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# Milling characteristics of extruded eutectoid Zn–Al alloy

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**Abstract**

Mechanical milling-induced phase transformations, microstructural changes and preferred crystal orientation of the extruded eutectoid Zn–Al-based alloy are reported. Decomposition of a metastable $\eta'_E$ phase and a four-phase transformation: $\alpha + \varepsilon \rightarrow T' + \eta$, were greatly accelerated by mechanical milling. The mechanism of the milling-induced microstructural change from a lamellar structure to a fine grain structure was found to be different from that which occurred under tensile and creep deformations in the extruded eutectoid Zn–Al-based alloy. A preferred crystal orientation was observed as well, in the alloy during milling, which was supported by a rolling-induced preferred orientation in the same alloy. 

*Keywords:* Milling; Extrusion; Phase transformation; Discontinuous precipitation; Structure change; Nanostructure; Preferred orientation; Zn–Al alloy

## 1. Introduction

Mechanical milling is an important process for both powder metallurgy and mechanical alloying. When milling metallic or other material powder or filings, they are repeatedly impacted, ground and compressed by stainless steel or marble balls. External stresses imposed on the materials result not only in changing of morphology, but also in the transformation of physical and chemical properties of the materials. It was reported that during mechanical milling, the pure metallic powder of the Zn–Al–Cu system underwent two stages of transformation, i.e. the first was the formation of phases from the pure elemental powder, and the second was the external stress-induced phase transformation [1]. Therefore, it is necessary to research what kind of phase transformation and microstructural change would occur under an external stress induced by mechanical milling.

The present work will report some results on milling characteristics of an extruded eutectoid Zn–Al alloy, i.e. a milling-induced phase transformation and microstructural change.

## 2. Experimental

Continuously casting ingots of the eutectoid Zn–Al alloy containing 2% Cu, [Zn76–Al22–Cu2 (wt.%)] were extruded at 250°C. Alloy filings were produced with water cooling from the extruded alloy ingots, and this was followed by ball milling at room temperature under an argon atmosphere in a stainless steel pot. The weight ratio of the stainless steel ball (12.7 mm in diameter) to the Zn–Al-based alloy filings was 36:1, methanol solution (1 wt.%) being added as a surfactant agent. The milling pot was rotated at a speed of 110 rpm. Small amounts of the milled alloy filings were taken after selected intervals of milling, then examined by scanning electron microscopy (SEM) and X-ray diffraction. Each time, relative amounts of the stainless steel balls were taken out from the milling pot to keep the weight ratio constant.

Procedures for X-ray diffraction, SEM and transmission electron microscopy (TEM) examinations were reported in a previous article [2].

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## 3. Results and discussion

### 3.1. Microstructure and phase relationships before milling

The extruded eutectoid Zn–Al-based alloy consisted of four-phases: $\alpha$, $\eta'_E$, $\varepsilon$ and $T'$, as shown in the X-ray diffractogram, Fig. 1. The $\alpha$ phase is an Al-rich f.c.c. phase. The $\eta'_E$ phase is a metastable Zn-rich h.c.p. phase in the as-extruded eutectoid Zn–Al alloy. The $\varepsilon$ is a compound ($Zn_4Cu$) and the $T'$ phase is a rhombohedral phase (Zn10–Al35–Cu55 in wt.%).

During 250°C extrusion, the dendritic structure of the cast alloy was destroyed, to form a fine lamellar structure in the supersaturated $\alpha'_S$ phase, which was surrounded by a coarse lamellar structure derived from the supersaturated $\beta'_S$ phase. The zinc-rich $\eta'_E$ and $\varepsilon$ phase particles were from the original interdendritic regions in the cast alloy [3–5]. Fig. 2(a) shows a SEM micrograph of the filings of extruded eutectoid Zn–Al-based alloy before milling. The $\alpha'_S$ and $\beta'_S$ were labeled on the fine lamellar and the coarse lamellar structure to indicate the original phases of both lamellar structures, which consisted of the dark-contrast $\alpha$ phase and the light-contrast $\eta$ and $\varepsilon$ phases. A small amount of $\varepsilon$ phase decomposed to the $T'$ phase in the extruded specimen in a four-phase transformation: $\alpha + \varepsilon \rightarrow T' + \eta$, as shown in Fig. 1 [6–10].

