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Preparation of bulk ultrafine-grained Mg−3Al−Zn alloys by consolidation of ball milling nanocrystalline powders

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Abstract: Powder metallurgy was used to fabricate a bulk ultrafine grain size (UFG) Mg−3Al−Zn alloys. Nanocrystalline alloy powders with an average grain size of 45 nm were synthesized via ball milling of elemental powders of Mg, Al and Zn. The milled powders canned in Al containers were subjected to cold (at room temperature) or hot press (for 40 min at 633K), respectively, in a vacuum furnace. The sintered samples were extruded at 423 K to further solidify. The results show that the average grain size is 180 nm for the cold samples, and that is 600 nm for the hot samples. The cold-press alloys show a yield stress of 426 MPa. The high strength of UFG Mg is attributed to the fine grain strengthening mechanism resulting from the strong dependence of strength on the grain size for HCP metals. The consolidated samples of the cold-press and hot-press alloys have a final density of (1.777±0.006) and (1.800±0.006) g/cm^3, respectively.

Key words: Mg−3Al−Zn alloys; ultrafine grain; nanostructured powders; powder metallurgy

1 Introduction

Nanocrystalline and ultrafine-grained (UFG) materials have received considerable attention in the last decade, owing to their improved properties as compared with conventional coarse-grained materials [1−2]. Following Hall-Petch relationship, it can be shown that grain size refinement is one of the most effective methods for improving the strength of the material. For Mg alloys, the strengthening due to grain refining can be very attractive because of their high k_y values [3−5]. For example, when the grain size was reduced to about 500 nm, the $MgZn_{3.3}Y_{0.43}$ 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 Mg alloy [2, 6−8]. Several approaches, such as equal channel angular extrusion (ECAE) [9], friction stir processing (FSP) [3], accumulative roll bonding (ARB) [10], high-pressure torsion (HPT) [11] and powder metallurgy (PM) [12] have been applied to the grain refinement of bulk Mg alloys. However, in most cases, the grain size of the 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 Mg materials can be produced, they were restrained in a thin layer form or precipitate hardened Mg alloys such as AZ91. But for pure Mg or solute solution hardened Mg 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. In the present work, an investigation the possibility of developing UFG microstructure of bulk Mg−3Al−Zn alloys by consolidation of ball milling nanocrystalline alloy powders is investigated. The effect of sintering temperature on the microstructure and mechanical properties of the alloy is also investigated.

2 Experimental

The alloy powder with a nominal composition of Mg−3Al−Zn alloys was produced by high energy mechanical milling (HEMM) of a mixture of Mg powder (99%, 45 μm), Zn powder (99%, 45 μm) and Al powder (99.5%, 45 μm) under high purity argon (99%). The milling was carried out with a QM21SP4 planetary ball milling machine. Before the formal experiment, the preparation experiment was carried out to determine the optimum ball milling parameters. The optimum ball milling parameters were as follows: shaft rotation were 360 r/min, mass ratio of ball to powder 40:1 and milling time 20 h. Prior to ball milling, the vial was sealed in a

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glove box filled with high purity argon (purity of 99.9%) to ensure the milling was done under an inert atmosphere. After milling, in order to avoid oxidation during sintering, the powders were removed from the vial and then canned into an Al container of 35 mm in diameter and 65 mm in length in a glove box with high purity argon. An Al plug of 35 mm in diameter and 19 mm in length was designed to ensure the densification of the alloy powders. The milled powders canned in Al containers were subjected to cold (at room temperature) or hot press (for 40 min at 633K), respectively and then pressed the plug until it fully went into the container in a vacuum furnace under a vacuum better than 1×10^{-2} Pa. The sintered compacts were extruded at 423 K, under an extrusion ratio of 6.25 and an extrusion rate of 22 mm/s using graphite as lubricant. To prevent the alloy from oxidation, the experimental materials were always kept in a glove box filled with pure argon (99.9%). The microstructure characterizations of the powders and extruded alloys were conducted on SEM and TEM, due to their small grain size. Density (ρ) measurements 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 ±0.000 1 g.

