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Desorption behaviour and microstructure change of nanostructured hydrided AZ31 Mg alloy powders

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Abstract: In order to optimize the dehydriding process for producing nanocrystalline Mg alloy powders by hydriding-dehydriding treatment, nano-structured as-hydrided Mg-3%Al-1%Zn (AZ31 Mg) (mass fraction) alloy powders were thermally dehydrided at various temperatures from 275 to 375 ℃. The kinetics of hydrogen desorption was examined by hydrogen discharge measurement during dehydriding. The microstructure of the as-hydrided and the subsequently fully dehydrided alloy powders was investigated by X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM), respectively. Both the desorption kinetics and the grain size of the alloy after complete dehydriding were found to be strongly dependent on the processing temperature. The higher the temperature, the faster the desorption, and the more significant the grain growth. When the desorption temperature was raised from 300 to 375 ℃, the time to achieve complete dehydriding was shortened from 190 to 20 min, and the average grain size increased correspondingly from 20 to 58 nm.

Key words: Mg hydride; dehydriding; Mg alloy; nanocrystalline material

1 Introduction

As one category of the lightest metallic structural materials, Mg alloys are gaining increasing importance for applications including aerospace, automotive, materials handling, communication, and portable electronic appliances[1−5]. However, Mg alloys are rarely used for high performance applications due to their relatively poor mechanical strength. In order to exploit the potential of Mg alloys for high performance structural applications, improvement of their mechanical strength is urgently demanded.

Grain refining is a general way to improve the mechanical strength of metallic materials. In most cases, the yield stress, σ_y, can be related to the grain size, d, by the Hall-Petch expression $\sigma_y=\sigma_0+k_y d^{-1/2}$, where σ_0 and k_y are positive constants for a specific material. For Mg alloys, the strengthening by grain refining can be very tempting because of their high k_y values[1, 6]. For example, when the grain size is reduced to 100−200 nm, the $Mg_{97}Zn_1Y_2$ (molar fraction, %) alloy presents a yield strength as high as 610 MPa[7−8].

Powder metallurgy (P/M) is a potential way to prepare nanocrystalline or ultrafine grained bulk alloys. In this process, nanocrystalline or amorphous alloy powders are used. For most Mg alloys, however, it is difficult to produce nanocrystalline alloy powders by means of rapid solidification (RS) due to their physical properties and limitations in thermodynamic aspects. For example, melt-spinning of the Mg-8.5%Al-1.0%Zn (mass fraction) alloy at a wheel speed of 2 200 r/min (35 m/s) only obtain alloy with average grain size of 1−3 μm [9]. Therefore, the search for ways of producing nanocrystalline Mg alloy powders is of great significance.

The process of hydrogenation, disproportionation, desorption and recombination (HDDR) is very effective in grain refining. By this technique, rare earth magnets with fine submicron grains of about 300 nm can be produced directly from as-cast materials[10−11]. Since Mg can absorb hydrogen to form MgH_2 and the reaction is reversible, this technique can be also used to produce submicron grains in Mg alloys, as indicated by

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TAKAMURA et al[12−13].

In an effort to establish a new way to produce nanocrystalline Mg alloy powders, we have recently developed a mechanically assisted hydriding-dehydriding process. It consists of two separate steps: 1) reaction milling of Mg alloy in hydrogen to form nanostructured Mg hydride, and 2) desorption of the nanostructured as-hydrided alloy powders. In our previous study, the validity of this new process has been well demonstrated[14]. The present work reports an investigation on the kinetics and microstructure change of nanostructured hydrided AZ31 Mg alloy powders upon thermally dehydriding, in an effort to optimize the processing parameters.

2 Experimental

Nanostructured hydrided AZ31 Mg alloy powders were prepared by the mechanically assisted hydriding technique, i.e., reaction milling in hydrogen. The starting material was the commercially available as-cast AZ31 Mg alloy. Before it was used for hydriding, the alloy was solutionised at 400 ℃ for 6 h to obtain a homogeneous Mg(Al, Zn) solid solution microstructure, and then crushed into coarse powders by using a mechanical hammer. The hydriding of the alloy powders was achieved by room-temperature reaction milling in hydrogen for 80 h. The ball-mill used was a planetary type QM-DY4. During milling, the hydrogen pressure in the vial was kept above 0.5 MPa. The ball to powder mass ratio was 120:1, and the mill shaft rotation was 400 r/min. By this process, the alloy can be fully hydrided, forming nanostructured MgH_2 phases with an average size of no more than 10 nm[14−15].

