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Softening Behavior of Nanocrystalline Mg-6Al-1Zn-1Si Alloy during Mechanical Alloying

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A B S T R A C T

Mg, Al, Zn and Si elemental powder mixtures were subjected to high-energy milling to produce Mg-6Al-1Zn-1Si (wt %) alloy. The milled powders were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and microhardness measurement. The Mg grain size was estimated from the broadening of XRD peaks using Williamson-Hall method. The results showed that the solubility of alloying elements in Mg extended compared to the equilibrium value with increasing the milling time up to 35 h. However, after longer milling time of 50 h, the hardening due to the decreasing grain size competed with softening due to the decomposition of supersaturated solid solution, leading to a decrease in hardness value of as-milled powder.

1. Introduction

The manufacturing of materials with a very small grain size in the nanometer range is an important way of improving the mechanical properties of metallic materials [1]. The solid state processing of materials has become of widespread interest because ofits capabilities to produce both equilibrium and non-equilibrium phases [2,3]. Mechanical Alloying (MA) is an appealing solid state technique to synthesize powders with controlled microstructure. This technique can produce very fine grain size down to nano-scale with flexibility in alloying [4]. One of the distinguishing attributes of mechanical alloying is the formation of solid solutions with extended solubility limits of elemental powders. This is often determined by X-Ray Diffraction (XRD), generally from changes in the lattice parameter values calculated from shifts in peak positions or even the absence of second phase peaks [5].

It is suggested that the formation of supersaturated solid solutions is closely related to the formation of nanocrystalline structure. The energy stored in the grain boundaries of nanocrystalline materials serves as a driving force for the formation of a solid solution. The large volume fraction of atoms in the grain boundaries in these materials is expected to enhance diffusion and consequently the solid solubility levels in these types of systems [2,6]. Instead of forming a solid solution, a fully decomposed two phase mixtures can be obtained after milling in some alloy systems such as Al–Zn and Al–Mg [7,8]. Tavoosi et al. [7] investigated the effect of milling time on structure and microhardness of Al-14 wt% Zn alloy. They

show that in early stage of the milling, the solubility of Zn in Al is extended compared to the equilibrium value. However, after longer milling times, decomposition of Al (Zn) supersaturated solid solution occurs leading to a decrease in hardness value of as-milled powder. Mazilkin et al. [8] studied the softening behavior of binary Al-Mg and Al-Zn alloys after Severe Plastic Deformation (SPD). They suggest that after SPD, work hardening and Hall–Petch hardening due to the decreasing grain size compete with softening due to the decomposition of supersaturated solid solution. They also report that by reducing the grain size during SPD, the supersaturated solid solution decomposes completely and closely approaches the equilibrium state corresponding to room temperature.

The current study is carried out to investigate the effect of milling time on structure, morphology and microhrdness changes of powder particles of Mg-6Al-1Zn-1Si alloy. This system is the base for numerous industrial alloys. In this system, the matrix is strengthened by precipitation of intermetallic compounds such as Mg_2Si [9]. Such phases form in Grain Boundaries (GB), which can strongly affect the GB energy, GB segregation, diffusion and mechanical properties of polycrystals [8]. So far, many researchers have investigated mechanical milling of Mg-based systems. However, softening behavior of Mg-Al system has not been reported yet. In view of that, a deeper understanding of microstructural and morphological formation of nanocrystalline structure of Mg-based system during ball milling is required.

2. Experimental Procedure

Elemental powders of Mg (>97%, Merck), Al (>98%, Merck), Zn (>99.9%, Merck) and Si (>98%, Sigma) were used as starting materials. The powder blend with nominal composition of Mg-6Al-1Zn-1Si (%wt) was mechanically alloyed in a Retsch PM100 planetary ball mill at room temperature under a high purity argon atmosphere for different milling times (15, 25, 35 and 50 h). Ball to powder weight ratio of 20:1 was selected and rotation speed was adjusted to 250 rpm. In order to prevent a large temperature increment during the process, the experiment was periodically stopped every 25 min for 5 min. Weighing, filling and handling of the powders were performed in a glove box under argon atmosphere.