3 Results and discussion

3.1 Structure and grain size of powder

The SEM images of the initial powders and milled powders in argon atmosphere for 20 h are shown in Fig. 1. From Fig. 1, it can be seen that the initial powder has various particles size in the range of less than 50 μm to more than 200 μm in diameter and layer-like shape. The powder size is not homogeneous. After 20 h ball milling, the powder particle is flake-shaped with a mean diameter of approximately 30 μm. The appearance of powder is smooth and the particles size homogeneously distributes. The size and shape of the particles is one of the key factors for the density of bulk alloy. The flake-shaped and homogeneously distributed powders are favorable for the density of the powders.

The bright field TEM micrographs, selected area electron diffraction (SAED) pattern, obtained from region with a diameter of 800 nm, and the grain size distribution of the powders milled for 20 h are shown in Fig. 2. As shown in Fig. 2, after 20 h milling, the nano-crystalline powders are mainly composed of equiaxed grains of 30−50 nm surrounded by a few smaller grains (<20 nm). The SAED pattern taken from the as-milled alloy powder exhibits the rings of diffracted spots, indicating the presence of boundaries with high angle of

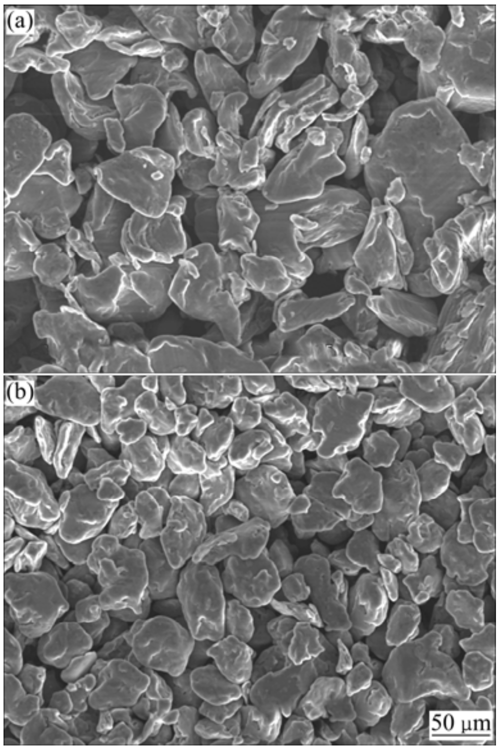

Fig. 1 SEM micrographs of Mg−3Al−Zn powders: (a) Initial powders; (b) After 20 h milling

orientation. These suggest that the dynamic recrystallization occurs during milling. Figure 2(c) shows the grain size distribution of the milled specimen, which is summarized from measuring 200 grain diameters in bright field images. It shows that the grain sizes are mostly scattered from less than 20 to 60 nm, and more than 80% of the grains are refined to less than 50 nm. In this work, the average grain size of magnesium alloy powders attainable by mechanical milling at room temperature is approximately 45 nm. The grain size value is also coincident with the previous report of milled pure Mg [13].

3.2 Structure and grain size of bulk alloy

The TEM observations are employed to further analyze the microstructure of bulk Mg−3Al−Zn alloys. The TEM images of the bulk Mg alloy after a combination process of cold or hot press and extruding at 423 K are shown in Fig. 3. 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 for the cold-pressed and the hot-pressed samples is about 180 and 600 nm, respectively. The microstructure of the both samples is sufficiently homogenous. Near equiaxed nano-sized grains are introduced and grain boundaries are well-defined. However, the grain size of the PM Mg−3Al−Zn alloys is much smaller than that of the ECAP Mg−3Al−Zn alloys with the average grain size of about 1 μm after 8 passes

