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Producing nanocrystalline bulk Mg–3Al–Zn alloy by powder metallurgy assisted hydriding–dehydriding

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ABSTRACT

Nanocrystalline bulk Mg–3Al–Zn alloy with an average grain size of 48 nm has been prepared by powder metallurgy assisted hydriding–dehydriding. Evolutions of nanograined structure powders and bulk alloy have been investigated by TEM, SEM and XRD, respectively. The results showed that by milling in hydrogen for 60 h, as-hydriding powder possessed an average grain size of 5.9 nm. After a subsequent process of desorption-recombination treatment (at 350 °C) and consolidation process (extruded at 200 °C) resulted in bulk samples with an average crystallite size of 48 nm and MgH_2 was fully turned into Mg. The consolidated samples of 60 h milled powder had a final density of 1.77663 ± 0.006 g/cm^3, which corresponded to 97.57 ± 0.3% of theoretical density. The highest microhardness of the nanocrystalline bulk alloy reached about 872.5 MPa, which is about three times higher than that of the coarse-grained AZ31.

1. Introduction

Nanocrystalline and ultrafine-grained materials have received considerable attention within the last decade, owing to their improved properties as compared with conventional coarse-grained materials [1–4]. Following Hall-Petch relationship, it has been shown that grain size refinement is one of the most effective methods for improving strength of the materials. For magnesium alloys, the strengthening due to grain refining can be very attractive because of their high K values [5,6]. For example, when the grain size was reduced to about 500 nm, $MgZn_{3.3}Y_{0.43}$ alloy showed a yield stress of 410 MPa with a 12% elongation [3]. In the recent years, new efforts were devoted to grain refinement of magnesium alloy [7–10]. Several approaches, such as equal channel angular extrusion (ECAE) [11], friction stir processing (FSP) [3], accumulative roll bonding (ARB) [12], high-pressure torsion (HPT) [13] and powder metallurgy (PM) [14] have been applied to the grain refinement of bulk magnesium alloys. However, in most cases, the grain size of final structure was still in the micrometer or submicrometer range. Even for EX-ECAP, the resulting microstructure still can never be refined to the nanoscale. Even though nanoscaled magnesium alloy materials can be produced, they were restrained in a thin layer form or precipitate hardened magnesium alloys (such as AZ91). But for pure magnesium or solute solution hardened magnesium alloys (such as AZ31) with a low content of alloying elements, it is difficult to achieve a nanostructure due to the rapid growth kinetics of the single-phase grains. The process of hydrogenation, disproportionation, desorption, and recombination (HDDR) is a very effective method in grain refining. The incorporation of HDDR with ball milling gave rise to a new way to produce nanocrystalline Nd–Fe–B magnets [15–17], attributed to the fact that the mechanically driven hydrogenation-disproportionation reaction took place at ambient temperature and it helped to prevent the as-disproportionated microstructure from grain growth. $Mg(M) + H_2 \leftrightarrows MgH_2 + M$ is a reversible reaction, where M represents the solute element in magnesium, the hydriding–dehydriding technique for grain refining should be also applicable to magnesium alloys. The present paper reported an investigation on the possibility of developing bulk nanocrystalline microstructure of Mg–3Al–Zn alloys via powder metallurgy assisted hydriding–dehydriding.

2. Experimental procedures

Nanocrystalline alloy powders were prepared by high energy mechanical ball milling from a mixture of Mg powder (99% pure, 325 mesh), Zn powder (99% pure, 325 mesh) and Al powder (99.5% pure, 325 mesh) under high purity hydrogen. The Mg, Al and Zn powders were mixed in stainless vial in mass ratio to 96:3:1 (wt.%). The mechanical ball milling was carried out with a QM21SP4 planetary ball milling machine made by Nan-jing University and the balls were stainless steel. The ball to powder mass ratio was 40:1 and the mill rotation was 360 rpm. The weight of alloy powders for each milling batch was 20 g. Because the samples absorbed hydrogen in the mechanical ball milling process, the hydrogen pressure cannot keep constant. The hydrogen pressure of the vials must be recharged to 1 MPa at intervals. To prevent the alloy powders from oxidation, the experimental powder materials were always kept in a glove box filled with pure argon. During desorption-recombination treatment and consolidation process, the powders were put into Al container of 35 mm in diameter and about 65 mm in length to avoid oxidation. An Al plug of 20 mm in diameter and 19 mm in length was designed to ensure the densification

