Journal of Alloys and Compounds 356–357 (2003) 804–808

Journal of ALLOYS AND COMPOUNDS

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Grain size refinement in Mg–Al-based alloy by hydrogen treatment

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Received 10 June 2002; accepted 15 November 2002

Abstract

The present paper describes the grain size refinement of AZ31 alloys by means of the HDDR process. Hydrogenation was carried out at 250~450 °C under a hydrogen pressure of 7 MPa for 24~36 h. Upon hydrogenation, the disproportionation reaction occurred, leading to the formation of MgH_2, $Mg_{0.42}Al_{0.58}$, and Al phases. In the subsequent desorption process, the three phases were recombined, and the AZ31 alloy was recovered. As a result of the HDDR process, the grain size of the AZ31 alloy powders was reduced from 50~300 μm to about 100 nm in the case of the heat treatment at 350 °C under a hydrogen pressure of 7 MPa for 24 h. The grain size tended to be increased with increasing process temperatures. In addition, the HDDR process was also applied to AZ31 alloy plates. By means of the HDDR process at 450 °C, the grain size was reduced to less than 500 nm, while the layer thickness being treated was limited to the range of about 20 μm from the surface after 36 h at 7 MPa pressure of H_2.

Keywords: Gas–solid reactions; X-Ray diffraction; Transmission electron microscopy; Grain-size refinement; HDDR phenomena

1. Introduction

Mg-based alloys have attracted attention because of their lightweight and high strength. In fact, Mg-based alloys, especially those based on Mg–Al–Zn (AZ-series), have been used in a variety of industrial fields, such as the casing of portable electronic devices and automobile parts. To enlarge the usage of Mg-based alloys, further improvements of their mechanical properties including ductility and strength are being demanded. Grain size refinement is obviously one of the answers. Among a number of grain refining techniques, equal channel angular pressing (ECAP) is quite effective for Mg-based alloy systems, and can lead to a grain size of about 1 μm [1]. However, since it is difficult to obtain fine submicron grains with this method, the development of new approaches is required.

As already known, hydrogen treatment, more precisely, the hydrogenation–disproportionation–desorption–recombination (HDDR) process is one of the most promising approaches to the task of reducing the grain size to submicron values. By using this technique, for example, rare-earth magnets with submicron-sized grains have been successfully developed [2–8]. Recently, we have found that the HDDR process can also be applied to the Mg–Al system, and can be applied to the grain size refinement of AZ31 solid-solution alloys (Mg–3 mass% Al–1 mass% Zn) [9,10]. This present paper describes a detailed consideration of the HDDR process for the AZ31 alloy, and the effect of process temperatures on the resultant grain size. In addition, the feasibility of utilizing the HDDR process for the AZ31 alloy with a plate-like shape is examined.

2. Experimental procedures

AZ31 solid-solution alloys (Mg–3 mass% Al–1 mass% Zn) were used as specimens. After removing the oxide scale from the surface of AZ31 alloy plates by using SiC paper, ultrasonic washing was carried out in acetone. The plates were then cut and ground into coarse powders with a diameter of less than 100 μm in an Ar-filled grove box. In addition to the powder, plate-like samples with dimensions of 8 mm×8 mm×1.5 mm were also subjected to the HDDR treatment. The hydrogenation was carried out at 250~450 °C under a hydrogen pressure of 7 MPa. Dehydrogenation was performed at the same temperature range by using a rotary oil-pump.

The hydrogen absorption–desorption behavior of the AZ31 alloy was measured by a volumetric technique using

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0925-8388/03/$ – see front matter
doi:10.1016/S0925-8388(03)00091-4

pressure–composition–temperature (*P–C–T*) apparatus. The phase changes accompanying the HDDR process was monitored by powder X-ray diffraction (XRD), and microstructural observations were performed by optical microscopy (OM) and transmission electron microscopy (TEM). For OM observations, 2,4,6-trinitrophenol alcoholic solution was used for etching the sample surface.

