The microstructure and corrosion resistance of SiC reinforced magnesium matrix composites with laminated gradient structure

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Abstract

The laminated gradient of the SiC reinforced Mg-MMCs has been report few. In this paper, the laminated gradient structure of Mg-3Al-35n + xSiC alloys (x = 0, 0.5, 1.0 and 2.0 wt%) were prepared via powder metallurgy and spark plasma sintering method, and the effects of different sintering rate (60 °C min, 70 °C min −1 and 80 °C min −1 ) on the phase, morphology and corrosion resistance of as-sintered and rolled-state samples with laminated gradient structure are characterized. The results shows that, from the surface to core, the grain size of samples gradually decreased with the contents of SiC addition decreasing. Compared to the as-sintered samples, the micro-hardness of rolled-state reach to 105 HV, and the electrochemical test results shows that corrosion resistance of rolled states samples prepared at 70 °C min −1 increased by 88%, and the corrosion potential (Ecorr) value is −1.3162 V SCE which is better than other samples; the samples prepared at 60 °C min −1 increased by 36%, and the samples prepared at 80 °C min −1 only decreased by 5%. It provides a new method to prepare the laminated gradient structure of magnesium alloy composites.

1. Introduction

In order to save energy and reduce emissions, the magnesium alloys serve as a lightweight and environmentally friendly materials are being increasingly used in industrial production, such as automotive, aerospace, materials-handling, portable microelectronics and telecommunication industries [1–3]. However, the low mechanical properties and poor corrosion resistant of magnesium alloys largely limit its further application [4]. Therefore, a substantial amount of research has been carried out on the improvement of the strength and corrosion resistant of magnesium alloys [5]. So the magnesium metal matrix composites (Mg-MMCs) have been developed. Because of the micro-sized silicon carbide particle (SiC) possess of low density, highspecific strength, high specific stiffness, high wear resistance and low coefficient of thermal expansion, so the SiC serve as reinforcement in Mg matrix composites have been studied by many researchers [6–9]. Some researchers found that appropriate SiC addition can significant improved the hardness, tensile properties and corrosion resistant of the Mg alloys. Matin et al [10] indicated that the hardness and tensile properties were significantly enhanced by adding 1.5 wt% of SiC nano-particles to an AZ80 magnesium alloy using stir casting. Viswanath et al [11] studied the creep behavior and mechanical properties of SiC/AZ91 composites was fabricated by stirring casting techniques, it found that the mechanical properties is improved with the addition of SiC. Powder metallurgy (P/M) technologies have been used to consolidate metal matrix and composite powders. Besides, spark plasma sintering (SPS) is characterized by an electric source of direct pulsed current, offer precise tailoring of the final microstructures allows for the production of desired material shapes unlike the conventional wrought magnesium alloys [12, 13]. The Lu et al [14] combined surface modification with metal nano-crystallization and put forward the concept of surface nano-crystallization. Recently, gradient nano structured metals have attracted much interest due to their high strength and high ductility. The preparation method of preparing
gradient nanostructures includes SMAT, surface mechanical grinding treatment (SMGT), torsion and USRP. So the gradient nano-structured is obtained in the magnesium alloys, which can improve its relevant mechanical properties. As all known, the corrosion resistant of magnesium alloys is poor, so it limit its further application. So the Mg-MMCs with gradient structured are very signifi-
can, which can improve the mechanical properties and corrosion resistant meanwhile to a certain extent. Before our research, there are some works in the Mg-MMCs, and materials with laminated gradient respectively, but combined with both characteristics are reported a few in the literature. So how to obtain the Mg-MMCs with gradient structured need to research further. Therefore, in this work, the work focused on investigating the micro-structure characteristics and corrosion resistance in the laminated gradient structure Mg-3Al-3Sn reinforced with SiC prepared by P/M technology and SPS technology, which is good for the application of magnesium alloy.