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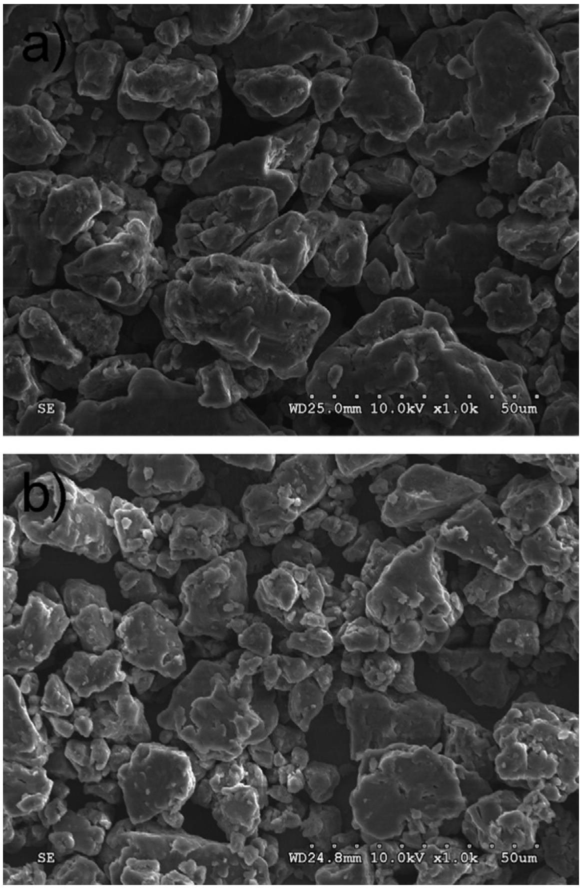

Fig. 1. SEM micrographs of Mg–3Al–Zn mixture after ball milling as a function of milling time: (a) 20 h and (b) 60 h.

of the powder. The Al container filled with as-disproportionated powders were carried out desorption-recombination treatment at 350 °C in a vacuum furnace. When the temperature of furnace reached 350 °C, the desorption-recombination of the as-disproportionated powders took place. The vacuum degree of furnace began to decrease, because of the hydrogen desorption behavior of the powders. When the vacuum furnace under vacuum degree better than 1×10^{-2} Pa, the plug was pressed until it fully went into the Al container. In order to further densify the sintered samples, they were extruded at 200 °C, under an extrusion ratio 6.25 and an extrusion rate 22 mm/s using graphite as lubricant. In order to study the desorption-recombination behavior of as-disproportionated powders, differential scanning calorimetry (DSC) were performed up to 500 °C under argon atmosphere at a heating rate of 20 °C/min. Microstructure characterization of the powder and bulk alloys were observed by XRD, SEM and TEM, respectively. Density (ρ) measurements of the bulk alloys were performed in accordance with Archimedes' principle. Four randomly selected extruded rod samples were tested and the average density was calculated. Distilled water was used as the immersion fluid. The samples were weighed using an ESJ200-4 electronic balance, with an accuracy of ±0.0001 g. Vickers hardness tests were conducted on the cross section plane using a Vickers indenter with a 1 kg load for 15 s.

3. Results and discussion

3.1. Structure and grain size of the powder

The SEM images for the powders milled in hydrogen atmosphere for 20 and 60 h are shown in Fig. 1. During the initial milling period, the particle size of the powder is distributed from a few μm to a few tens of μm. Increasing milling time to 60 h, the average particle size in the observed region rapidly decreases to about 10–20 μm. From the SEM observations, we can find that, with increasing of milling time, the structures of as-milled powders become more and more homogenous and the particle size become smaller and smaller. However, though ball milling was performed at the room temperature, with increasing of milling time to 60 h, as shown in Fig. 1(b), the milled particles tend to form agglomerates due to cold welding.