The desorption of the nanostructured hydrided AZ31 Mg alloy powders was performed by using a home-made apparatus consisting of a closed volume set up with digital vacuum/pressure gauges, an electric heating and temperature monitoring system, and a vacuum pumping system. The mass of the powder sample for each run of desorption treatment was (0.5±0.01) g. The hydrogen was desorbed from the sample kept at a constant test temperature in the initially evacuated volume with a vacuum of 1×10^{-2} Pa. To investigate the effect of temperature on the desorption kinetics, the desorption was carried out at various temperatures form 275 ℃ to 375 ℃. The morphology of the powder samples before and after desorption treatment was observed by scanning electron microscopy (SEM). The phase and microstructure change due to the desorption treatment were characterized by XRD and TEM, respectively.

3 Results and discussion

3.1 Hydrogen desorption kinetics

Fig.1 shows the hydrogen desorption kinetics curves of the nanostructured hydrided AZ31 Mg alloy powders at various temperatures. It is seen that the hydrogen desorption rate is strongly dependent on the desorption temperature. The higher the temperature, the larger the hydrogen desorption rate. At 275 ℃, the desorption was rather slow, and only about 30% of the hydrogen in the hydrided alloy was released after desorption for 200 min. Indeed, we found that a complete dehydriding could not be achieved even after desorption treatment for 12 h at this temperature. However, at 375 ℃, a complete dehydriding was achieved upon desorption treatment for 20 min. Overall, the desorption kinetics of the nanostructured hydrided AZ31 Mg alloy powders was well comparable to that of the ball-milled nanocrystalline MgH_2 powders reported by YONKEU et al[16]. By hydrogen discharge measurement, the time needed to achieve complete dehydriding at 300, 325, 350 and 375 ℃ was found to be about 190, 65, 40 and 20 min, respectively. The accelerated hydrogen desorption rate with increasing temperature can be attributed to the enhanced rate coefficient for both the decomposition reaction of MgH_2 to Mg and the diffusion of H atoms in the Mg lattice. This is due to the positive effect of temperature increase on the corresponding Arrhenius factors, $\exp(-E_{dec}/RT)$ and $\exp(-E_{dif}/RT)$, the expressions of decomposition rate coefficient, $k= k_0\exp(-E_{dec}/RT)$, and diffusion coefficient, $D=D_0\exp(-E_{dif}/RT)$, where E_{dec} and E_{dif} are the activation energies for the MgH_2 decomposition and the H is the diffusion in the Mg lattice, respectively.

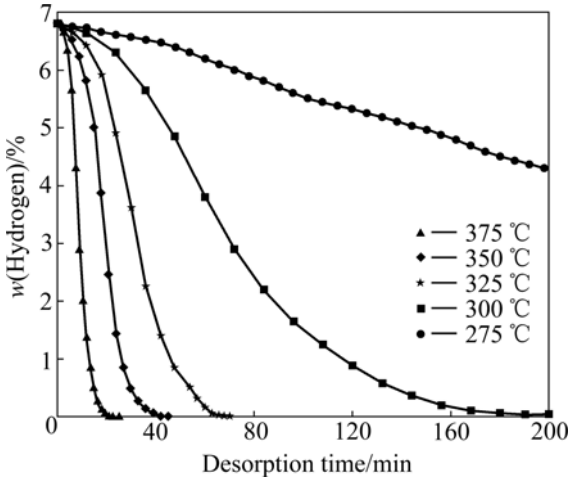

Fig.1 Desorption kinetics of mechanically assisted hydrided AZ31 Mg alloy powders

3.2 XRD analysis

Fig.2 shows the XRD patterns of both the as-hydrided and the subsequently dehydrided AZ31Mg alloy powders by desorption treatment at various temperatures. For the as-milled hydrided alloy powders, only MgH_2 diffraction peaks were observed, suggesting that the Mg phase was completely transformed into MgH_2 after mechanically milling in hydrogen for 80 h by the solid-gas reaction[14]:

$$Mg(M)+H_2 \rightleftharpoons MgH_2+M \quad (1)$$

Based on the XRD results shown in Fig.2, the average grain size of both the MgH_2 and the Mg phase was estimated by the broadening of X-ray diffraction peaks. It was revealed that the average grain size of the MgH_2 phase in the as-hydrided state was about 8 nm, which is a bit finer than the value of 10 nm reported in our earlier studies[14−15], possibly due to the fact that more intensive milling parameters and a longer period of milling time were used in the present study. After desorption treatment, the average grain size of Mg in the completely dehydrided sample was in the range of 20−58 nm, depending upon the temperature used for the desorption treatment, as shown in Fig.3. Though the final Mg phase was in a grain size coarser than the starting MgH_2 phase due to grain growth during dehydriding, it was still typically nanocrystalline. From Fig.3, it is seen that the higher the applied desorption temperature, the more significant the growth of the newly formed Mg grains during dehydriding, despite the fact that the time needed for achieving complete dehydriding is much shorter at a higher temperature. This suggests that temperature is the key factor which dominates the grain growth of the newly formed Mg during dehydriding, owing to the positive effect of temperature on the

