Trans. Nonferrous Met. Soc. China 19(2009) s355−s358

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Effect of Al and Zn additives on grain size of Mg-3Ni-2MnO$_2$ alloy

FANG Wa(房 娃), SUN Hong-fei(孙宏飞), FANG Wen-bin(房文斌), WANG Bin(王 彬)

School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

Received 10 June 2009; accepted 15 August 2009

Abstract: The effect of Al and Zn additives on the grain size of Mg-3Ni-2MnO$_2$ alloy was investigated. The nanostructured Mg-3Ni-2MnO$_2$ and Mg-3Ni-2MnO$_2$-3Al-Zn were made by ball milling process under hydrogen atmosphere. The XRD results and TEM analysis reveal that Al and Zn additives almost have no effect on the grain size of Mg-3Ni-2MnO$_2$ alloy. The present study provides us a feasibility of producing nano-structured magnesium alloys, based on hydrogenation, disproportionation, desorption and recombination(HDDR), by adding beneficial elements to hydrogen storage materials.

Key words: nanocrystalline; magnesium alloy; hydrogenation-disproportionation-desorption-recombination(HDDR); ball milling

1 Introduction

Magnesium and magnesium alloys are attractive materials due to their low density, good thermal conductivity, good electromagnetic shielding characteristics, and high elastic modulus, etc. These favorable properties can contribute significantly to the aspect of mass saving in the design and construction of automobiles, mobile phones, aerospace components and computers[1−2]. However, the application of Mg alloys is very limited due to their lower mechanical properties [3−4]. Thus, it is very significant to develop novel high performance Mg alloys. As we know, for Mg alloys grain refinement has great significance in that the achievement of a fine grain size can fundamentally improve their formability and combination properties [5−8]. The process of hydrogenation, disproportionation, desorption and recombination (HDDR) is very effective in grain refining. The nanocomposite Mg-3Ni-2MnO$_2$, which is made by ball milling process under hydrogen pressure, can completely absorb hydrogen during mechanically milling process and desorb at a relatively low temperature[9−10]. Thus, Mg-3Ni-2MnO$_2$ is a good choice for hydrogenation, disproportionation, desorption and recombination(HDDR). By this technique, nanocrystalline Nd-Fe-B magnets were produced[11−12], attributed to the fact that the mechanically driven hydrogenation–disproportionation reaction takes place at ambient temperature and it helps to prevent the as-disproportionated microstructure from grain growth.

Al and Zn were selected as the alloying elements due to the following reasons. Aluminium can be added into Mg alloys to improve corrosion resistance and mechanical properties at room temperature[13−15], and zinc can be added to improve corrosion resistance and creep resistance. Up to now, there are only a few reports about the microstructure evolution of magnesium alloys assisted by hydrogenation, disproportionation, desorption and recombination(HDDR), and the studies on adding beneficial elements to hydrogen storage materials are also very few. Hence, the aim of the present study is to reveal the microstructure evolution of Mg-3Ni-2MnO$_2$ and to investigate the effect of Al, Zn additives on the grain size of Mg-3Ni-2MnO$_2$ alloy.

2 Experimental

The nanocomposites were prepared with the mixture of three kinds of powders of Mg, Ni and MnO$_2$ in stainless steel vial in mass ratio of 95:3:2 and five powders of Mg, Ni, MnO$_2$, Al and Zn in mass ratio of 91:3:2:3:1. Mg (>99 %), Ni (>99.5%), MnO$_2$ (>99 %), Al (>99%) and Zn powders (>99%)) were provided by Shanghai Chemical Reagent Company and Northwest Light Alloy Company, respectively. The milling was carried out with a QM21SP4 planetary ball milling machine made by Nanjing University, and the mass ratio of ball to powder was 10:1 and the rotation speed was fixed at 360 r/min. The mass of alloy powders for each

Foundation item: Project(DCQQ24404018) supported by Scientific and Technological Program of Heilongjiang Province, China
Corresponding author: FANG Wa; Tel: +86-451-86403365; E-mail: fangwa1@sina.com

milling batch was 20 g. The grinding was performed under hydrogen atmosphere (about 1 MPa). Because the samples can absorb hydrogen in the ball milling process, the hydrogen pressure cannot keep constant. The hydrogen in the vial must be recharged to 1 MPa at intervals. All handling was in glove box filled with argon. Small amount of powder was taken for analysis. X-ray diffraction was performed on a Rigaku apparatus with Cu K_α radiation. The microstructure of alloy powders was characterized by SEM and TEM.