3. Results and discussion

To investigate the HDDR process in the AZ31 alloy, initially, the hydrogenation conditions were examined. As is widely known, in order to hydrogenate Mg and Mg-based alloys, relatively high temperatures of over 300 °C and long reaction times are required because of its slow reaction rate. Fig. 1 shows pressure–concentration isotherms of the AZ31 alloy powders taken at 350 °C. As expected, the AZ31 alloy was capable of absorbing hydrogen of about 7.4 mass% at 350 °C, and a plateau regime was observed at around 0.6 MPa for the hydrogenation and dehydrogenation processes. This hydrogen content was almost equal to that of pure Mg, indicating that the AZ31 alloy was fully hydrogenated. To ensure the hydrogenation of whole samples, in this study the hydrogenation was performed at 350 °C under 7 MPa for 24 h.

The phase change during the hydrogenation process was observed by XRD. Fig. 2 shows the XRD patterns of the AZ31 alloy before and after hydrogenation at 350 °C under 7 MPa for 24 h. As reported in Ref. [10], the AZ31 alloy exhibited a disproportionation reaction resulting in the formation of MgH_2, $Mg_{0.42}Al_{0.58}$ (often designated as R or ε), and Al phases. The lattice constants of the resultant MgH_2 ($a=0.4520$ and $c=0.3023$ nm) was, within experimental errors, found to be the same as those of pure MgH_2 ($a=0.4520$ and $c=0.3022$ nm). This indicates that most of the solute atoms (Al and Zn) in the AZ31 alloy were expelled from the matrix phase during hydrogenation. Even though Zn or Zn-containing phases should have also been formed during hydrogenation, such phases were not detected by XRD analysis because of the small amount of Zn (1 mass%). The XRD showed that the AZ31 alloy was decomposed into a hydride and Al-containing phases that were unable to form hydrides, in other words, hydrogenation–disproportionation reactions occurred in the

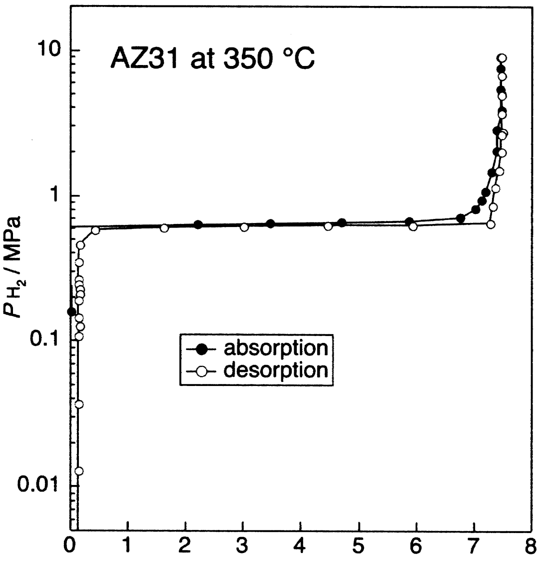

Fig. 1. Pressure–concentration isotherm of AZ31 alloy powders at 350 °C.

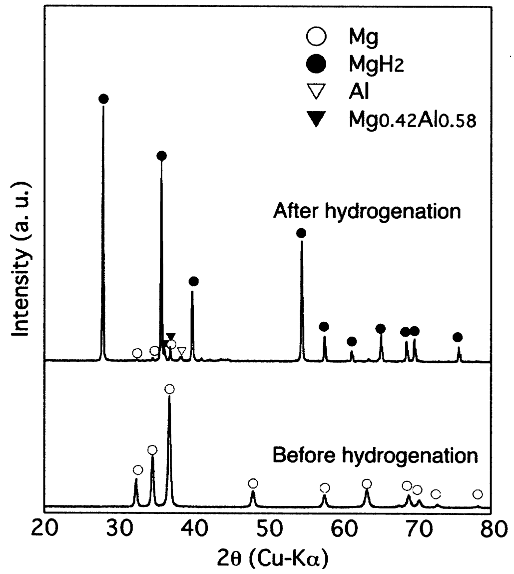

Fig. 2. XRD patterns of the AZ31 alloy before and after hydrogenation at 350 °C under 7 MPa for 24 h.