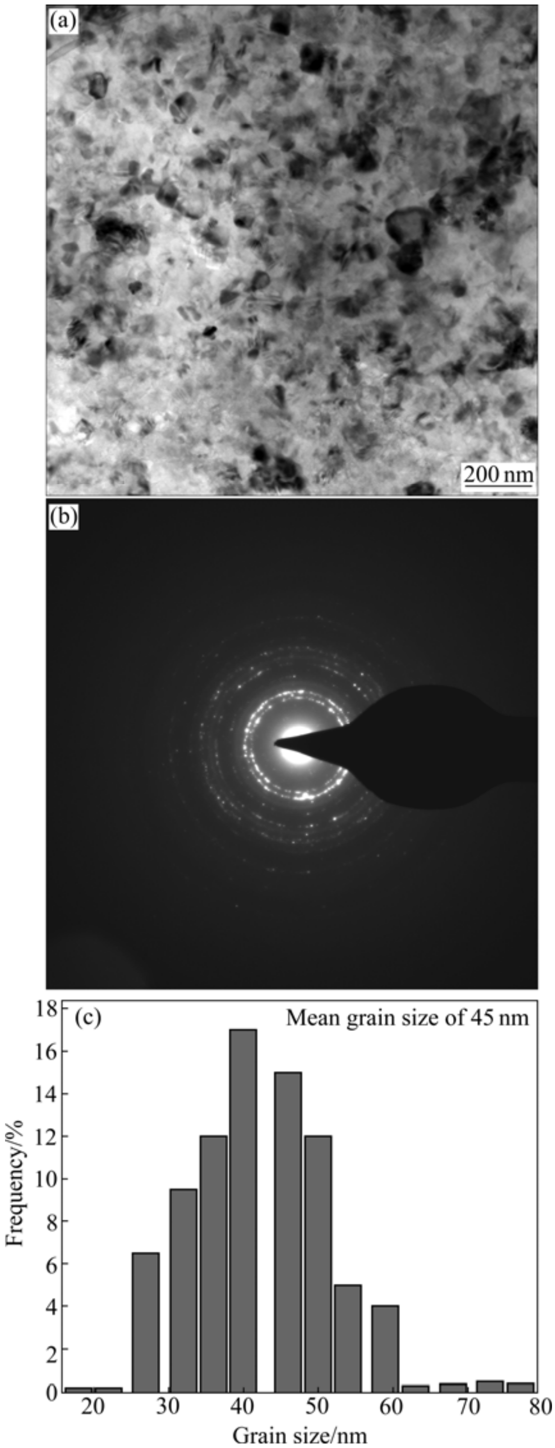

Fig. 2 TEM images of Mg−3Al−Zn powders by ball milling for 20 h: (a) Bright field image; (b) SAED pattern; (c) Grain size distribution (mean grain size of 45 nm)

ECAP at temperatures as low as 373 K [9]. A very small grain size of 180 nm for Mg alloy is obtained by the consolidation of ball milling nanocrystalline alloy powders.

3.3 Density of bulk alloy

After consolidation, the dense structured rods are extracted from the Al tubes. The average densities for the tested cold-press and hot-press samples are (1.777±0.006) and (1.800±0.006) g/cm^3, respectively. Since the nominal density of an Mg−3Al−Zn alloy is 1.821 g/cm^3, the consolidated samples have the theoretical density of (97.6±0.3)% and (98.9±0.3)%, respectively. From the comparison of the density for the two alloys, it can be found that the hot press is better for the densification of the alloy. It is also worth mentioning that no macroscopic pores or cracks are observed throughout the samples.