The dark field TEM micrographs and selected area electron diffraction (SAED) pattern, obtained from region with a diameter of 800 nm, for the Mg–3Al–Zn powders milled of 20 h and 60 h in hydrogen atmosphere are shown in Fig. 2(a) and (b). The corresponding grain size distributions for these two cases are shown in Fig. 2(c) and (d). As shown in Fig. 2(a) and (b), microstructures are sufficiently homogenous for the two milling time powders, after 20 h milling, the nanostructured powders are mainly composed of equiaxed grains of 15–40 nm surrounded by a few smaller grains (<10 nm) and some larger ones about 45–50 nm. Increasing milling time to 60 h, the average grain size decreases rapidly to about 6 nm, even though there are also some larger grains. The grains and the grain boundaries are clearly observed for the two milling time powders. The SADP taken from the as-milled alloy exhibits the rings of diffracted spots, indicating the presence of grain boundaries with high angle of misorientation. Fig. 2(c) and (d) shows the grain size distribution of the milled powder for 20 h and 60 h respectively, which is summarized from measuring 200 grain diameters in dark field images. From Fig. 2(c), we can see that the grain sizes are mostly scattered from less than 15 to 35 nm, and more than 80% of the grains are refined to less than 35 nm. The average grain size of powder milling for 60 h is 5.9 nm. The grain size value in this study is comparable with the literature data reported by Ref. [18]. An average grain size of 8–10 nm was reported in their study, when the cast AZ31 was milled 60 h in hydrogen atmosphere, the ball to powder mass ratio was 100:1 and the mill shaft rotation was 375 rpm.

3.2. DSC analysis

Fig. 3 shows the DSC curves of the nano-structured as-disproportionated Mg–3Al–Zn powders obtained by milling for 20 and 60 h. It can be seen that, in the temperature range from 200 to 425 °C, there are two well-pronounced endothermic peaks in the DSC curve for the two milling time powders. This suggests that hydrogen desorption from the nanostructured as-disproportionated magnesium alloy powders occurs in two stages. The first stage corresponds to the endothermic peak between 250 and 255 °C, which can be attributed to the hydrogen desorption associated with both the partial dehydrogenation of the magnesium and the dehydrogenation of hydrogenated nanocrystalline grain boundaries, which are at least hundreds of times more than in the conventionally disproportionate alloy. The second stage corresponds to the endothermic peak between 280 and 400 °C, which indicates the full de-hydriding of the magnesium alloy. In addition, the DSC curve in Fig. 3 shows an exothermic peak at about 260 °C, which can be interpreted as the release of strain energy accumulated in the alloy powders due to intensive milling. The temperature of endothermic peaks for 60 h milling powders is a little higher than that of 20 h ones, this maybe can attribute to 60 h powders absorbing more hydrogen. Based on the DSC analysis, the desorption-recombination processing temperature for the as-disproportionated powders can be chosen as 350 °C.

3.3. Structure and grain size of bulk alloy

Fig. 4 shows the XRD patterns of the Mg–3Al–Zn alloy. Fig. 4(a) and (b) are powders subject to disproportionation for 20 and 60 h; Fig. 4(c) and (d) are the as-extruded material for these two cases, respectively. From Fig. 4(a) and (b), it can be clearly seen that the intensity of the diffraction peaks of magnesium phase is reduced and the width of peaks is increased with the increasing of milling time. At the same time, the intensity and the width of the peaks of