The phase constituents of the milled powders were analyzed by X-Ray Diffraction (XRD, X'Pert Pro MPD, PANalytical) with CuK_α radiation. The grain size and lattice strain of Mg-phase were estimated from the broadening of XRD peaks using Williamson–Hall method [10]:

$$\beta \cos\theta = \frac{K\lambda}{d} + 2\varepsilon \sin\theta \qquad (1)$$

Where β is the full width at half maximum of a diffraction peak, θ is the Bragg angle, λ is the used X-ray wavelength and ε is the microstrain. The microstructure and morphology of MA-processed particles are characterized using scanning electron microscopy (SEM, KYKY EM-3200). The hardness is measured by a Vickers diamond indenter in a micro-hardness tester at applied load of 10 g. The cross section of the powder particles is prepared by mounting a small amount of powder in a resin followed by conventional grinding and polishing methods. A total of 10 measures are taken for each sample and average values are reported.

3. Results and Discussion

Fig. 1 shows the size and morphology of the powder particles at different milling times. During the milling, the powders are repeatedly flattened, cold welded, fractured and rewelded [5].

The starting powders have an irregular morphology, as shown in Fig. 1a. After 15 h of milling time (Fig. 1b), the particles are flattened due to the introduction of the compressive forces into the particles generated by ball-powder-ball collisions [11]. Subsequent to milling for 25 h, welded particles with equiaxed morphology are observed, indicating welding is the predominant phenomenon at this stage of milling (Fig. 1c). With further milling (35 h), the fracture of the powder particles is predominant leading to the formation of smaller particles with narrower distribution of particle size (Fig. 1d). For milling times longer than 35 h (Fig. 1e), the change of particle size is not significant indicating that an equal rate of agglomeration and fragmentation of powder particles is achieved. It is known that after milling for a certain length of time, steady-state equilibrium is attained when a balance is achieved between the rate of welding, which tends to increase the average particle size, and the rate of fracturing, which tends to decrease the average particle size [12].

The XRD patterns of the powder mixture after various times of mechanical alloying process are presented in Fig. 2. The change in intensity and broadening of the Mg (101) peak after various milling times are also observed in Fig. 3. As can be seen, with increasing the milling time, all diffraction peaks are broadened and decreased evidently due to mechanicallyinduced lattice strainandcrystallite size reduction [13]. The absence of Zn and Sipeaks in the XRD pattern is due to their low concentrations. The peak shifting of Mg reflections to peaks in the XRD pattern is due to their lowpeaks in the XRD pattern is due to their low concentrations. The peak