### 3.2. Milling-induced phase transformation

During milling, the intensity of the (0002) diffraction peak of the metastable Zn-rich $\eta'_E$ phase shifted gradually to the lower $2\theta$, accordingly the d-spacing of the (0002) crystal planes of the phase increased from 0.2449 nm for the extruded alloy filings to 0.2461 nm for the 15 h milled filings, and finally reached 0.2466 nm after 100 h milling, while the $(10\bar{1}0)$ and $(10\bar{1}1)$ diffraction peaks of the $\eta'_E$ remained unchanged, as shown in Fig. 1. This was in agreement with observations in the specimens of cast, furnace-cooled and extruded eutectoid Zn–Al-based alloys under tensile, creep and fatigue deformations [3–5,11–15]. This is a characteristic of the decomposition of the Zn-rich $\eta'_E$ phase, which takes place as $\eta'_E \rightarrow \eta + \alpha + T'$ during isothermal holding [3].

It was also observed that the X-ray diffraction intensity of the $\varepsilon$ phase decreased with milling time, whereas the intensity of the $T'$ phase increased, as shown in Fig. 1. The decomposition of the $\varepsilon$ phase takes place in a four-phase transformation, $\alpha + \varepsilon \rightarrow T' + \eta$, as reported in many previous publications [6–10].

Comparing the aging characteristics of the extruded alloy (without external stress applied to the specimen during aging after extrusion [3,4]), both the decompositions of $\eta'_E$ and $\varepsilon$ phases were accelerated by mechanical milling. The $\eta'_E$ phase decomposed completely after $\approx 20$ h aging at 91.4°C (the temperature of the local boiling water) and the four-phase transformation was completed after 20 h aging at 150°C. The same phase