2. Introduction

The laminated gradient Mg-3Al-3Sn + xSiC (3 wt% Al, 3 wt% Sn, 94 wt% Mg, besides x = 0, 0.5, 1 and 2 wt%) magnesium composites, the raw materials powders were weighed in argon atmosphere inside a glove box to minimize any contamination resulting from powder handling in the atmosphere. After weighing, all the raw materials were put in a stainless steel crucible, then thoroughly mixed-together through ball- milled in a speed at 300 rpm for 10 h under high purity argon inert gas protection, the stearic acid of 98% purity amounting to 0.5 wt% of the total powder charge was used as the process control agent. The milled powders were sintering by using the sintering system of Dr Sinter (Model SPS-632Lx). A cylindrical graphite die of 40 mm inner diameter filled with milled powder was set in the equipment, and the mixed powders were laying one layer by one layer as showed in figure 1 (a). The sintering temperature was kept at 520 °C, at a heating rate of 60 °C min−1, 70 °C min−1 and 80 °C min−1 respectively as the figure 1 (b) show. Then the specimens were rolled into the thickness of 2.2 mm at 300 °C, by one pass. The optical microstructures of the as-sintered and rolled- state specimens were observed by using an ICX41M-type inverted optical microscope (OM) after machining. The grain size was calculated by the average linear intercept method. The phase constitution of specimens was measured by using a Powder-type x-ray diffractometer with monochromatic Cu-Kα radiation at a 2θ range of 20–80°. To ensure accurate analysis, the specimens were polished to remove the oxide layer of the surface before the XRD test. The chemistry of some particles was observed by scanning electron-microscopy (SEM, Model SUPRA40, Germany) equipped with an energy-dispersive x-ray spectroscopy (EDS) analysis system. The elemental analysis were detected by XRF x-ray fluorescence spectrometer.

The hardness was tested by an HVS-100 full automatic micro-hardness tester fitted with a Vickers indenter, with a load of 100 g and a holding time of 10 s. The electrochemical corrosion behavior of samples in 0.1 mol l−1 NaCl aqueous solution at room temperature was studied by electrochemical workstation (CHI660A). A three electrode system was established in a horizontal electrolytic cell, in which 1 cm² Pt was used as auxiliary electrode, SCE as reference electrode and sample as working electrode.

3. Results and discussion

3.1. Microstructure characteristics

The microstructure of the as-sintered samples at different heating rates are shown in figure 2. The grain size have a obviously difference, from the layer-1 to the layer-4, with the contents of SiC decreasing, average grain size
Figure 2. Optical micrographs of as-sintered samples at different heating rates: (a) 60, (b) 70, (c) 80 °C min⁻¹, and (d) illustration of forming behavior of the samples at the sintering state.

Figure 3. (a) SEM images from core to surface, EDS map of (b) Mg, (c) Al, (d) Sn, (e) Si, (f) C.
increases from 37 $\mu$m to 75 $\mu$m. And the elongated magnesium grains observed in the light areas decrease in size, the light areas of the grains contain many small grains, the grain size reach to 5 $\mu$m, and the SiC observed in the dark areas are distributed. The area factions of the SiC have a laminated gradient structure present, and also the SiC were add to magnesium alloys can reduce the grains size, for more nucleation particles are provided for the formation of Mg grains, and the critical nucleation energy is reduced, thus promoting the heterogeneous nucleation and increasing the nucleation rate [15].

The morphology of the rolled-state samples with different heating rates are shown in figures 4(a)–(d). It can be seen that after rolling, the density of samples have increased, and the elongated magnesium grains are observed along rolling direction, it indicated that the samples prepared with the heating rate of 70 $^\circ$C min$^{-1}$, have a highest density. The existence of SiC at the interface, the grain boundary migration is hindered and the grain growth rate is reduced during the sintering process, and during the hot deformation, SiC can also promotes the nucleation of dynamic recrystallization (DRX) and hinders the grain growth of DRX, and many precipitates along grain boundary distributed [16]. The SiC has been detected by EDS, it is shows in figure 5(a). Moreover, the micro-hardness curves of the as-sintered and rolled-states samples are represented in figure 5(b). It shows that the micro-hardness of all samples is decreasing gradually, with the decreasing of SiC contents from surface to core, so the micro-hardness of the layer-1 is higher than other layers. And along with the increasing of the heating rates, the micro-hardness of the samples also improved gradually; When the heating rates at 80 $^\circ$C min$^{-1}$, the rolled-states samples have the highest micro-hardness, reach to 105.5HV. The stress-strain curves of rolled sample are showed in figure 5(c), it indicated that the rolled states samples prepared at 70 $^\circ$C min$^{-1}$ have a good tensile mechanical properties, the yield stress (YS, 251MPa) and ultimate tensile stress (UTS, 308 MPa).