3 Results and discussion

3.1 XRD analysis

The XRD spectra as a function of milling time for the Mg-3Ni-2MnO$_2$ and Mg-3Ni-2MnO$_2$-3Al-Zn samples are shown in Fig.1. It can be seen clearly that for both of the samples, the intensity of the diffraction peaks of magnesium decreases rapidly while the width of the peaks increases with increasing milling time. At the same time, the intensity and the width of the peaks of MgH_2 increase rapidly. After 60 h milling, the diffraction peaks of MgH_2 become very broad, indicating that the crystalline size of MgH_2 diminishes into the nanocrystalline range. From the width of Mg peaks, it is considered that the crystalline MgH_2 partly becomes amorphous. As shown in Fig.1(a), after 20 h milling the diffraction peaks of Mg for Mg-3Ni-2MnO$_2$-3Al-Zn are more distinctly reduced and the width of the peaks is more obviously increased than that of Mg-3Ni-2MnO$_2$. But with milling time increasing, the differences between peaks of Mg and MgH_2 for the two samples become very slight (Fig.1(b)). When the milling time reaches 60 h, there are almost no peaks of Mg in Mg-3Ni-2MnO$_2$ alloy. But the intensity and width of peaks of MgH_2 for Mg-3Ni-2MnO$_2$-3Al-Zn are larger than those of Mg-3Ni-2MnO$_2$ (Fig.1(c)).

The grain size was calculated using the Scherrer equation based on the XRD patterns. After 20 h milling, the average grain size of Mg-3Ni-2MnO$_2$ is 3−4 nm, and that of Mg-3Ni-2MnO$_2$-3Al-Zn is 4−5 nm. With the extension of milling time, the grain size becomes smaller and smaller. After 40 h milling, the average grain size of Mg-3Ni-2MnO$_2$ decreases to 2.5−3 nm, and that of Mg-3Ni-2MnO$_2$-3Al-Zn decreases to 3−4 nm. When the milling time reaches 60 h, the average grain sizes for the two samples don’t become smaller, which are almost equal to that of 40 h milling. It can be concluded that Al and Zn have no effect on the grain size of Mg-3Ni-2MnO$_2$ alloy, and with the extension of milling time, the grain size becomes smaller and smaller. When the milling time reaches 40 h, the effect of milling time on grain size refining becomes weak.

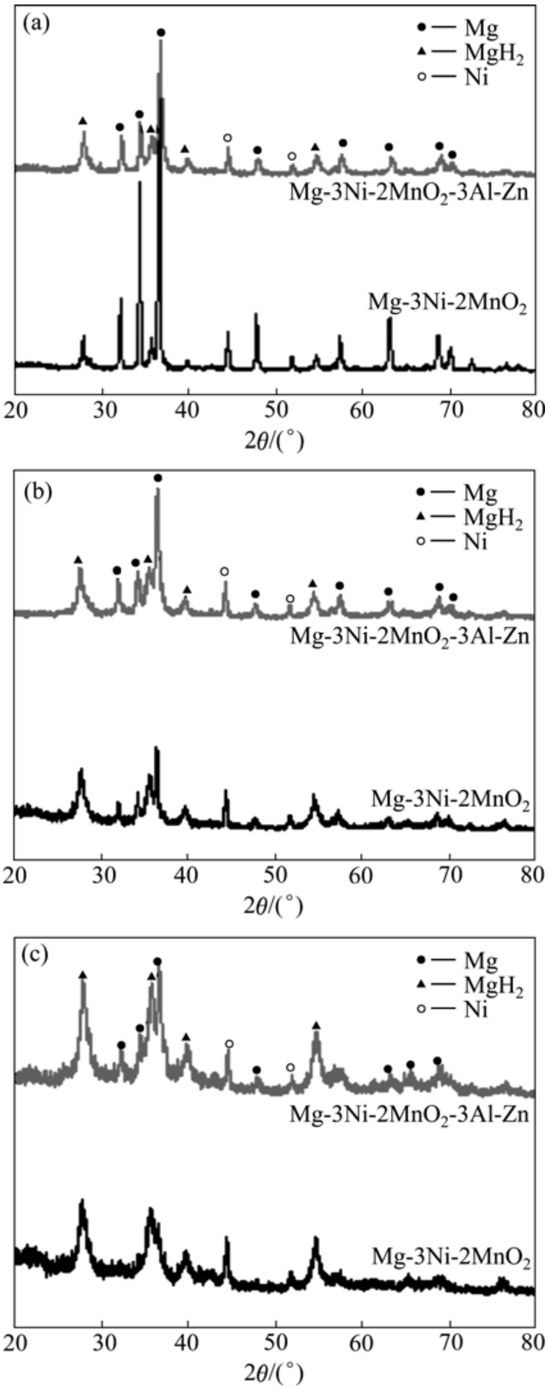

Fig.1 XRD patterns of Mg-3Ni-2MnO$_2$ and Mg-3Ni-2MnO$_2$-3Al-Zn after different milling time: (a) 20 h; (b) 40 h; (c) 60 h

