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Characteristics of Mechanical Alloying of Zn–Al-Based Alloys

Three pure elemental powder mixtures of Zn–22%Al–18%Cu, Zn–5%Al–11%Cu, and Zn–27%Al–3%Cu (in wt.%) were mechanically alloyed by steel-ball milling processing. The mechanical alloying characteristics were investigated using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy techniques. It was explored that mechanical alloying started with the formation of phases from pure elemental powders, and this was followed by mechanical milling-induced phase transformation. During mechanical alloying, phases stable at the higher temperatures formed at the near room temperature of milling. Nano-structure Zn–Al-based alloys were produced by mechanical alloying.

Keywords: Mechanical alloying; Tensile deformation; Stress-induced phase transformation; Zn–Al alloys

1 Introduction

Mechanical alloying (MA) has attracted considerable attention as a means of solid state reaction by repeated mechanical deformation such as impacting, grinding, and compressing etc. A great advantage of this technique is to produce alloys with nano-structure by mechanical milling at near room temperature other than the conventional casting or condensation from vapor-quenching methods, without special considerations for oxidation during alloy producing or a large difference in the melting point or vapor pressure [1–4]. During mechanical alloying, the solubility could be extended into supersaturated solid solution region, thus expanding the compositional alloying ranges. Various non-equilibrium metastable phases were observed [5, 6]. However, the mechanism of formation and decomposition of these metastable phases has not been well understood.

The present paper will deal with characteristics of the mechanical alloying of Zn–Al-based alloys: formation and transformations of various metastable phases, and microstructural evolution, based on a systematic investigation of the phase transformations of the alloy system [7–18].

2 Experimental

Three elemental powder mixtures were produced from pure metallic powders of Zn, Al, and Cu. The chemical compositions of the powder mixtures were Zn–22%Al–18%Cu, Zn–5%Al–11%Cu, and Zn–27%Al–3%Cu (in wt.%). The pure elemental powder mixtures were milled sepa-

rately in stainless steel vials under argon atmosphere. The grinding medium was 12.7 mm diameter stainless steel balls, and methanol solution was used as surfactant agent. The weight ratio of the stainless steel balls to the pure elemental powder mixture was 36:1. The milling vials were rotated at a speed of 110 rounds per minute. Small amounts of the milled powder mixtures were taken from the vials after selected intervals of milling for examination of the microstructure and identifying of the phase transformation, using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques.

XRD was carried out in a Siemens diffractometer with Ni-filtered Cu K α radiation at a scanning speed of 1 degree per minute. The characteristic X-ray diffraction peaks were obtained within a diffraction angle (2θ) range from 35 to 47 degrees. Back-scattered electron mode images were applied for SEM examination. The milled powder mixtures were deposited on a carbon electron microscopy grid for TEM examination. The TEM examination was performed at 120 kV in a Jeol-1200EX transmission electron microscope.

3 Results and Discussion

3.1 Phase Formation and Transformation in MA

In order to explore the microstructure evolution and phase transformations occurring in mechanical alloying, XRD examination was carried out on the three elemental powder mixtures before mechanical milling and after various periods of milling. The X-ray diffractograms are shown in Fig. 1.

The characteristic XRD and their indexes of the original elemental powders, i.e. the 0 h milled powder mixtures, are shown in Fig. 1 and listed in Table 1. The XRD patterns of the elemental powder mixture are similar. But the diffraction intensities of the pure elements Zn, Al, and Cu are varying due to the difference in composition of the powder mixtures.

For the elemental mixture of Zn–22%Al–18%Cu, both the XRD peak position and the relative intensities of the diffraction peaks had changed after 1 h ball milling. According to the well established identification of the phases involved [9–14], the elemental powders had started to transform into phases.