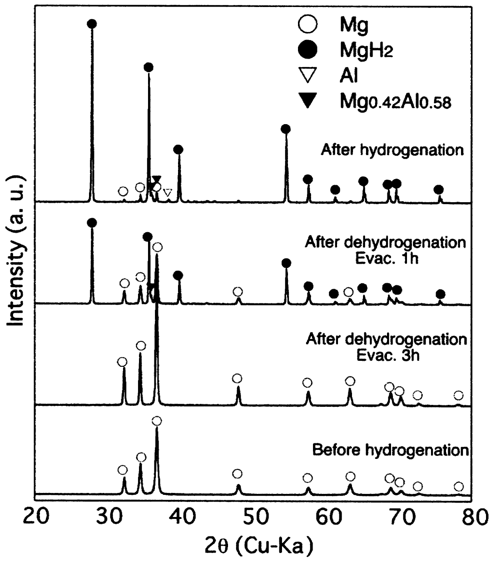

Fig. 3. XRD patterns of the AZ31 alloy dehydrogenated at 350 °C for 1 or 3 h.

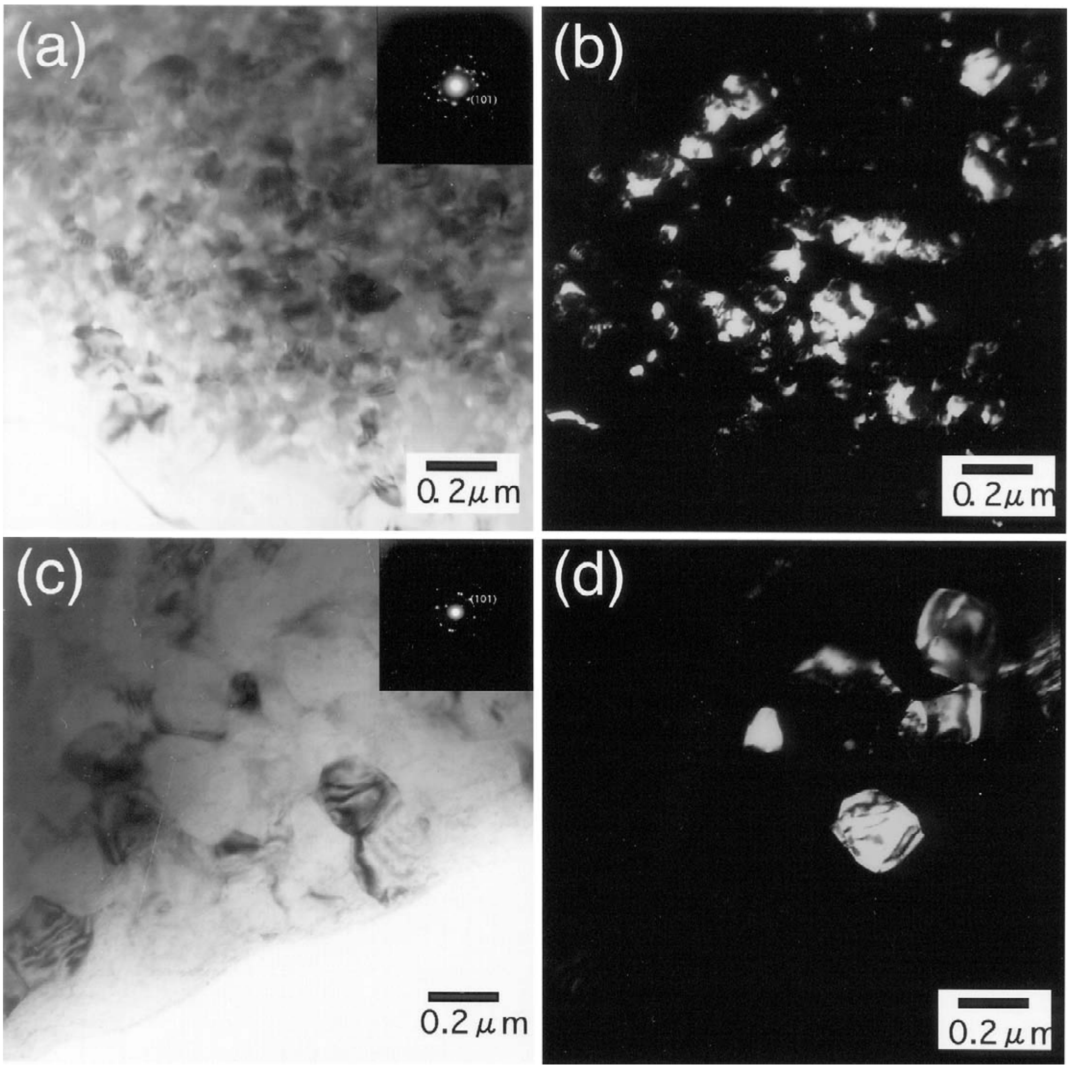

Fig. 4. TEM micrographs of the HDDR-treated AZ31 alloy. (a) and (b) correspond to bright and dark [Mg(101)] images taken from the sample hydrogenated at 350 °C under 7 MPa for 24 h followed by dehydrogenation at 350 °C. (c) and (d) are bright and dark [Mg(101)] images of samples hydrogenated at 450 °C, 7 MPa for 24 h followed by dehydrogenation at 450 °C, respectively.

AZ31 alloy. The hydrogenation–disproportionation reactions of the AZ31 alloy were also investigated at every 50 °C from 250 to 450 °C. Except for the sample treated at 250 °C, the same reactions as above were confirmed to occur. According to the Mg–Al binary phase diagram, the $Mg_{0.42}Al_{0.58}$ phase can be formed by a peritectic reaction of Mg_2Al_3 (β) and $Mg_{17}Al_{12}$ (γ) in a limited temperature range of 320~370 °C. However, in this study, this phase was found to exist in the samples hydrogenated at 300 °C and over 400 °C. This suggests that the $Mg_{0.42}Al_{0.58}$ phase

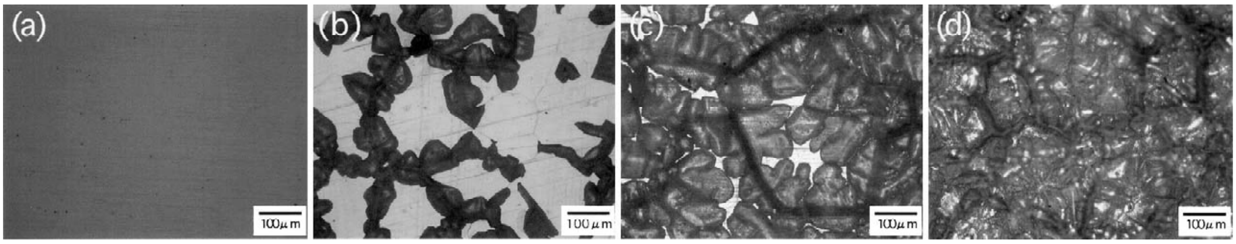

Fig. 5. Optical micrographs of hydrogenated AZ31 alloy plate. (a) Before hydrogenation. (b)~(d) From samples hydrogenated at 450 °C under 7 MPa for 12, 24, and 36 h, respectively.

is a *meta*-stable phase that can be formed by hydrogenation.