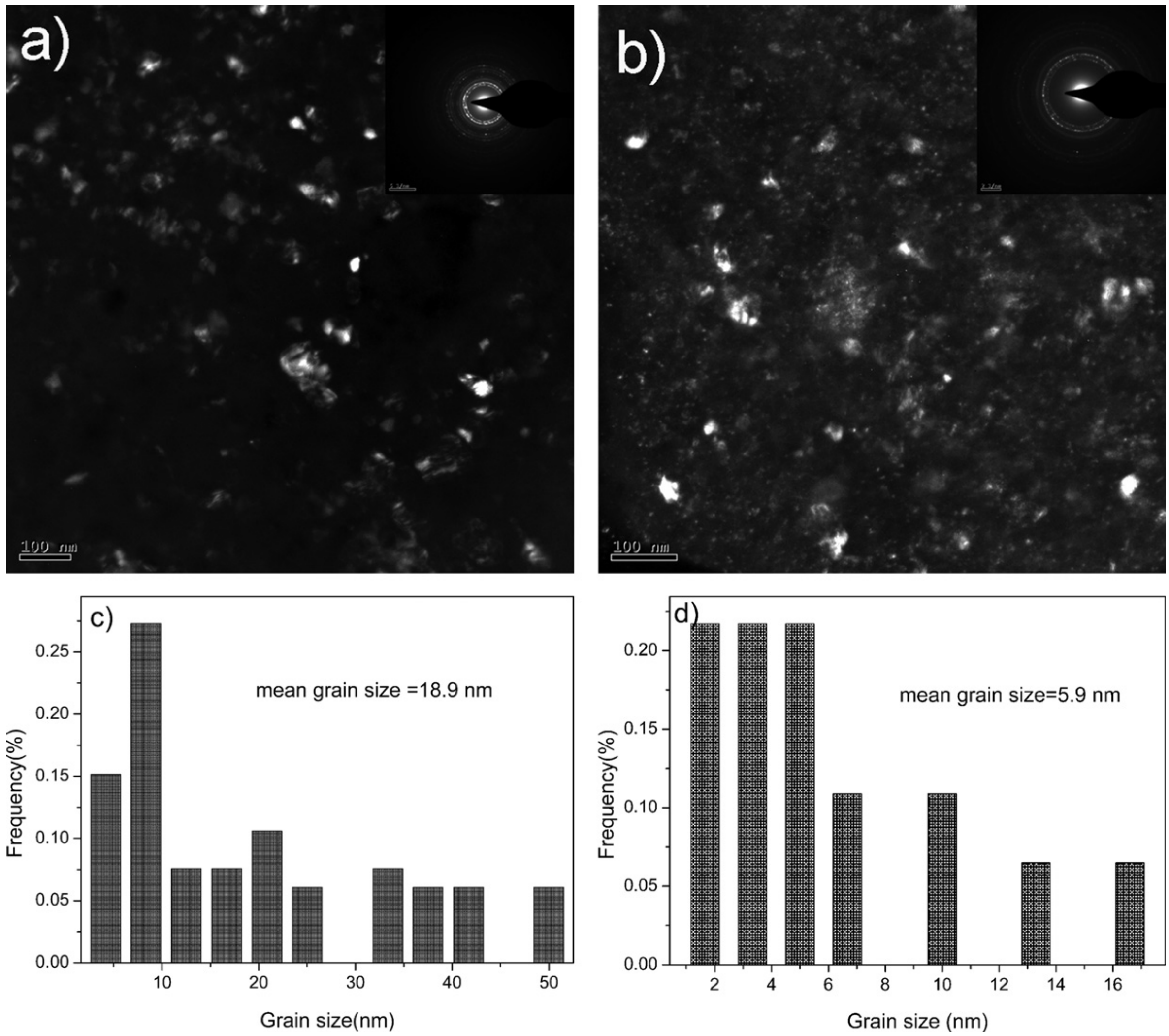

Fig. 2. Dark field image (with SAED pattern as an insert) of Mg–3Al–Zn powders ball milled in hydrogen atmosphere for different time: (a) 20 h and (b) 60 h. The grain size distributions corresponding to the materials in (a) and (b) are shown in (c) and (d), respectively.

MgH_2 phase are increased rapidly. The diffraction peaks of MgH_2 phase and magnesium phase become very broad, which proves that the crystalline size of MgH_2 phase and magnesium diminish into the nanocrystalline range. From Fig. 4(c) and (d), it can be seen that after the desorption-recombination treatment and consolidation process, no diffraction peaks of MgH_2 phase are observed, except for those of the newly formed magnesium phase. This suggests that the MgH_2 phase is fully dehydrided and the microstructure is transformed into magnesium phase again. No diffraction peaks of Al phase and Zn phase are observed, this suggests the elements Al and

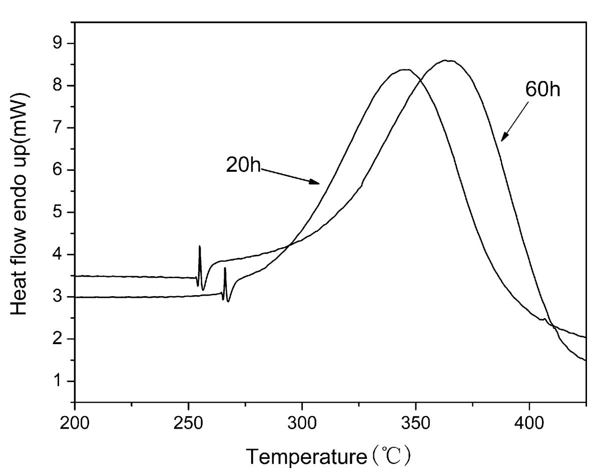

Fig. 3. DSC curves of as-disproportionated Mg–3Al–Zn powders for 20 and 60 h milling.