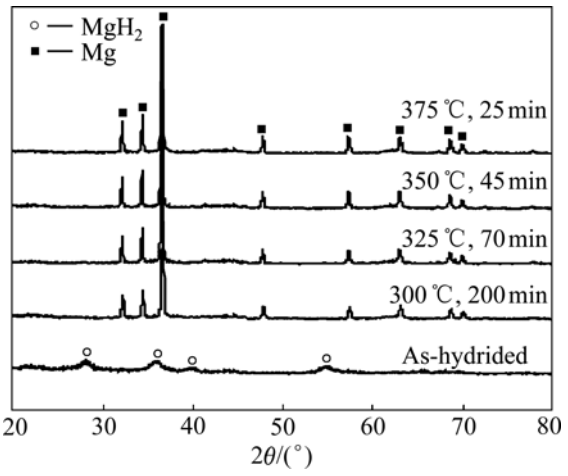

Fig.2 XRD patterns of as-hydrided and subsequently dehydrided AZ31 Mg alloy powders

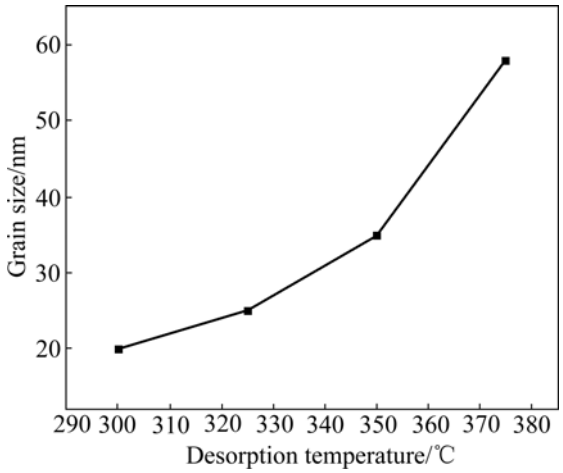

Fig.3 Dependence of Mg crystallite grain size on desorption temperature

Arrhenius factor $\exp(-E_g/RT)$ in the grain growth equation, $d^n-d_0^n=k_0\exp(-E_g/RT)t$, where t is time and E_g is the activation energy for grain growth. With the view of achieving a moderate dehydriding kinetics and at the same time preventing the Mg grains from overgrowth, the optimal desorption temperature is around 325 ℃.

3.3 SEM and TEM observation

Fig.4 shows SEM morphologies of both the as-hydrided and the subsequently dehydrided AZ31 Mg alloy powders by desorption treatment at 325 ℃ for 70 min. The as-hydrided powders were featured by individual submicron-sized particles with a size of 0.5−1 μm and some agglomerates consisting of such submicron-sized particles (Figs.4(a) and (b)). After full dehydriding, though it seems that a small fraction of individual submicron-sized particles agglomerated to form larger composite particles, little change could be observed in both the morphology and the size of most powders (Figs.4(c) and (d)). This suggests that, in general, the thermal dehydriding process carried out in the present study will not lead to sintering or severe agglomeration of the powder particles.

Fig.5 shows representative TEM images and corresponding electron diffraction patterns of the mechanically assisted hydrided and the subsequently thermally dehydrided alloy samples, respectively. In the as-hydrided state (Figs.5(a) and (b)), MgH_2 was identified to be the exclusive phase, and the grain size was about 8 nm in average. After desorption treatment at 325 ℃ for 70 min, the as-hydrided alloy was fully dehydrided with the formation of a single Mg phase, and the size of most Mg grains was estimated to be about 25 nm (Figs.5(c) and (d)). Obviously, TEM observations