After 22 h milling, four phases: Zn-rich η and ϵ , Al-rich α and T' (Zn–35%Al–55%Cu in wt.%) were clearly detected on the X-ray diffractograms. The d spacings and the

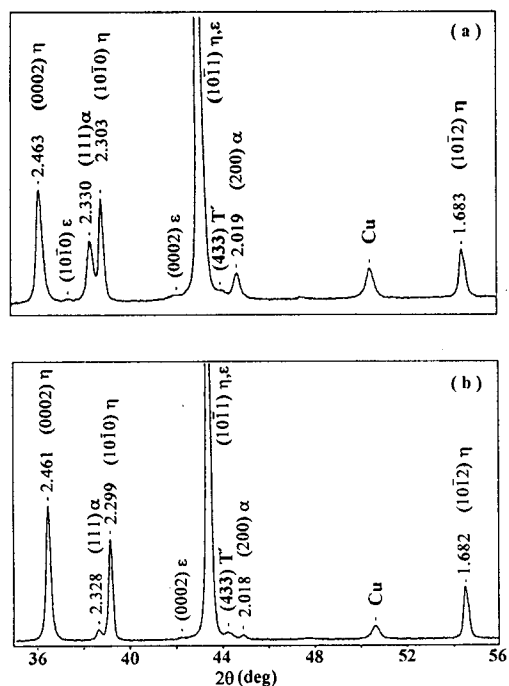


Fig. 2. X-ray diffractograms for (a) Zn–22%Al–18%Cu (22 h milled) and (b) Zn–5%Al–11%Cu (4 h milled).

related characteristic XRD peaks (0002), (10 $\bar{1}$ 0), (10 $\bar{1}$ 1), and (10 $\bar{1}$ 2) lattice planes of the η phase and (111) and (200) of the α phase are shown in Table 1. It was noticed that the d spacings of (0002), (10 $\bar{1}$ 0), and (10 $\bar{1}$ 1) of the η phase had decreased to 2.463; 2.303; and 2.086 Å from 2.471; 2.305; and 2.088 Å of the original pure Zn element, respectively. The d spacings of (111) and (200) of the original pure Al had decreased from 2.335 and 2.022 Å to 2.330; 2.303; and 2.019 Å of the Al-rich α phase, respectively. Both (10 $\bar{1}$ 0) and (0002) peaks of the ϵ phase were observed in Fig. 2a. In comparison with the XRD for 0 h milled elemental powder, the pure face-centred cubic (fcc) Cu (200) peak had decreased.

On further milling, both (10 $\bar{1}$ 0) and (0002) peaks of the ϵ phase decreased, while the diffraction intensity from the (433) planes of the T' phase increased distinctly, as shown in Fig. 1a. This implied that the four metastable phases (η , ϵ , α and T') had undergone a four-phase transformation ($\alpha + \epsilon \rightarrow T' + \eta$) during mechanical milling. Meanwhile, the pure fcc Cu (200) peak decreased further, but still existed after 46 h milling. This meant that the formation of the phases from the pure elemental powders had not yet been completed after 46 h milling. After 118 h milling, the pure fcc Cu (200) peak had vanished and the intensity from (433) planes of the T' phase had increased strongly. The formation of the phases from the pure elemental powders was completed, while the four-phase transformation ($\alpha + \epsilon \rightarrow T' + \eta$) went on during the prolonged mechanical milling. The final products of the mechanical milling were α , T' and η for the elemental mixture of Zn–22%Al–18%Cu, as shown in Fig. 1a. From the XRD results, it was clear that the mechanical alloying consisted of two stages:

(i) From 0 to 118 h, the formation of the metastable phases η , ϵ , α and T' from the pure elemental powders.

Table 1. d spacings (Å) of the pure elemental powders Zn, Al, and Cu, 22 h milled Zn–22%Al–18%Cu, and 4 h milled Zn–5%Al–11%Cu alloys.

Material	(0002)	(10 $\bar{1}$ 0)	(10 $\bar{1}$ 1)	(10 $\bar{1}$ 2)	(111)	(200)
Pure elements	2.471	2.305	2.088	1.686	2.335	2.022
22 h milled Zn–22%Al–18%Cu	2.463	2.303	2.086	1.683	2.330	2.019
4 h milled Zn–5%Al–11%Cu	2.461	2.299	2.083	1.682	2.328	2.018

(ii) From 22 h to the end of milling, the four-phase transformation: $\alpha + \epsilon \rightarrow T' + \eta$. Finally, the ϵ phase completely decomposed and disappeared on the XRD.