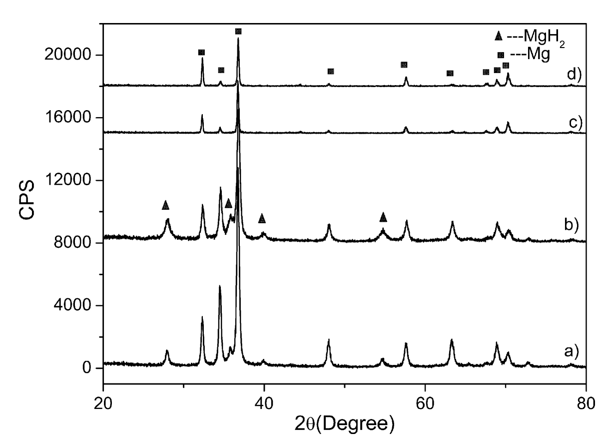

Fig. 4. XRD diffraction patterns for Mg–3Al–Zn alloy.

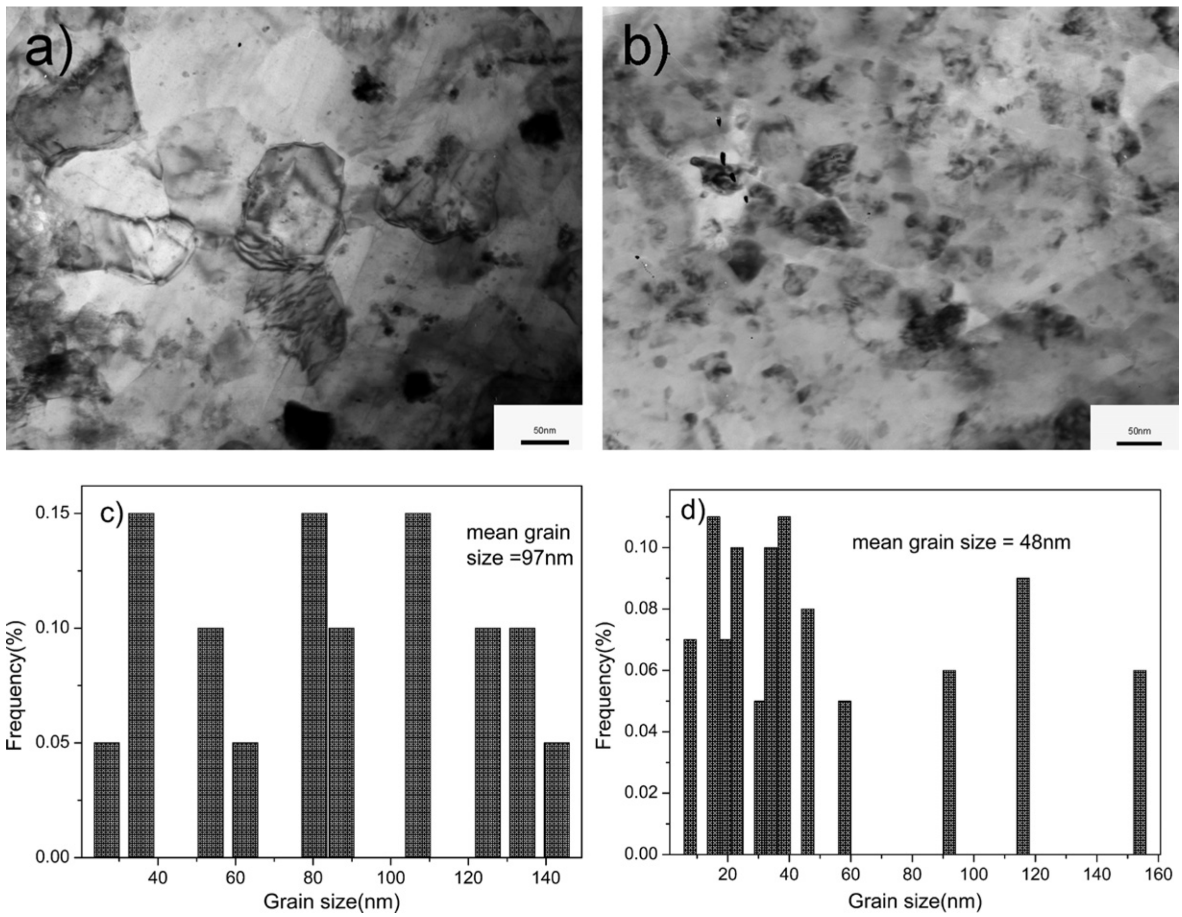

Fig. 5. Bright field image of bulk Mg–3Al–Zn alloy extruded at 200 °C ball milled for different time: (a) 20 h and (b) 60 h. The grain size distributions corresponding to the materials in (a) and (b) are shown in (c) and (d), respectively.

Zn dissolve in magnesium, forming Mg (Al, Zn) solid solution. Based on the XRD results, the average crystallite sizes of MgH_2 and magnesium phase of powder milled for 60 h are estimated to be about 4.6 and 20 nm, respectively, by calculation using the Scherrer equation, which is in agreement with the TEM observations. The average crystallite size of bulk alloy milled for 60 h is estimated to be about 45 nm. Because the reasonable processing parameters are used, the grain growth is not significant after desorption-recombination treatment and consolidation process, in comparison with those of as-disproportionate powders. The value of average crystallite size of bulk alloy demonstrates that the feasibility of achieved a nanocrystalline microstructures bulk Mg–3Al–Zn alloy by powder metallurgy assisted hydriding–dehydriding.

TEM observations of Mg–3Al–Zn alloy after 20 and 60 h milling durations and extruded at 200 °C are shown in Fig. 5. It is noticeable that there are no voids or pores at the interfaces and the powder particles are well bound for the two alloys. The average grain size of the 20 h sample is about 97 nm. However, the average grain size of the 60 h sample is about 48 nm, which is in agreement with the XRD results. The microstructure of the both extrusion samples is sufficiently homogenous. Near equiaxed nano-sized grains are introduced and grain boundaries and well-defined for the both samples. It is also possible to find small inclusions (approximately 2–6 nm) spaced approximately 20–100 nm apart. The inclusions are deduced to be oxide particles originating from the surface films of the initial powder that are broken down during milling. Fig. 5(c) and (d) shows the grain size distribution of the bulk alloys