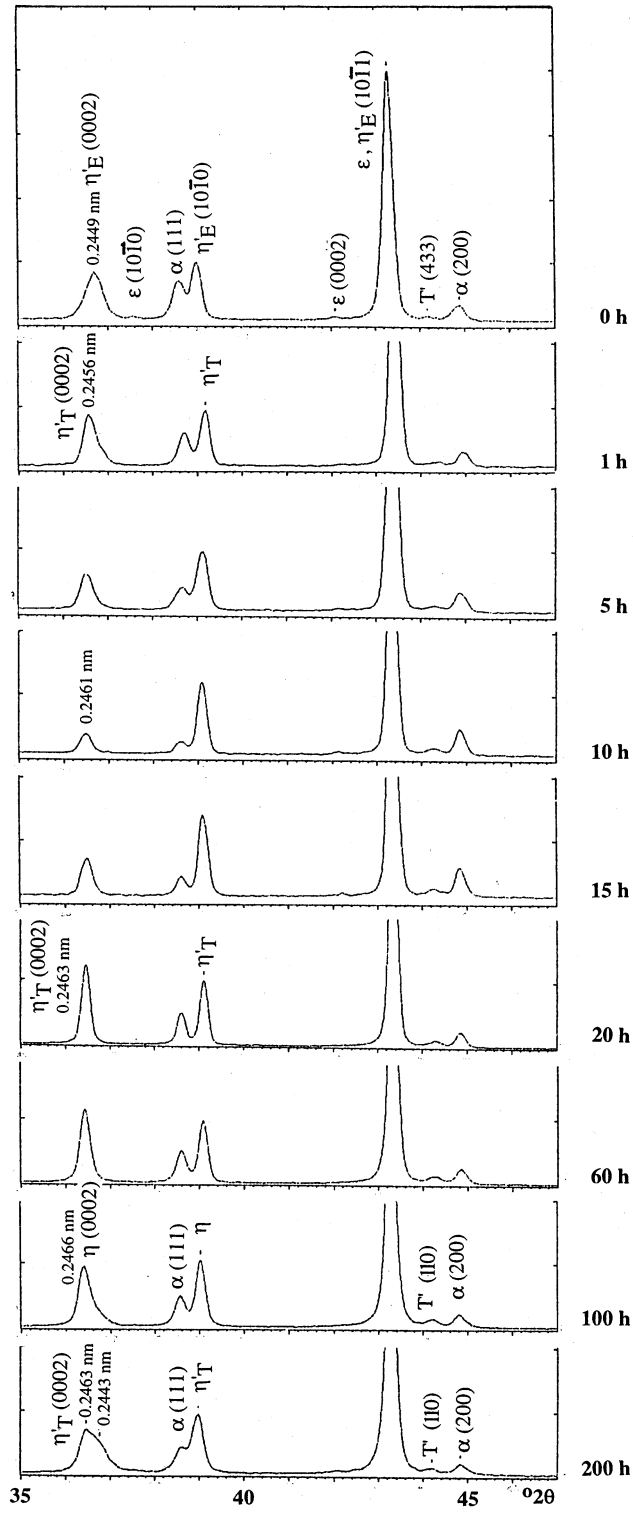
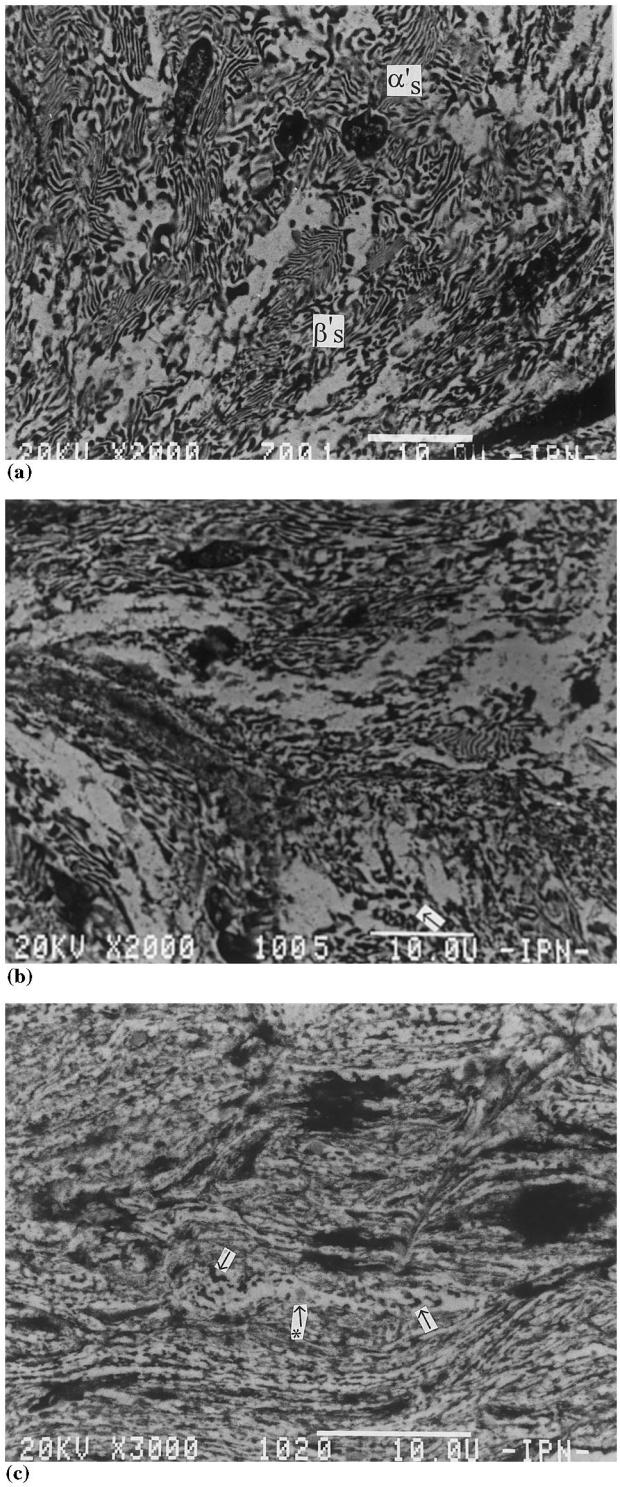



Fig. 1. X-ray diffractograms of extruded eutectoid Zn–Al alloy filings after various time intervals of milling at room temperature: 0, 1, 5, 10, 15, 20, 60, 100 and 200 h.




(a)

(b)

(c)

Fig. 2. Scanning electron micrographs of extruded eutectoid Zn–A1 alloy filings after various time intervals of milling at room temperature: (a) 0, (b) 5, (c) 20 h.

transformations occurred only in a few hours milling at room temperature.

It was interesting to find that after 200 h milling, the (0002) diffraction peak shifted back to the higher $2\theta$; accordingly the d-spacing of the (0002) crystal planes decreased from 0.2466 to 0.2443 nm. This implied that the external stress induced by mechanical milling resulted in the alloy changing from a stable state back to a metastable state again.

### 3.3. Milling induced microstructural change

During milling, the precipitation inside the light contrast $\eta'_E$ and $\varepsilon$ phase particles was developed. After 5 h milling, fine grains of $\approx 0.2$–$0.5$ μm diameter appeared as discontinuous precipitates, and this fine grain structure was developed after 20 h milling, as arrows pointed in Fig. 2 (b) and (c). Both the fine and coarse lamellar structures were replaced by a fine grain structure.