3.2 SEM observation

Fig.2 shows the microstructures of Mg-3Ni-2MnO$_2$ and Mg-3Ni-2MnO$_2$-3Al-Zn samples milled for various times. From Figs.2(a) and (b), we can see that for both of the samples various sized particles exist in the range of less than 1 μm to more than 20 μm. Because the milling time is not long, the powder size is imhomogeneous and the large sized particles are still present in the powders. The difference of particle size between the two samples

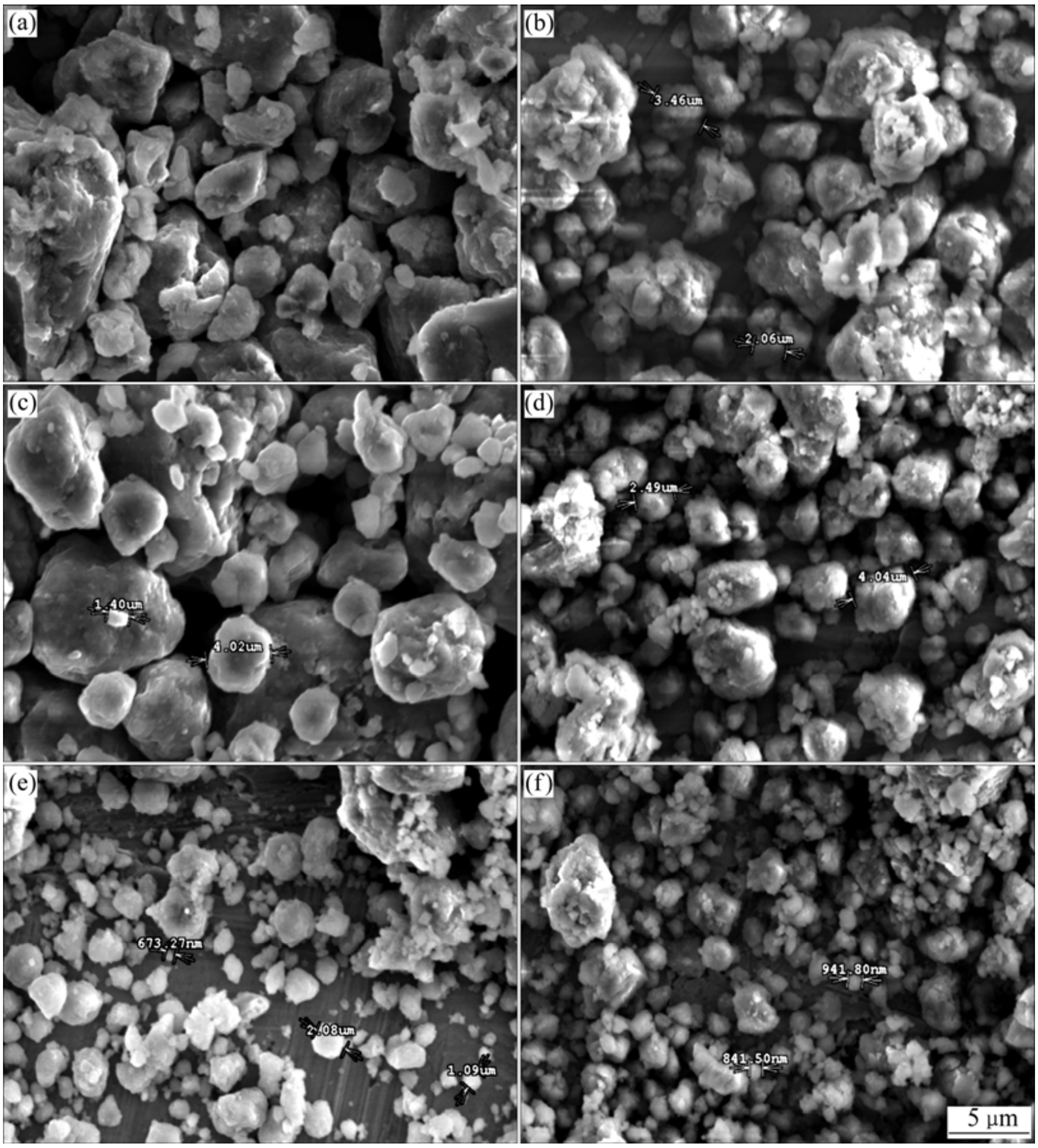

Fig.2 SEM morphologies of Mg-3Ni-2MnO$_2$ (a, c, e) and Mg-3Ni-2MnO$_2$-3Al-Zn (b, d, f) alloy samples milled for 20 h(a, b), 40 h (c, d) and 60 h (e, f)