3.2. Phase analysis

The XRD characterization of as-sintered and rolled-state samples are shown in figure 6. It shows that the dominant peaks belong to the hexagonal Mg phase, and also contains precipitates of Mg$_2$Sn and Si$_3$Mg$_{6.2}$Al$_{1.8}$

![Figure 4.](image-url) The morphology of rolled-state samples at different heating rates: (a) 60, (b) 70 and (c) 80 $^\circ$C min$^{-1}$ (d) the density of the sintered and rolled sample.
diffraction peaks, the broad diffraction peak (002) at $2\theta = 34.4$ degree corresponding to the $\alpha$-Mg phase. It indicated that with the increasing of heating rate, the intensity of the diffraction peaks have an obviously change, and a notable increasing of the amount of Mg$_2$Sn has been observed, while the volume of the Si$_4$Mg$_6.2$Al$_{1.8}$ phase
volume is decreased gradually. The diffraction peak (101) at $2\theta = 36.6$ degree corresponding to $\text{Mg}_2\text{Sn}$ phase, and after rolling, the intensity of diffraction peak is decreased, the intensity ratios tendency of the samples at diffraction peak (002) and (101) in the figure 6(d). It indicate that after rolling, the metals sheets have an obvious preferred grain orientation, and the textures are existed in metal. The table 1 shows the specific parameters of diffraction peaks intensity at $I(002)$ and $I(101)$ for all the specimens. For as-sintered and rolled states samples are prepared at 70 °C min$^{-1}$, the diffraction angle of the sample shift from 36.6278 to 36.6538, the diffraction peak shifts to higher angle more than other two samples; And the intensity of $I(101)$ diffusion peaks for as-sintered and rolled states samples are 5920.382 and 1907.324 respectively, the ratio of the $I_a(101)/I_a(101)$ is 3.1040, which is lower than the samples sintered at 60 °C min$^{-1}$ and 80 °C min$^{-1}$. This variation results illustrated that the grain size is decreased and the lattice is distorted, which is due to the SiC addition. Moreover, the sintering process is very important to the distribution and formation of the precipitates phase, as well as the numbers, shapes, sizes and crystalline of the precipitates phase. So during the rolling process, because of the SiC pinning effect, it influence the driving force and binding energy of precipitates phase, which it affects size and quantity of precipitates phase. The table 2 shows the element composition of the sintered sample, it indicated that the all samples have been slightly oxidized during the preparation process.

### 3.3. Corrosion properties analysis

The figure 7 shows the polarization curves for the as-sintered and rolled-states samples at different heating rate in 0.1 mol l$^{-1}$ NaCl solution. It is clearly seen that, the polarization curves of the as-sintered and rolled states specimens at different heating rates have no obvious passive behavior. For the as-sintered and rolled-states samples, the corrosion potential ($E_{corr}$) and corrosion current densities ($I_{corr}$) have an obvious difference. For the as-sintered samples, when the heating rates is 70 °C min$^{-1}$, the value of corrosion potential ($E_{corr}$) is lower than other samples about 8.5–30 mV, the $E_{corr}$ value of the rolled states samples at 70 °C min$^{-1}$ reach to maximum $-1.3162$ V$_{SCE}$, which is higher than the other research, which is show in table 3. Moreover, the rolled states samples at heating rates at 70 °C min$^{-1}$, the $I_{corr}$ reach to minimum 0.001084, and the corrosion resistance has increased 88% compare to as-sintered samples at 70 °C min$^{-1}$; However, the as-sintered and rolled states samples at 60 °C min$^{-1}$, the corrosion resistance has increase 36%, the as-sintered and rolled states samples at 80 °C min$^{-1}$, the corrosion resistance has only increase 5%. The figure 7(d) for shows the tendency of corrosion potential (Ec) as-sintered and rolled states specimens at different heating rates. Why the tendency has this difference? Because of the samples after rolling, the density has improved, and many second precipitates $\text{Mg}_2\text{Sn}$ become refine and distribute along grain boundary, and SiC possess of a good corrosion resistance, all of the factors attribute to the corrosion behaviors.