For comparison, two kinds of discontinuous precipitation in the $\eta'_E$ and $\varepsilon$ phases were identified in the extrusion-aged and extrusion-tensile tested eutectoid Zn–Al-based alloy specimens, as shown in Figs. 5 and 6, where $\rightarrow$ and $*\rightarrow$ represented precipitates in the $\eta'_E$ and $\varepsilon$ phases, respectively ([13]; unpublished research).

Fig. 3 shows the microstructures of alloy filings after 80, 100 and 200 h milling. The alloy filings were segmented into very small particles of several micrometers in diameter, whilst the decomposition of the $\eta'_E$ and $\varepsilon$ phases was well developed. After 100 h milling, a nanostructure of 20–50 nm grains formed, as shown in the TEM micrograph in Fig. 4.

The microstructural change from a lamellar structure to a fine grain structure in the milled alloy filings is quite different from that in the tensile-tested specimen of the same alloy. For comparison, the microstructural evolution and the typical microstructure of the ruptured part of the tensile-tested alloy are shown in Figs. 6 and 7 [5,13]. It was clearly observed that the change from a coarse lamellar structure to a fine grain structure and the fine lamellar remained unchanged in the extruded alloy after tensile deformation at 100°C, shown in Fig. 6. This was because the strain induced by tensile deformation was not great enough to rupture the fine lamellae, but sufficient to break the coarse lamellae. As the distance from the rupture frontier decreased, the fine grain structure developed, accompanying the precipitations in the light contrast $\eta'_E$ and $\varepsilon$ phase particles, shown in Fig. 7. In the case of milling, the fine grain structure was mainly from the decompositions of the $\eta'_E$ and $\varepsilon$ phases, the strain induced by each impacting and grinding was not sufficient for rupture of the lamellar structure, even for the coarse lamellae, but great enough for the decompositions of the $\eta'_E$ and $\varepsilon$ phases. Repeated impacting and grinding resulted in good development of the decompositions, 'etching' almost all the specimen and forming the fine grain structure.

### 3.4. Milling-induced preferred orientation

Another phenomenon induced by mechnanical milling was the preferred crystal orientation of the both metastable Zn-rich $\eta'_E$ and $\eta'_T$ phases. As shown in Fig. 1, both the (0002) X-ray diffraction of the metastable $\eta'_E$ and $\eta'_T$ phases at $2\theta$ 36.9° and 36.8° decreased in