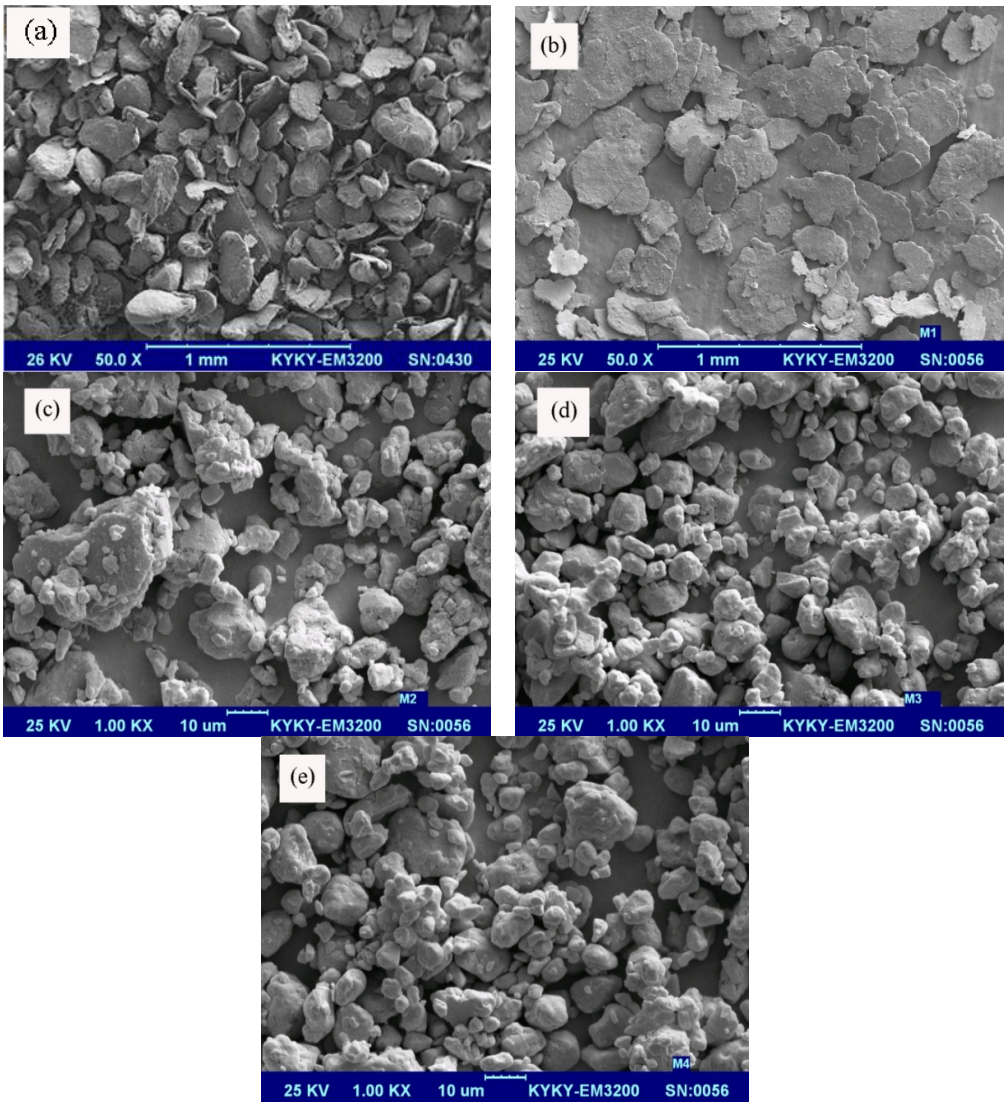

Figure 1. SEM micrographs of powder mixtures for un-milled (a) and milled for: 15 h (b); 25 h (c); 35 h (d); 50 h (e).

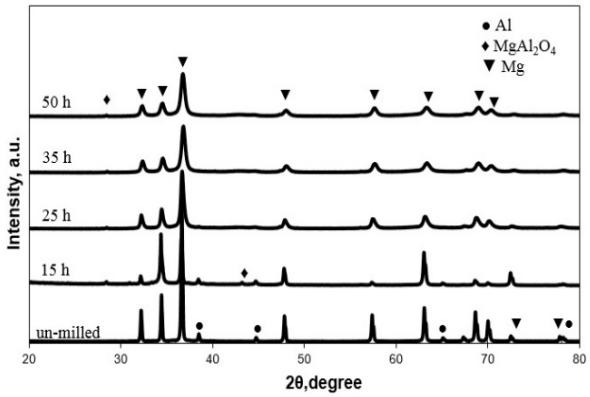

Figure 2. XRD patterns of the MAed powders as a function of milling time.

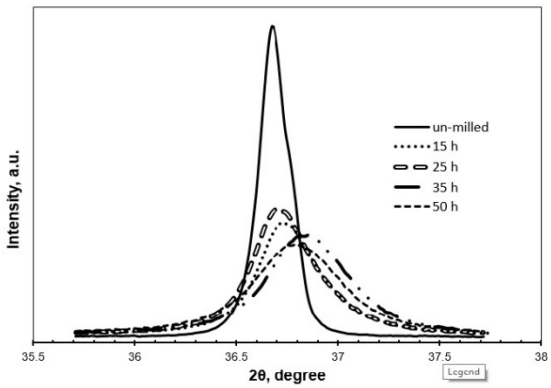

Figure 3. The displacement of Mg (101) XRD peak during MA.

shifting of Mg reflections to higher 2θ values is also observed up to 35 h milling. This suggests the formation of Mg-based solid solution during milling. The atomic sizes of Al, Zn and Si elements are smaller than that of the Mg element, thus the dissolution of these elements is expected to reduce the lattice parameter of Mg. After 15 h milling,

all peaks of Mg and Al are still existed in diffraction pattern, whereas their intensities significantly decrease. The appearance of XRD peaks of $MgAl_2O_4$ determines the oxidation magnesium during the process.