### Table 1. The parameters of diffraction peaks intensity at $I(002)$ and $I(101)$ for all the specimens.

|                | 2 Theta $I_{002}$ | 2 Theta $I_{101}$ | $I_{002}/I_{101}$ | $I_{101}/I_{002}$ |
|----------------|-------------------|-------------------|-------------------|-------------------|
| As-sintered    | 34.4048           | 36.6278           | 0.4481            | 2.9344            |
| 60 °C min$^{-1}$| 7835.756          | 7115.278          |                   |                   |
| Rolledstate    | 34.4048           | 36.6408           |                   |                   |
| 60 °C min$^{-1}$| 17486.18          | 2424.861          |                   |                   |
| As-sintered    | 34.4048           | 36.6278           | 0.4158            | 3.1040            |
| 70 °C min$^{-1}$| 6121.628          | 5920.382          |                   |                   |
| Rolled state   | 34.4308           | 36.6538           |                   |                   |
| 70 °C min$^{-1}$| 14723.57          | 1907.324          |                   |                   |
| As-sintered    | 34.4048           | 36.6278           | 0.3103            | 2.1164            |
| 80 °C min$^{-1}$| 7248.962          | 6278.294          |                   |                   |
| Rolled state   | 34.4048           | 36.6408           |                   |                   |
| 80 °C min$^{-1}$| 23361.4           | 2966.439          |                   |                   |

### Table 2. The element composition of the sintered sample.

| Elements | Mg | Al | Sn | Si | C | O |
|----------|----|----|----|----|---|---|
| Sintered samples | 60 °C min$^{-1}$ | Bal. | 2.73 | 2.68 | 1.21 | 1.02 | 0.21 |
| | 70 °C min$^{-1}$ | Bal. | 2.70 | 2.61 | 1.34 | 1.22 | 0.15 |
| | 80 °C min$^{-1}$ | Bal. | 2.67 | 2.65 | 1.31 | 1.14 | 0.18 |
4. Conclusions

In this study, the laminated gradient structure of Mg-3Al-3Sn + xSiC (x = 0, 0.5, 1.0 and 2.0 wt%) composites have been successfully synthesized via a powder metallurgy and spark plasma sintering method. Through the SiC addition and the design of the laminated gradient structure meanwhile, the influences of heating rates on the micro-structure characteristics and corrosion resistance of the laminated gradient composite samples with different weight fractions of SiC were investigated.

The results are summarized as follows:

1. The laminated gradient structure of the samples are prepared with different heating rates at 60, 70 and 80 °C min⁻¹, the grain size have a obvious difference, from the surface to the core, the grain size decrease gradually;

2. With the increasing of heating rate, the intensity of I(002) and I(101) diffraction peaks around at 34.4 degree and 36.6 degree of allsamples firstly increased, and then reduced. For as-sintered and rolled states samples
are prepared at 70 °C min⁻¹, the diffraction angle of the sample shift from 36.6278 to 36.6538, and the ratio of the I₆₆ (101)/I₅₆ (101) is 3.104, which is higher than others, and it indicate that Mg-Sn refine more;

(3) After rolling, the density have improved, and the second precipitates Mg₂Sn become refine and distribute along grain boundary, for all of the rolled states samples, the corrosion resistance have improve; Compared to as-sintered samples, the corrosion rate of rolled states samples prepared at 70 °C min⁻¹ increased by 88%, the samples prepared at 60 °C min⁻¹ increased by 36%, and the samples prepared at 80 °C min⁻¹ only increased by 5%; It provides a new method to prepare Mg-MMCs with gradient structure, which can improve the mechanical properties and corrosion resistance, so it can be used widely.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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