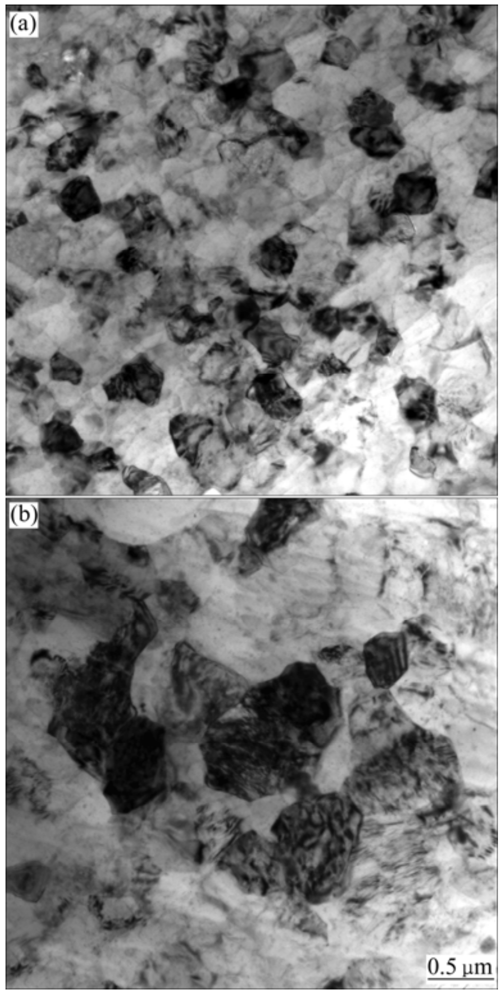

Fig. 3 TEM images of as-extruded Mg−3Al−Zn alloy: (a) Cold pressed; (b) Hot pressed

3.4 Mechanical properties

Mechanical testing provides evidence of the superior properties of UFG Mg alloy compared to other AZ31 alloys. Figure 4 shows the room temperature uniaxial compressive true stress—strain curves for the alloys pressed at 293 and 633 K, having the average grain sizes of 180 and 600 nm, respectively, under an initial strain rate of 10^{-3} s^{-1}. In both cases, the samples are tested till failure. From the comparison of the two true stress—strain curves, it can be seen that the yield

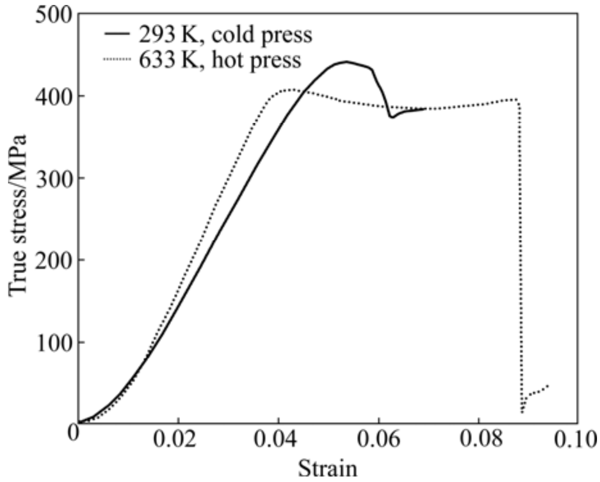

Fig. 4 True stress—strain curves for Mg−3Al−Zn alloys measured in compression deformed under strain rate of 10^{-3} s^{-1} at room temperature

stress of the alloy is higher for the cold-press sample with smaller grain size; however, the strain is directly opposite. And the Mg−3Al−Zn alloys exhibit the higher compressive stress values compared with other Ref. [7], for the cold-press samples, which is 440 MPa, for the hot-press samples, which is 406 MPa. Following Hall-Petch relationship, the ultrafine-grained size is the mean reason resulting in a higher yield stress. It is interesting to point out that using powder metallurgy method results in yield stress of the alloy increased by 20% compared with UFG AZ31 in Ref. [12]. Form Fig. 4, it can be seen that all of the compressive true stress—strain curves of the UFG Mg−3Al−Zn alloys are that a short region with high strain hardening rate follows by a long region with strain softening, and then strain hardening occurs again. It should be pointed out that the curve shapes of this study are distinctly different from those of the conventional polycrystalline Mg alloy. But that is a common shape for NC and UFG materials because the smaller grain size inhibits the dislocation generation and storage necessary for work hardening, based on the research results of MEYERS et al [14]. The same strain softening was found by BARNETT et al [6] in the compression of AZ31 alloys with grain size of 3 μm.