The hydrogenated AZ31 alloy was subsequently evacuated to remove hydrogen from the hydride phase. Fig. 3 shows the XRD patterns taken from the AZ31 alloy dehydrogenated at 350 °C for 1 or 3 h. After evacuation for 1 h, the Mg-rich metallic phase started to recover, and the Al phase disappeared. However, the $Mg_{0.42}Al_{0.58}$ phase still remained in this early dehydrogenation stage. After evacuation for 3 h, however, $Mg_{0.42}Al_{0.58}$ had vanished, and the AZ31 alloy was totally recovered. Since the lattice constants of the recovered AZ31 alloy ($a=0.3198$ and $c=0.5195$ nm) was, within the experimental errors, the same as those of the original AZ31 alloy ($a=0.3199$ and $c=0.5195$ nm), the dehydrogenation–recombination reactions were considered to be accomplished by evacuation for 3 h. These observations indicate that the HDDR process takes place for the AZ31 alloys. The HDDR steps observed in the AZ31 alloy can be summarized as follows: during hydrogenation, Al solute was expelled from the AZ31 alloy in the process of forming MgH_2. At this stage, in addition to Al, the $Mg_{0.42}Al_{0.58}$ phase was formed. Upon dehydrogenation, the initial Mg metallic phase was recovered, and Al atoms were dissolved into the Mg matrix phase. At the final stage of the recombination process, $Mg_{0.42}Al_{0.58}$ was incorporated into matrix.

Fig. 4a and b show TEM micrographs of the HDDR-treated AZ31 alloy. The sample was hydrogenated at 350 °C under 7 MPa for 24 h followed by dehydrogenation at the same temperature for 3 h in vacuum. The electron diffraction pattern taken from a selected area of approximately 1 μm in diameter consisted of a number of spots which were attributed to grains with different orientation. From a dark field image taken from a Mg(101) diffraction spot, the grain size was found to be reduced to about 100 nm from 50~300 μm for the original AZ31 alloy. This observation indicates that the HDDR treatment is effective in refining the grain size of the AZ31 alloy. The TEM observations were also conducted for the AZ31 alloy HDDR-treated at a higher temperature of 450 °C. Fig. 4c and d show the TEM micrographs of the sample treated at 450 °C. Even though a certain level of grain growth occurred, the grain size was still around 200 nm. This result suggests that the HDDR-treated AZ31 alloy powders could be shaped into a plate or rod by using hot extrusion without significant grain growth. The effect of hydrogenation at 350 °C followed by dehydrogenation at 450 °C and vice versa was also examined. From TEM observations, the grain size of both samples was found to be around 100~200 nm, and there was no large difference in the microstructure.

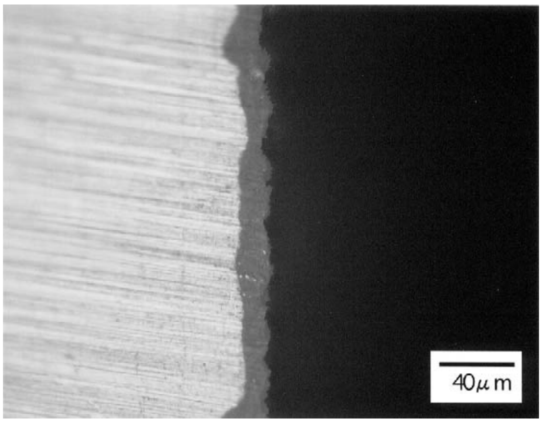

Fig. 6. Optical micrograph of a cross section of the AZ31 alloy plate hydrogenated for 36 h at 450 °C and 7 MPa of H_2.