is very slight. Al and Zn additives do not change the particle size of Mg-3Ni-2MnO$_2$ alloy. And the difference of particles size between the two samples decreases as milling time increases (Figs.2(c) and (d)). The particle size of Mg-3Ni-2MnO$_2$-3Al-Zn is a little bigger than that of Mg-3Ni-2MnO$_2$. The reason may be that the surface of the particles is covered by the product of reaction of Mg and a small amount of Al, which results in the reaction rate of Mg and H_2 reducing. The final result is that MgH_2 content is reduced and hydrogen brittleness is receded. When the milling time reaches 60 h, the average particle size of the two samples is about 2 μm, and the distribution of particles size becomes homogeneous. Effect of Al and Zn additives on the particles size is slight, but Al and Zn additives make the agglomeration of the powders decreased (Figs.2(e) and (f)). This can be attributed to Al and Zn additives acting as lubricating agent, so the welding between Mg and Mg is restricted and the reaction of Mg and H_2 is intensified with the ball continually striking.

3.3 TEM analysis

Fig.3 shows the TEM images of Mg-3Ni-2MnO$_2$ and Mg-3Ni-2MnO$_2$-3Al-Zn samples milled for 60 h, respectively. The average grain size of Mg-3Ni-2MnO$_2$ is estimated to be 8−10 nm and the distribution of the grain is very homogeneous. In comparison, after adding Al and Zn, the average grain size is also estimated to be 8−10 nm, which is in agreement with the XRD results. So, we can conclude that Al and Zn additives do not change the microstructure of nanocrystalline Mg-3Ni-2MnO$_2$.

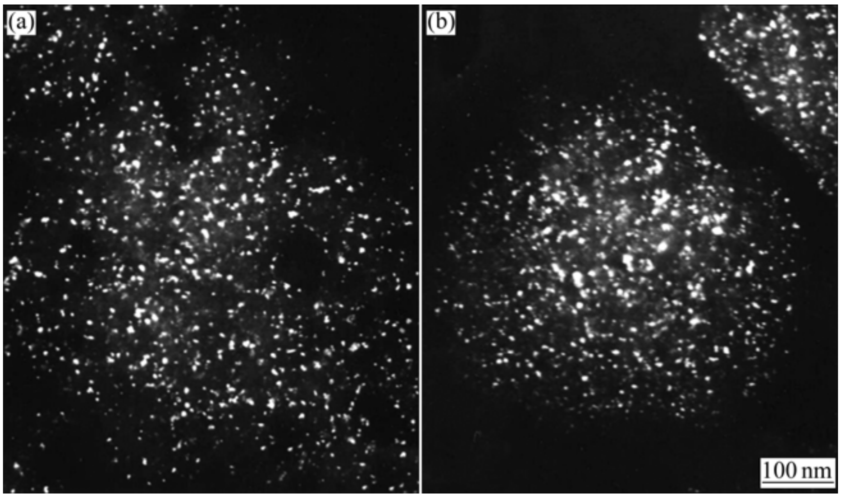

Fig.3 TEM images of Mg-3Ni-2MnO_2 (a) and Mg-3Ni-2MnO_2-3Al-Zn (b) alloy

4 Conclusions

1) The nanocomposite Mg-3Ni-2MnO_2 and Mg-3Ni-2MnO_2-3Al-Zn were made by ball milling process under hydrogen atmosphere. The process of hydrogenation, disproportionation, desorption, and recombination(HDDR) is an effective grain refinement method for magnesium alloys.

2) Al and Zn additives do not change the grain size and the microstructure of nanocrystalline Mg-3Ni-2MnO_2 alloy. The effect of Al and Zn additives on the grain size of Mg-3Ni-2MnO_2 alloy essentially takes place before 20 h and the effect is very slight.

3) Al, and Zn additives can strengthen the property of magnesium alloys on premise of unchanging the microstructure of the materials. The present study provides us a feasibility of producing nano-structured magnesium alloys, based on hydrogenation, disproportionation, desorption and recombination (HDDR) through adding elements to hydrogen storage materials. To obtain excellent nano-crystal magnesium alloys, more factors should be taken into account and further efforts are under way.

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(Edited by YUAN Sai-qian)