A similar way of mechanical alloying was observed for the elemental powder mixture of Zn–5%Al–11%Cu, as shown in Fig. 1b. After 1 h steel ball milling, both the peak positions and the relative intensities of the XRD had changed, which was comparable to the effect observed in the powder mixture of Zn–22%Al–18%Cu. The XRD peak of the (433) plane of the T' phase appeared.

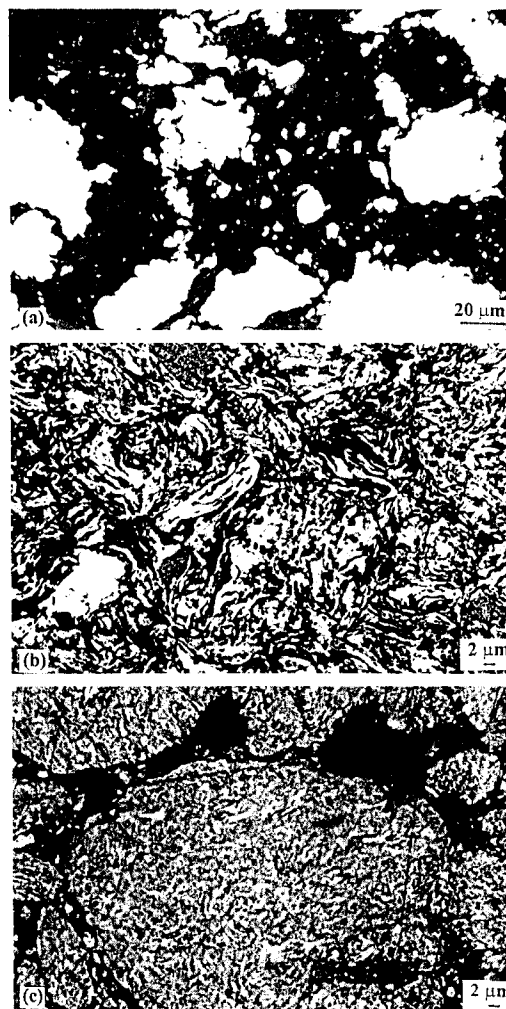


Fig. 3. Back-scattered SEM images of Zn–22%Al–18%Cu after various periods of mechanical milling: (a) 0 h, (b) 22 h, and (c) 70 h.

After 4 h milling, four phases (η , ϵ , α and T') coexisted in the powder mixture. The peak indexes and the related d spacings of the characteristic XRD of the phases are shown in Fig. 2b and Table 1. Further milling, the (0002) XRD peak of the ϵ phase became more clear, accompanied with the decreasing of the XRD peaks of the α phase. This implied that the four-phase transformation ($\alpha + \epsilon \rightarrow T' + \eta$) was occurring after 4 h milling. The existence of the pure fcc Cu (200) peak indicated the stage of formation of the metastable phases from pure elemental powders had not yet been completed after 22 h milling, while the milling-induced phase transformation already occurred after 4 h milling. The stage of the formation of the phases had been completed after 46 h milling, when the pure fcc Cu (200) peak disappeared from the X-ray diffractogram, as shown in Fig. 1b. During the prolonged milling, both of the XRD intensities of the T' and η phases were found to increase to the maximum. The final products of the mechanical milling were ϵ , T' and η for the elemental mixture of Zn–5%Al–11%Cu, as shown in Fig. 1b.

From the XRD results, the two stages of mechanical alloying for the elemental mixture of Zn–5%Al–11%Cu were observed as follows:

(i) From 0 to 46 h, the formation of the metastable phases (α , ϵ , η , and T') from the pure elemental powders.