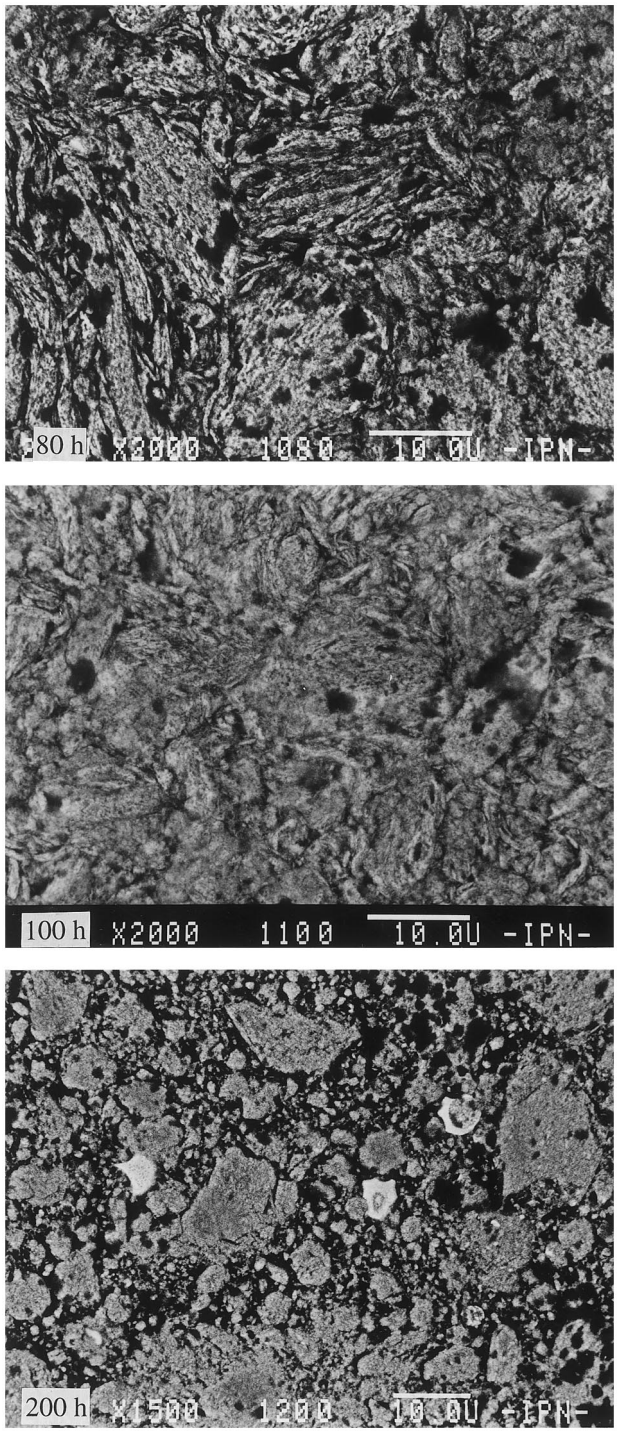



Fig. 3. Scanning electron micrographs of extruded eutectoid Zn–A1 alloy filings after various time intervals of milling at room temperature: 80, 100 and 200 h.

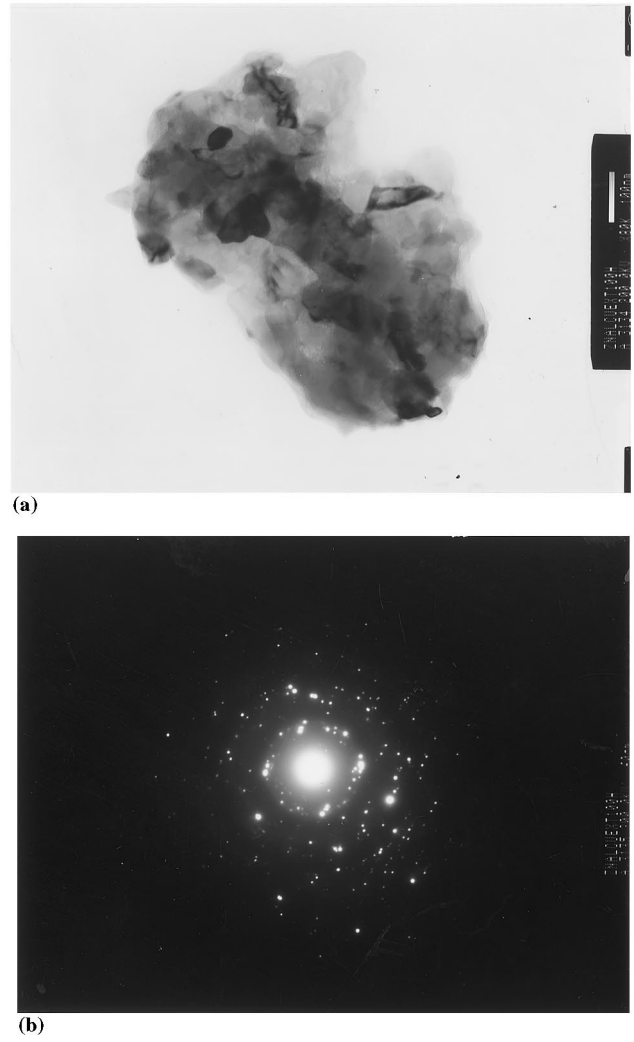



Fig. 4. TEM micrograph (a) and the selected area diffraction pattern (b) of the particle after 100 h milling.

diffraction intensity during the first 10 h milling; meanwhile the intensity of the $(10\bar{1}1)$ X-ray diffraction of the $\eta'_E$ and $\eta'_T$ phases at 43.3° increased. Further milling the intensity of the (0002) X-ray diffraction of the metastable $\eta'_E$ and $\eta'_T$ phases increased and recovered the original intensity after 20 h milling. This implied that the crystal orientation of the Zn-rich $\eta'_E$ and $\eta'_T$ phases changed during milling, i.e. there was a preferred orientation of both $\eta'_E$ and $\eta'_T$ phases under external stress induced by mechanical milling. By studying evolution of the plastic deformation of the alloy filings, it was found that the changing of the diffraction intensity of the phases were caused by the milling induced external stress.