3.5 Fracture analysis

In order to better understand the mechanical properties of UFG alloys, the microstructures of the fracture surface are observed by SEM. The fracture morphologies are found to be similar to those in the conventional Mg alloy. All specimens are fractured by the microvoid coalescence mechanism. The fracture surface shows dimpled rupture (Fig. 5) and the dimples are 1−4 μm in size. At the bottom of the dimples, micro-cavities, which are the initiation sites for fracture, are found. The deeper and more uniformly distributed dimples in Fig. 5(b) can be observed when compared with Fig. 5(a). The dimples distribute uniformly among the tearing edges for the hot-press samples, which indicates that improved ductility is obtained for the hot press alloy.

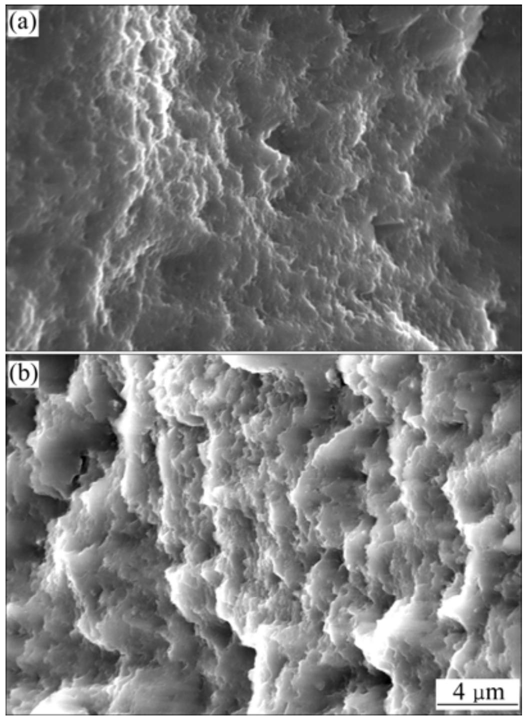

Fig. 5 SEM fracture micrographs of Mg−3Al−Zn alloy solidified by cold press (a) and hot press (b) after compressive test at room temperature with initial strain rate of 10^{-3} s^{-1}

4 Conclusions

1) Nanocrystalline Mg−3Al−Zn alloy powders with the mean grain size of 45 nm were successively developed after 20 h ball milling under argon atmosphere. An ultrafine size and uniform grained structure bulk Mg−3Al−Zn can be produced, and the mean grain size can be refined to 180 nm for cold-press alloys.

2) The ultrafine-grained structure can drastically increase yield stress of bulk Mg−3Al−Zn alloy. The extruded alloys reveal extraordinary high strength; an ultimate strength of 479 MPa and a yield stress of 464 MPa were obtained by this study. The high strengths are obtained due to the grain boundary strengthening because of small grain size.

3) After consolidation, the consolidated samples of cold-press and hot-press alloys have the theoretical densities of (97.6±0.3)% and (98.9±0.3)%, respectively.

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固化球磨纳米晶粉末制备块体超细晶 Mg−3Al−Zn 合金

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摘 要：采用粉末冶金技术制备块体超细晶 Mg−3Al−Zn 合金。首先采用球磨 Mg、Al、Zn 混合粉末来制备纳米晶粉末，所得的粉末的平均晶粒尺寸为 45 nm。随后将球磨好的粉末封入铝包套内，分别在室温和 633 K 温度下，在真空烧结炉内进行真空热压。然后将烧结后的样品在 423 K 下挤压以进行进一步的致密化处理。结果表明：致密后的冷压样品的晶粒尺寸为 180 nm，而热压坯的晶粒尺寸为 600 nm，冷压样品的屈服强度达 464 MPa；超细晶镁合金的强化机制主要是细晶强化，这主要是由于 HCP 结构的材料晶粒尺寸对材料的影响更为明显。固化后冷压样品的最终密度为(1.777±0.006) g/cm^3，而热压样品的最终密度为(1.800±0.006) g/cm^3。

关键词：Mg−3Al−Zn 合金；超细晶；纳米晶粉末；粉末冶金

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