for 20 h and 60 h respectively, which is summarized from measuring 200 grain diameters in bright field images. However, the average grain size of the PM Mg–3Al–Zn alloy is much smaller than that of the ECAE AZ31 alloy with the average grain size about 1 μm after 8 passes ECAE at temperatures as low as 100 °C [11]. A very small grain size of 48 nm for magnesium alloy is attained by the powder metallurgy assisted hydriding–dehydriding.

Recent studies by Takamura et al. [19,20] have shown that the microstructure of AZ31 can be refined to submicron scale by a thermal hydriding–dehydriding treatment. However, the conventional thermally driven process can never produce nanocrystalline magnesium alloy, because of the long holding time for the thermal hydriding–dehydriding process as long as 36 h at 350 °C, led to grain overgrowth. In contrast, for mechanical ball milling assisted by hydriding–dehydriding process, the MgH_2 phase, will not grow upon with prolonged milling time, after it forms as a consequence of a certain colliding event, because the hydriding of the magnesium alloy takes place at ambient temperature, with the mechanical energy transferred by the colliding balls serving as the driving force. And meanwhile the bulk nanostructures Mg–3Al–Zn specimens produced by desorption-recombination treatment (at 350 °C) and consolidation process (extruded at 200 °C) can be accomplished as quickly as 1 h. It well explains why we could produce nanostructured as-hydrided magnesium alloy powders with the average grain size of about 5.9 nm and bulk Mg–3Al–Zn alloy with the average grain size of 48 nm.

3.4. Density of bulk alloy

After consolidation, the dense structured rods are extracted from the Al tubes. The average density for tested 20 and 60 h samples is 1.8003 ± 0.006 and $1.77663 \pm 0.006\,g/cm^3$, respectively. Since the nominal density of Mg–3Al–Zn alloy is $1.82088\,g/cm^3$, the consolidated samples have the theoretical density of $98.87 \pm 0.3\%$ and $97.57 \pm 0.3\%$, respectively. It is also worth mentioning that no macroscopic pores or cracks are observed throughout the samples.