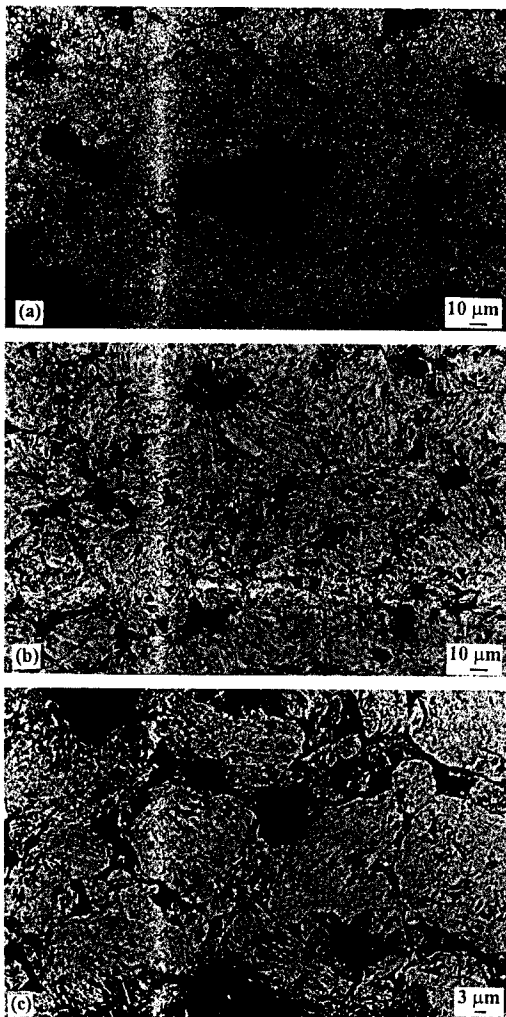


Fig. 4. Back-scattered SEM images of Zn–5%Al–11%Cu after various periods of mechanical milling: (a) 0 h, (b) 22 h, and (c) 70 h.

(ii) From 4 h to the end of milling, the four-phase transformation ($\alpha + \epsilon \rightarrow T' + \eta$).

Finally, the α phase totally decomposed and disappeared on the XRD.

For the elemental powder mixture of Zn–27%Al–3%Cu, the formation of the metastable phases from the pure elemental powders was established during mechanical milling, as shown in the X-ray diffractograms (Fig. 1c). Because of only 3% of copper in this powder mixture, it was hard to observe the ϵ phase as detected in the powder mixture of Zn–22%Al–18%Cu. The XRD of the pure (200) Cu disappeared after 118 h milling. That meant the first stage of mechanical alloying, i. e. the formation of phases from the pure elemental powder was from 0 h to about 118 h. After the phases formed from the elemental powders, the milling-induced phase transformation occurred and the final phases were α , T' , and η , just similar to the case of the elemental mixture of Zn–22%Al–18%Cu, as shown in Fig. 1c.

From the XRD results described above, it was reasonable to deduce that the mechanical alloying was a process of two stages. It started with the formation of the phases from the pure elemental powders, and this was followed by the mechanical milling induced phase transformation. At the first stage, i. e. the formation of the phases from the pure elements were 0–118 h and 0–46 h for the elemental powder

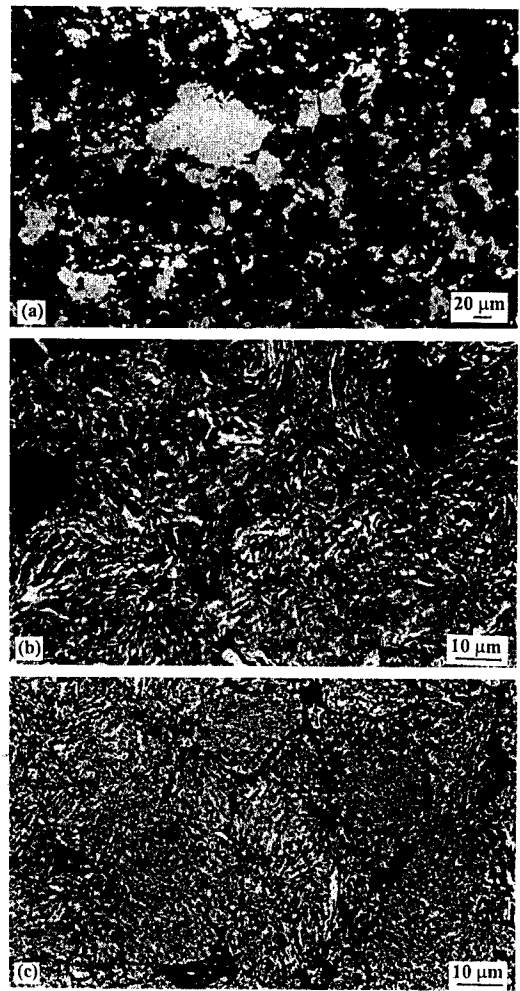


Fig. 5. Back-scattered SEM images of Zn–27%Al–3%Cu after various periods of mechanical milling: (a) 0 h, (b) 22 h, and (c) 70 h.

