property, and can reach 70%, 73%, 73%, and 62% of the actual hydrogen absorption capacity at 200, 225, 250, and 275°C within 0.5 min respectively. However, the dehydrogenation amount of the hypereutectic alloy at 200, 225, 250 and 275°C was only 0.30, 1.3, 2.7, 2.9 wt% respectively.

When substitution amount equals to 2 at.%, the hydrogen absorption rate of $Mg_{40}Ni_8Cu_2$ alloy increases with the increase of temperature in the first 0.5 min, but after the reaction for 7 min, the hydrogen absorption rate of the alloy at 250°C and 275°C is lower than that at 200°C. According to the van't Hoff relation (formula "1"), the increase in temperature means a higher equilibrium pressure and a smaller pressure differential, the change of the driving force leads to a change in its reaction rate and amount of hydrogen storage[14].

$$\ln p = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (1)$$

When the substitution amount x equals to 2 at. %, the hydrogen absorption properties of the alloy at different temperatures is greatly improved, especially at 200°C, the hydrogen absorption capacity is significantly increased, and the effect of Cu supersede Ni on the hydrogen desorption performance of the rich Mg₂Ni-based alloy is relatively complicated. First of all, with the increase of Cu substitution amount at 200°C, the hydrogen desorption properties of the alloy gradually improved. Within 20 min of hydrogen desorption, both the hydrogen desorption rate and the amount have been obviously improved. However, in the Mg-based hydrogen storage alloys, the catalytic effect of Cu is lower than that of Ni, so the addition of excessive Cu will cause the decrease of hydrogen absorption properties.

4 Conclusion

(1) The Mg₄₀Ni₁₀ and Mg₄₀Ni₈Cu₂ alloys were prepared by melting casting method. Cu substituted Ni did not change the microstructure of the alloy, but was still composed of primary phase (Mg₂Ni) and eutectic (Mg-Mg₂Ni/Mg₂Cu). With the increase of substitution amount, the primary phase and eutectic grow up, and the eutectic structure change from lamellar to strip and bar.

(2) The activation property of Mg₄₀Ni₈Cu₂ alloy becomes worse due to the aggregation of Mg₂Cu phase. It takes 4 to 5 cycles of hydrogen absorption and desorption to be fully activated. The alloys can be completely hydrogenated at different temperatures.

(3) Element Cu has an obvious influence on the kinetic property of hydrogen absorption reaction of Mg₄₀Ni₈Cu₂ alloy. The kinetic property of hydrogen absorption of the alloy enhanced, except for the dehydrogenation reaction at 200°C.

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