Fig. 8 shows the evolution of the plastic deformation of the alloy filings during 20 h milling. During the first 10 h of milling the alloy filings were flattened due to the directional stress imposed by repeated impacting and grinding. This directional stress resulted in the preferred orientation at $(10\bar{1}1)$ crystal planes of the $\eta'_E$ and $\eta'_T$

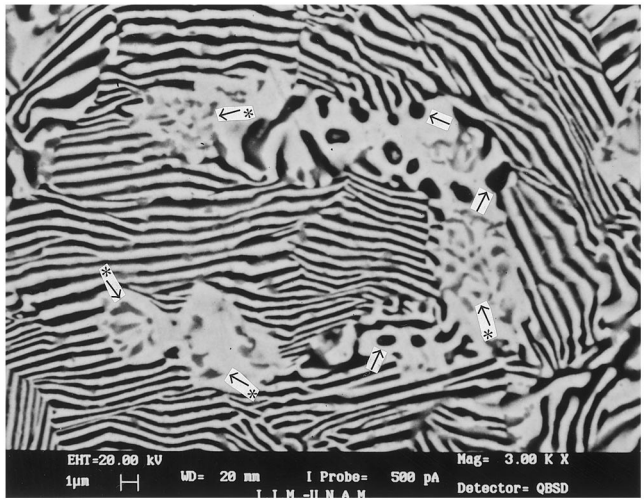



Fig. 5. Discontinuous precipitation within the light contrast $\eta'_E$ and $\varepsilon$ phase particles in the extruded Zn–A1 alloy after 50 h aging at 170°C (without external stress during aging after extrusion): →, precipitation of the $\eta'_E$ phase; *→, precipitation of the $\varepsilon$ phase.

phases. With furthering milling, the flattened alloy filings segmented to intergranular small particles, and the directional external stress gradually disappeared. Therefore, the preferred orientation of the phases recovered the original crystal orientation.

A similar preferred orientation was observed during rolling in the alloy. Shown in Fig. 9, the X-ray diffractograms of the solution-treated, quenched eutectoid Zn–Al-based alloy after rolling to various reductions (unpublished research). It was found that the (0002) X-ray diffraction of the metastable $\eta'_T$ phase decreased apparently in intensity after rolling to a 90% reduction; accordingly the intensity of the $(10\bar{1}1)$ diffraction of the phase increased greatly. The rolling is a mechanical process with one direction

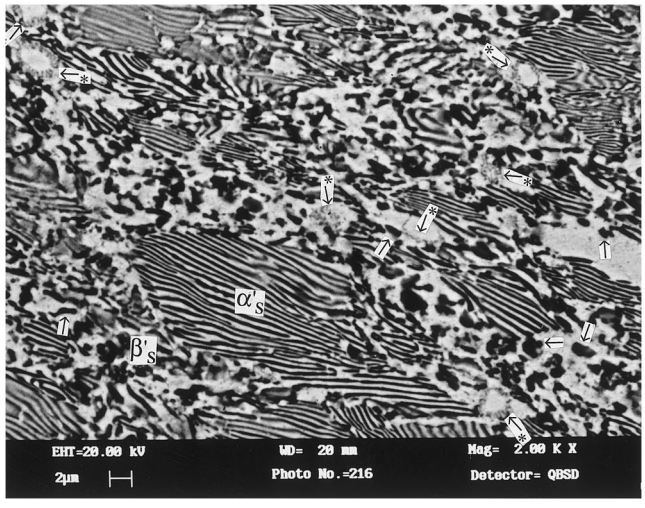



Fig. 6. Scanning electron micrograph of the rupture part of extruded eutectoid Zn–A1 alloy after tensile testing at 100°C.