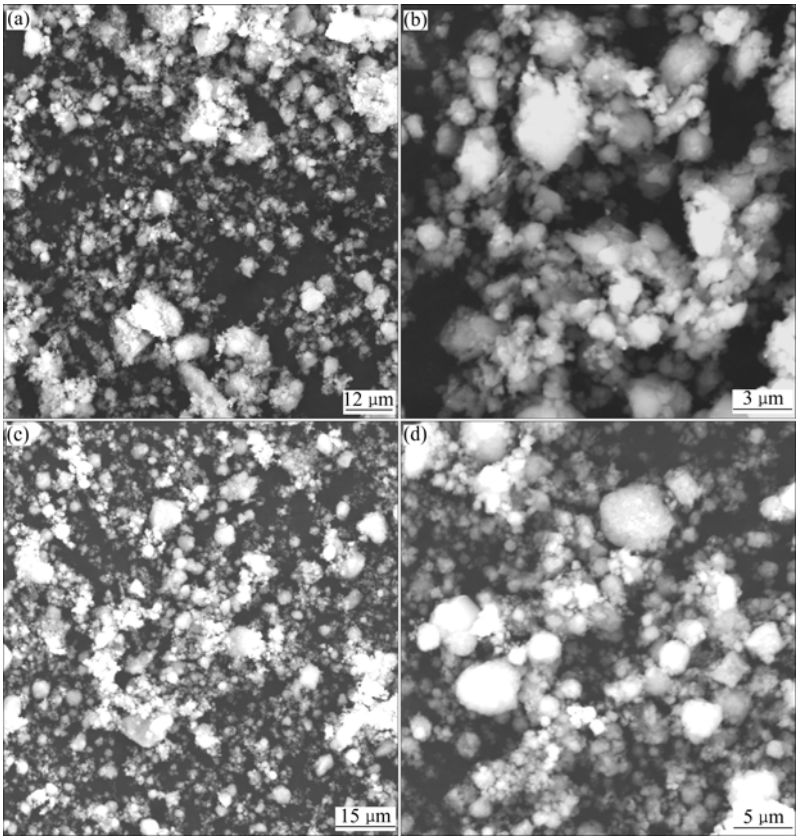

Fig.4 SEM images of as-hydrided and subsequently dehydrided AZ31 Mg alloy powders: (a) and (b) As-hydrided; (c) and (d) Dehydrided at 325 ℃ for 70 min

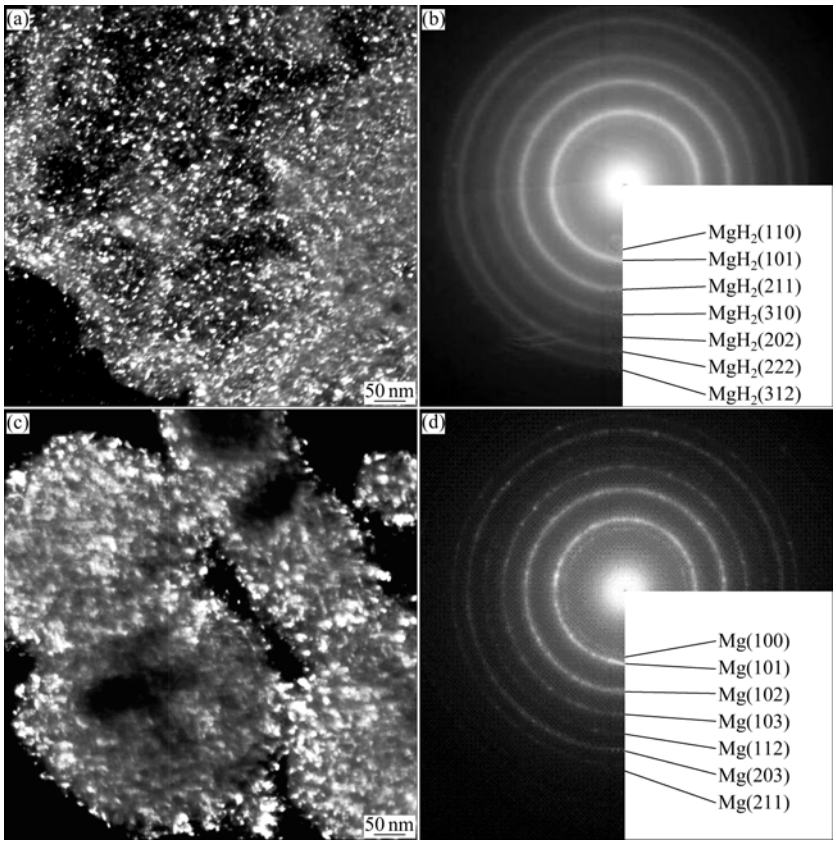

Fig.5 TEM images and diffraction patterns of as-hydrided and subsequently dehydrided AZ31 Mg alloy powders: (a) and (b) As-hydrided; (c) and (d) Dehydrided at 325 ℃ for 70 min

well support the XRD results.

4 Conclusions

1) The desorption kinetics of nanostructured hydrided AZ31 Mg alloy powders is strongly dependent on the processing temperature. The higher the temperature, the larger the desorption rate. The time needed to achieve complete dehydriding at 300, 325, 350 and 375 ℃ was found to be 190, 65, 40 and 20 min, respectively.

2) The mechanically assisted hydrided AZ31 Mg alloy powders were featured by a single MgH_2 phase microstructure with an average grain size of about 8 nm. By subsequent dehydriding at temperature in the range of 300−375 ℃, nanocrystalline AZ31 Mg alloy powders could be obtained, with the average size of newly formed Mg grains of 20−58 nm.

3) To prevent Mg grains from overgrowth and achieve fast desorption kinetics, the optimal processing temperature is around 325 ℃. By dehydriding at 325 ℃ for 70 min, the nano-structured hydrided AZ31 Mg alloy can be completely dehydrided, with the formation of nanocrystalline Mg with average grain size of about 25 nm.

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