3.5. Microhardness of bulk alloy

The degree of refinement and the extent of homogeneity of the final microstructure are two aspects that are most noticeable in the material prepared by powder metallurgy assisted hydriding–dehydriding. These nanometer grains are also proved by microhardness tests. The measured hardness values of 20 h milled samples are scattered within 661–729.8 MPa and 60 h milled samples are scattered within 740–872.5 MPa, which is about three times the value of the coarse-grained AZ31 (about 264 MPa), indicating that the nanograined microstructure has strengthened significantly for the Mg–3Al–Zn alloy.

4. Conclusions

In short, nanocrystalline Mg–3Al–Zn alloy has been successfully produced by powder metallurgy assisted hydriding–dehydriding. Microstructure and microhardness of the materials have been investigated. The following conclusions can be drawn from this study:

Nanocrystalline Mg–3Al–Zn alloy powders have been successively developed by 20 and 60 h ball milling under hydrogen atmosphere. The mean grain size of the 60 h milled powder observed from TEM micrographs is about 5.9 nm, which is similar to XRD result. After a desorption-recombination treatment at 350 °C and extruded at 200 °C, the MgH_2 phase is fully dehydrided and the microstructure is transformed into magnesium phase again. Nanocrystalline and uniform grained structure bulk alloy can be achieved. The grain boundaries are well defined and the mean grain size can be refined to about 48 nm. The highest microhardness for bulk nanocrystalline alloy reaches 872.5 MPa, which is about three times that of the coarse-grained AZ31.

After consolidation, the relative densities of consolidated samples are more than $97.57 \pm 0.3\%$.

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References

[1] S. Takaki, K. Kawasaki, Y. Kimura, in: R.S. Mishra, et al. (Eds.) Ultrafine Grained Mater. (2000) 247.
[2] C.I. Chang, X.H. Du, J.C. Huang, Scripta Mater. 59 (2008) 356–359.
[3] C.I. Chang, X.H. Du, J.C. Huanga, Scripta Mater. 57 (2007) 209–212.
[4] M.Y. Zheng, S.W. Xu, X.G. Qiao, K. Wu, Mater. Sci. Eng. A 483–484 (2008) 564–567.
[5] E. Mora, G. Garcés, E. OnÕrbe, P. Pérez, Scripta Mater. 60 (2009) 776–779.
[6] M.R. Barnett, Z. Keshavarz, A.G. Beer, D. Atwell, Acta Mater. 52 (2004) 5093–5103.
[7] Y.C. Pan, X.F. Liu, H. Yang, Z. Metallkd Metallkd. 96 (2005) 1398–1403.
[8] Y.C. Lee, A.K. Dahle, TMS Annu. Meet. (2000) 211–218.
[9] I.R. Harris, P.J. McGuiness, J. Less-Common Met. 174 (1991) 1273–1284.
[10] Do Hyung Kim, Ju Yeon Lee, Hyun Kyu Lim, Mater. Sci. Eng. A 487 (2008) 481–487.
[11] Li Jin, Dongliang Lin, Mater. Sci. Eng. A 423 (2006) 247–252.
[12] M.T. Pérez-Prado, J.A. delValle, O.A. Ruano, Scripta Mater. 51 (2004) 1093–1097.
[13] J. Čizek, I. Procházka, Mater. Sci. Eng. A 462 (2007) 121–126.
[14] L. Lu, M.O. Lai, Y.H. Toh, L. Froyen, Mater. Sci. Eng. A 334 (2002) 163–172.
[15] P.J. McGuiness, X.J. Zhang, K.G. Knoch, I.R. Harris, J. Magn. Magn. Mater. 104 (1992) 1169–1173.
[16] G. Shi, L.X. Hu, B. Guo, X.D. Sun, Mater. Sci. Forum 475–479 (2005) 2185–2188.
[17] G. Shi, L.X. Hu, E.D. Wang, J. Magn. Magn. Mater. 301 (2006) 319–324.
[18] Lianxi Hu, Yang Wu, Yuan Yuan, Mater. Lett. 62 (2008) 2984–2987.
[19] T. Miyazawa, Y. Kobayashi, A. Kamegawa, M. Okada, Mater. Trans. 45 (2) (2004) 384–387.
[20] H. Takamura, T. Miyashita1, A. Kamegawa, M. Okada, J. Alloys Compd. 356–357 (2003) 804–808.