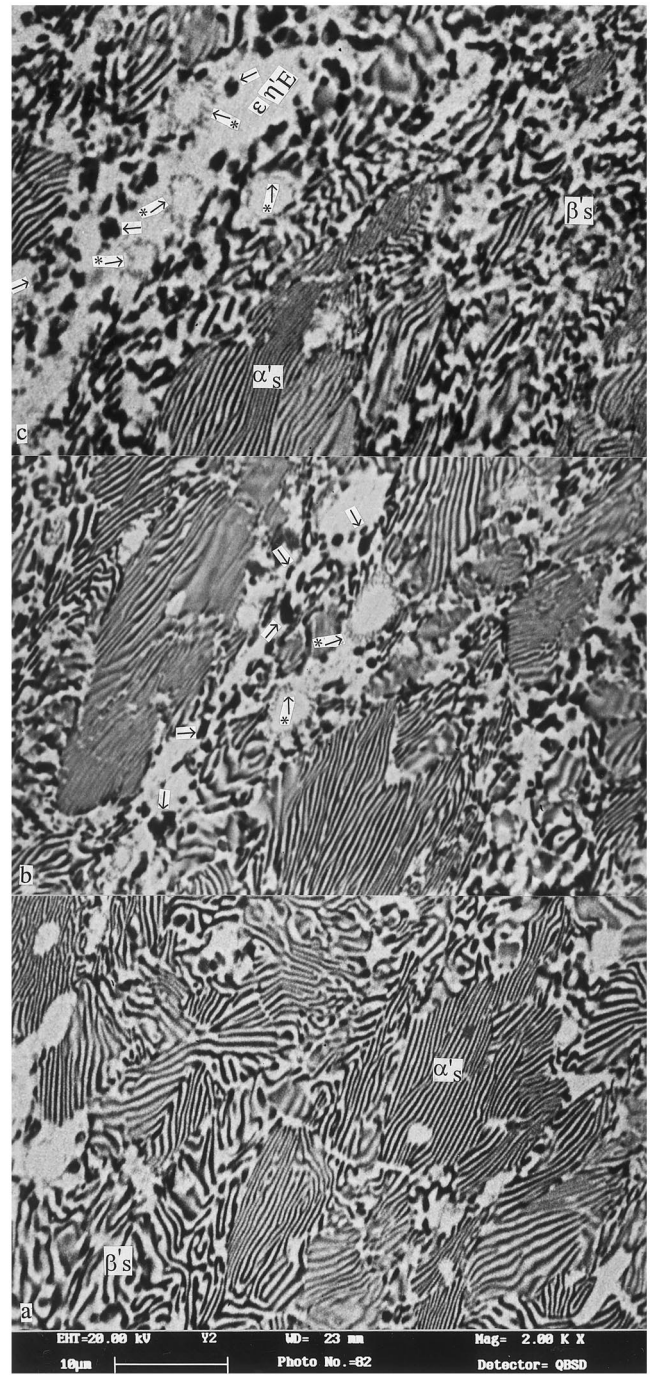



Fig. 7. Scanning electron micrographs of various parts of extruded eutectoid Zn–A1 alloy specimen after tensile testing at 100°C: (a) bulk part, (b) neck zone and (c) rupture part.

compression which is imposed on the alloy specimen. Apparently, the rolling-induced directional external stress resulted in a preferred crystal orientation in the eutectoid Zn–Al alloy. In the case of milling, the directional external stress was destroyed as the flattened alloy filings were ground into small intergranular particles, and the preferred orientation returned back to the 0 h milling original state.