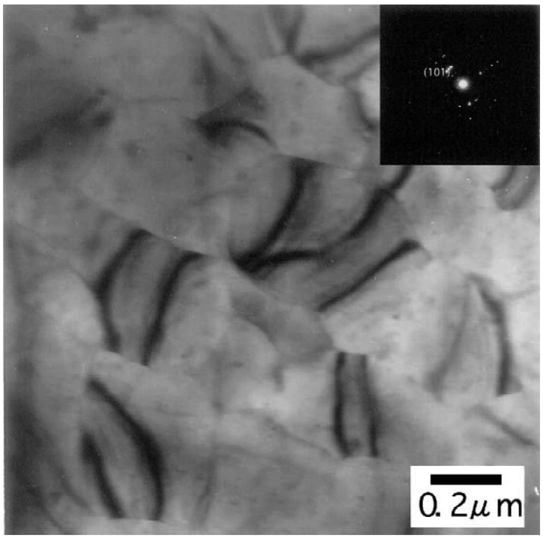

Fig. 7. TEM micrographs taken from the HDDR-treated AZ31 alloy plate, which was hydrogenated at 450 °C under a hydrogen pressure of 7 MPa for 36 h, and dehydrogenated at the same temperature for 30 min.

All the experiments mentioned above were conducted for the AZ31 alloy powders to ensure full hydrogenation and dehydrogenation, and it was also suggested that a shape-forming process such as hot extrusion may be employed using the HDDR-processed material. However, it is more preferable if this HDDR process can be directly adopted for the microstructural evolution of the AZ31 alloy plate. Therefore, the feasibility of utilizing the HDDR process for AZ31 alloy plates was investigated. Fig. 5 shows optical micrographs of an AZ31 alloy plate hydrogenated at 450 °C under 7 MPa for 0~36 h. It was found that a hydride phase (dark contrast region) started to be formed in the vicinity of the grain boundaries (Fig. 5b), and with time, it moved towards the interior of grains. After 36 h, the surface of the alloy was fully covered with the hydride phase (Fig. 5d). The formation of the hydride phase was also confirmed by XRD. Fig. 6 shows a cross section of the AZ31 alloy plate hydrogenated for 36 h. The hydride layer of 20 μm in thickness was found to be formed. Subsequently, dehydrogenation at 450 °C was carried out, and from the XRD analyses, it could be concluded that evacuation for 30 min was enough to recover the metallic phase for this specimen.

Fig. 7 shows TEM micrographs taken from the HDDR-treated AZ31 alloy plate. The grain size appeared to be increased compared with that shown in Fig. 4c. However, even though the hydrogenation process was performed for 36 h, it was still less than 500 nm. Thus it can be stated that the HDDR process can be applied to refining the grain size of the surface of the AZ31 alloy plates, while the layer thickness being treated was limited to the range of about 20 μm at this time.

4. Conclusions

Grain size refinement of an AZ31 alloy by the HDDR process has been studied. Upon hydrogenation, the disproportionation reaction leading to the formation of MgH_2, $Mg_{0.42}Al_{0.58}$, and Al phases occurred. In the subsequent desorption process, the three phases were recombined, and the AZ31 alloy was recovered. As a result of the HDDR process, the grain size of AZ31 alloy powders was reduced to about 100 nm in the case of the heat treatment at 350 °C under a hydrogen pressure of 7 MPa for 24 h. The grain size tended to be increased with increasing process temperatures. However, a fine grain size of around 200 nm was still obtained even at 450 °C. From this, the HDDR process was found to be an effective approach to refining the grain size of AZ31 alloys. In addition, the HDDR process was also applied to AZ31 alloy plates by hydrogenation at 450 °C, 7 MPa for 36 h; under these conditions, the surface of the AZ31 alloy plate was fully covered with the hydride phase. After the dehydrogenation process, the grain size of the surface layer was reduced to less than 500 nm. The surface layer thickness was limited to the range of about 20 μm from the surface.

Acknowledgements

This work has been supported in part by Grant-in-Aids for Scientific Research on the Priority Group of New Protium Function and on the Priority Group of Platform Science and Technology for Advanced Magnesium Alloys from the Ministry of Culture, Science, and Education.

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