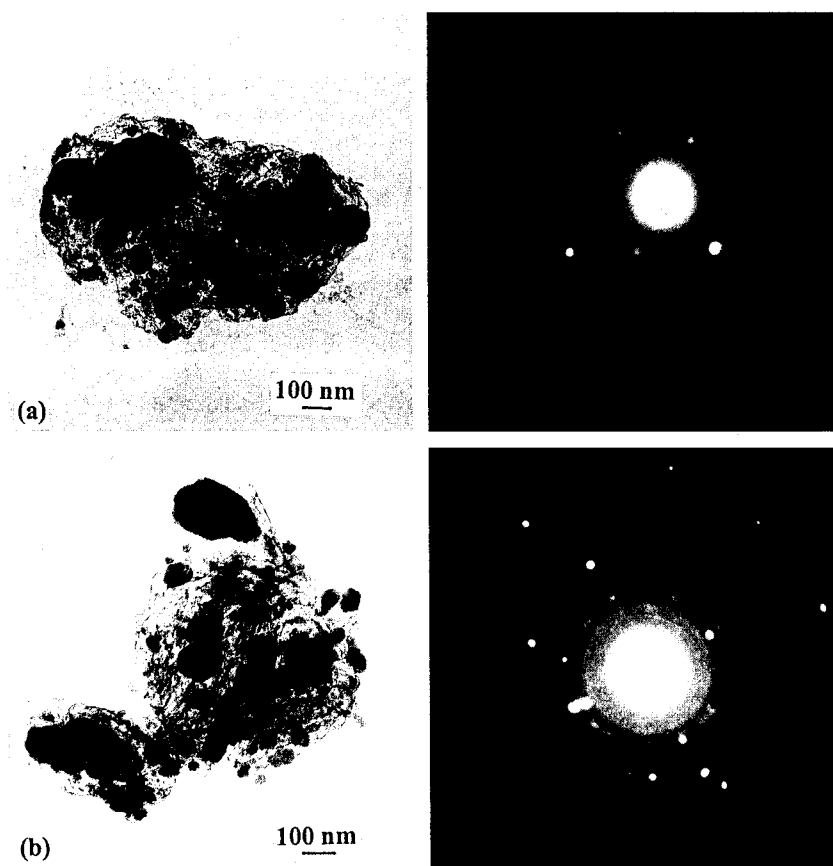


Fig. 6. TEM bright field micrographs and the corresponding electron diffraction patterns of the 300 h milled powder mixtures: (a) Zn-22%Al-18%Cu, (b) Zn-5%Al-11%Cu.

mixtures of Zn-22%Al-18%Cu and Zn-5%Al-11%Cu alloys, respectively. Once the four metastable phases (α , ε , T' , and η) formed after 22 and 4 h milling in the powder mixtures of Zn-22%Al-18%Cu and Zn-5%Al-11%Cu, respectively, the second stage, i. e. the mechanical milling-induced phase transformation started. The final products of the mechanical alloying for both the elemental powder mixtures were α , T' , η , and ε , T' , η , respectively, depending on the composition of the powder mixture.

It is necessary to notice that there is a four metastable phases coexistence ($\alpha + \varepsilon + T' + \eta$), i. e. an equilibrium: $\alpha + \varepsilon = T' + \eta$ at 268 °C in the ternary Zn–Al–Cu alloy system, as reported in previous investigations [9–14]. The four phases: α , ε , T' , and η (in coexistence), that formed in the first stage of mechanical alloying at near room temperature, were actually the equilibrium phases: α , ε , T' , and η at 268 °C. Therefore, this four-phase coexistence in the mechanical alloying was in correspondence with the equilibrium: $\alpha + \varepsilon = T' + \eta$ at 268 °C.