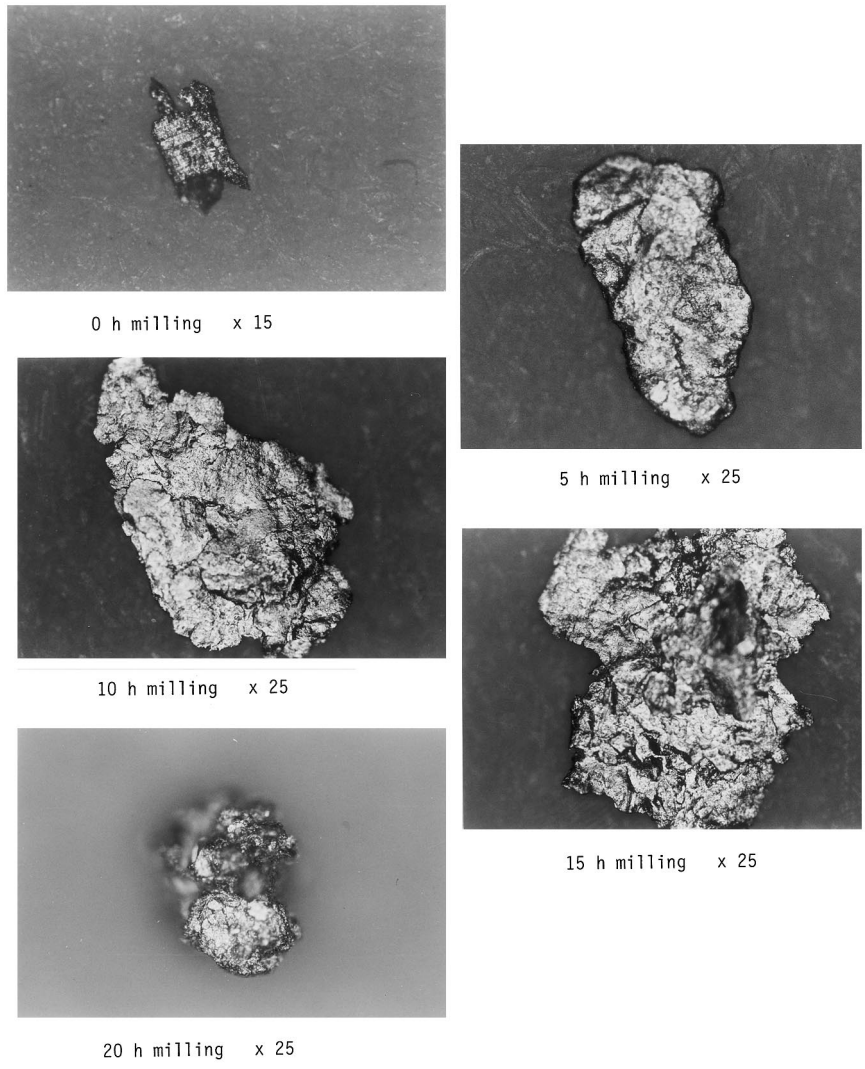



Fig. 8. Deformation evolution of extruded eutectoid Zn–A1 alloy filings during milling.

## 4. Conclusions

(1) Both metastable phases, $\eta'_E$ and $\varepsilon$, decomposed during mechanical milling at room temperature. These phase transformations were accelerated by mechanical milling, compared with what occurred in isothermal holding. After a long milling time, the alloy filings reached a final stable state at room temperature, further milling resulted in the destabilization of the alloy filings.

(2) The microstructure of the extruded Zn–Al-based alloy filings changed from a lamellar structure to a fine grain structure during mechanical milling at room temperature, which became obvious with milling time, and formed a nanostructure during prolonged milling.

(3) The microstructural change took place by decomposition of the Zn-rich $\eta'_E$ and $\varepsilon$ phase in the extruded Zn–Al-based alloy during milling, which was different from what occurred during tensile deformation. The latter appeared as only partial spheroidization of the coarse lamellar structure.

(4) The directional external stress induced by mechanical milling resulted in a preferred crystal orientation of the metastable $\eta'_E$ phase.

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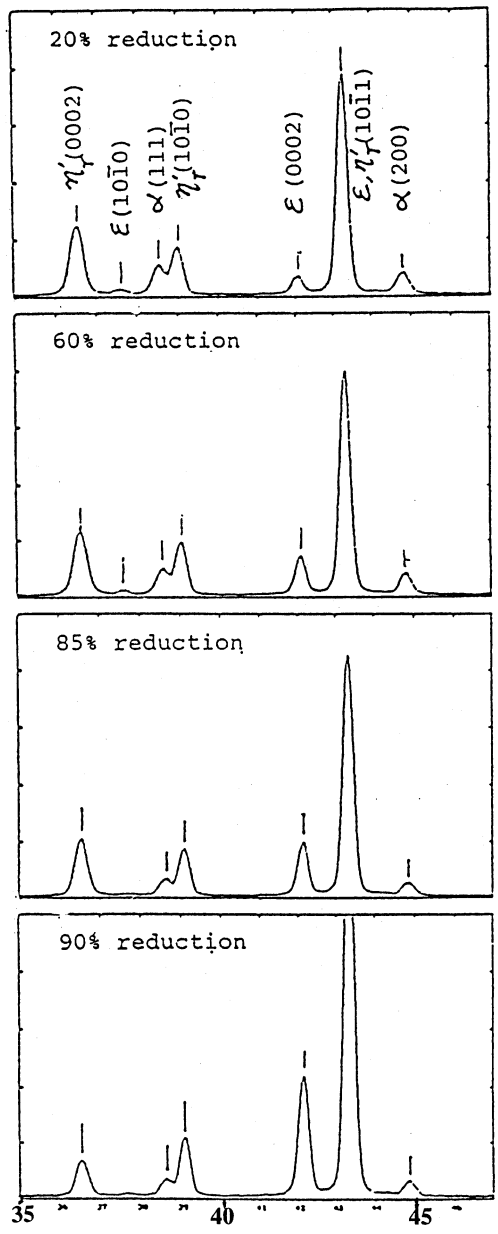


Fig. 9. X-ray diffractograms of the solution-treated, quenched-eutectoid Zn–Al alloy after various reduction rolling, to show the preferred orientation.

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