The higher intensity of the Mg (002) compared to that of (101) peak can be attributed to texture effect. This can be realized considering the anisotropy in theelastic modulus of magnesium. In fact, at the initial stages of milling, grains within a powder particle are deformed into thin layers in the soft direction in (002) plane, perpendicular to the direction in which the powder particle is flattened by milling ball.When the sample is prepared to carry out the X-ray pattern, theses flattened powders are arranged parallel to the sample-holder [14,15]. With the milling time extended up to 25 h and 35 h, the diffraction peaks corresponding to Mg and Al become broader with low intensity, while those corresponding to $MgAl_2O_4$ intensify, showing the presence of higher amount of this phase with increasing milling time. No new phase formation is noticed at these times. The phase constituents remain unchanged during a further milling time of up to 50 h. However, at this time, the Mg peaks shift slightly to the lower 2θ values, suggesting that alloying elements are rejected from Mg lattice. In fact, the internal energy of the powder mixture during milling increases because of the formation of a supersaturated solid solution and a high density of dislocations [7]. Therefore, system tends to reduce its internal energy by decomposition of supersaturated solid solution at longer milling times.

In equilibrium state, intermetallic phases are formed by addition of alloying elements to Mg [16]. No detection of intermetallic phases in the XRD patterns of milled powders can be attributed to the formation of stable oxides films on Mg particles, which prevents elements from alloying directly with Mg. In fact, direct synthesize of intermetallic phases by mechanical milling is usually difficult, as stated by Wang et al. [17] for the formation of nanocrystalline Mg_2Si through solid-state reaction.

Fig. 4 shows the grain size and lattice strain of mixed powders as a function of milling time. As can be seen, the grain size initially decreases with increasing the milling time up to 35 h and then approaches a constant value at longer milling time as the rate of creation and annihilation of dislocations becomes identical. In contrast, the lattice strain increases sharply with increasing the milling time up to 35 h. Afterwards it decreases as a result of two factors; recovery phenomenon and the rejection of alloying elements from Mg lattice.

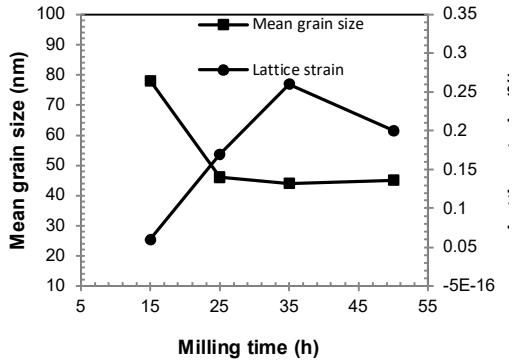

Figure 4. The grain size and lattice strain of Mg matrix as a function of MA time.

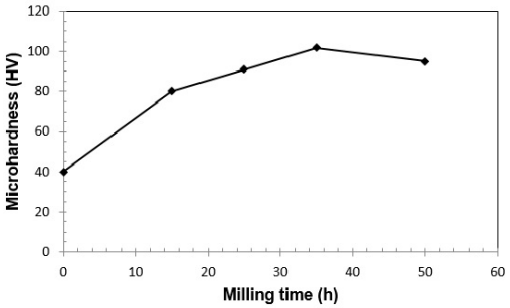

Figure 5. The microhardness value of Mg-6Al-1Zn-1Si powder particles versus milling time

The microhardness values as a function of milling time are shown in Fig. 5. With increasing the milling time up to 35 h, the hardness of powder particles increases due to the refinement of grain size, introduction of lattice strain, and solid solution hardening effect of alloying elements. However, after 35 h of MA time the hardness decreases as the milling time increases. According to Fig. 4, it is expected that the hardness increases and then maintains as MA increases due to the Hall-Petch relationship. This discrepancy can be explained by the decomposition of Mg solid solution, in consistence with shifting of the Mgpeaks to the lower 2θ values and recovery of lattice strain, leading to the softening of the alloy.

4. Conclusion

In the current study, the effect of mechanical alloying on the structure, morphology and microhardness of Mg-6Al-1Zn-1Si (wt %) alloy has been investigated. The findings can be summarized as follow.

1. The grain size initially decreases with increasing the milling time up to 35 h and then approaches a constant value at longer milling time.
2. The lattice strain increases sharply with increasing the milling time up to 35 h. Afterwards it decreases as a result of two factors;

recovery phenomenon and the rejection of alloying elements from Mg lattice.

3. After longer milling time of 50 h, decomposition of Mg supersaturated solid solution occurs leading to a decrease in hardness value of as-milled powder.

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