Below 268 °C, the alloys located within the four-phase field ($\alpha + \varepsilon + T' + \eta$) became metastable and decomposed in the way of a four-phase transformation: $\alpha + \varepsilon \rightarrow T' + \eta$. The final stable phases would be either $\alpha + \eta + T'$ or $\varepsilon + \eta + T'$, or $\eta + T'$, depending on the composition of the alloy [9–14]. Under external stress circumstances (such as extrusion, tensile, creep, and fatigue etc.), the decomposition of the various metastable phases was considerably accelerated. Moreover, the phase transformation that occurred in the part of the specimens less with external strain was related with the early stage of the phase transformation during ageing, while the phase transformation during the prolonged ageing

occurred in the neck zone and the rupture part of the specimens, where the higher strain was concentrated [15–18].

During mechanical alloying, after the metastable phases formed in the early stage of milling, they started to transform to a more stable state under external stresses induced by mechanical milling (in combination of impact, grinding, and fatigue, etc.). The observed decomposition of these metastable phases, i. e. the milling induced phase transformation (one kind of external stress induced phase transformation), $\alpha + \varepsilon \rightarrow T' + \eta$, was essentially also related with the four-phase equilibrium at 268 °C: $\alpha + \varepsilon = T' + \eta$.

It was also found that the four metastable phases (α , ε , T' , and η) formed earlier in the powder mixture Zn-5%Al-11%Cu (after 4 h milling) than in the powder mixture Zn-22%Al-18%Cu (after 22 h milling). In the Zn–Al-based alloys, the solid state reactions or phase transformations were, in most cases, related with the diffusion of atoms involved. The Zn atoms have a higher diffusion coefficient than Al and Cu [19]. In the mechanical milling, the formation of the phases would be more rapid in the Zn-richer powder mixture.

The final products of the mechanical milling were α , T' , η , and ε , T' , η , respectively, which were in agreement with the equilibrium phases at room temperature for the Zn–Al-based alloys. Therefore, the characteristics of the mechanical alloying, such as the formation and transformation of the phases, were essentially in accordance with the equilibrium phases at higher temperature and the decomposition of these high-temperature equilibrium phases at the near room temperature of mechanical milling, respectively.

3.2 Microstructure of Mechanically Milled Alloys

Another characteristic of mechanical alloying of the elemental powders was the formation of a nano-microstructure. The microstructural evolution of the elemental powders: Zn–22%Al–18%Cu, Zn–5%Al–11%Cu, and Zn–27%Al–3%Cu, is shown in Figs. 3–5. Similar microstructure changes were observed in these powder mixtures in the whole mechanical alloying.

Accompanying with the formation and transformation of the phases, the elemental powders were repeatedly impacted, ground, welded and deformed into flake-shaped particles at the early stage of milling. In the back-scattered SEM images, the Zn-rich η and ε phases appeared in bright contrast, while the Al-rich α phase was dark in contrast. During the prolonged milling, these flake-shaped particles were deformed into very fine equiaxed particles of nanometer size (40–100 nm), as shown in TEM bright field micrographs and the corresponding electron diffraction patterns of the 300 h milled powder mixtures (Fig. 6). Because of the very fine particle sizes, the concentric rings corresponded to a polycrystalline structure. The reflection images of the phases involved were overlapping.

4 Conclusions

1. Four metastable phases (α , ε , T' and η) formed in both 22 h milled Zn–22%Al–18%Cu and 4 h milled Zn–5%Al–11%Cu powder mixtures, which was followed by a four-phase transformation ($\alpha + \varepsilon \rightarrow T' + \eta$) during the prolonged mechanical milling. The final products of the mechanical milling were α , T' , η , and ε , T' , η , respectively, which are in agreement with the equilibrium phases at room temperature in Zn–Al alloys.
2. Mechanical alloying is a process consisting of two steps. It starts with the formation of phases from the pure elemental powders, followed by a phase transformation induced by mechanical milling.
3. The characteristics of the mechanical alloying, i. e. formation and transformation of the phases, were essentially related with the equilibrium phases at higher temperature, and a decomposition of these high-temperature equilibrium phases occurred at the near room temperature of mechanical milling, respectively.

4. Nano-microstructure was obtained by mechanical alloying of Zn–Al-based alloys.

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