JOURNAL OF MATERIALS SCIENCE **34** (1999) 3653–3658

Phase decomposition in extruded Zn-Al based alloy

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Ageing characteristics of an extruded eutectoid Zn-Al based alloy were investigated using X-ray diffraction and scanning electron microscopy techniques. The extruded alloy consisted of Al rich α phase and Zn rich η'_E and ε phases. The original cast eutectoid Zn-Al alloy was extruded at 250 °C. Both supersaturated α'_s and β'_s phase decomposed during extrusion and appeared as fine and coarse lamellar structures. The η'_E and ε phases particles formed in the original interdendritic region. It was found that two Zn rich phases η'_E and ε decomposed sequentially during ageing at 170, 140 °C. The decomposition of the η'_E phase occurred as a discontinuous precipitation in the early stage of ageing and the decomposition of the ε phase took place in a four phase transformation: $\alpha + \varepsilon \rightarrow T' + \eta$ in the prolonged ageing. Two typical morphologies of the decomposition of the Zn rich phases η'_E and ε were distinctive in back-scattered scanning electron microscopy.

1. Introduction
Alloy materials suffer always various external stresses during their manufacturing and service application. The investigation of the stress induced phase transformation and microstructural change in most alloy materials is of practical importance.

Decomposition of Zn-rich metastable phases in an extruded eutectoid Zn-Al based alloy become recently an interesting topic because of its correlation with dimensional stability of the material [1–3]. When the eutectoid Zn-Al based alloy (Zn76Al22Cu2 in wt %) was extruded at 210–290 °C, the Zn-rich phase η'_E formed as a metastable phase, and decomposed during isothermal holding. It was observed that the decomposition of the metastable η'_E phase resulted in dimensional shrinkage of the material. Another Zn-rich metastable phase ε decomposed during prolonged aging, which caused expansion of the material.

In this paper the decomposition of both the metastable phases η'_E and ε in the extruded alloy was in detail investigated during isothermal holding.

2. Experimental
The eutectoid Zn-Al based alloy material Zn76Al22Cu2 (wt %) was continuously cast into rod of 178 mm in diameter, then extruded into rod of 20 mm in diameter after heating up to 250 °C. The extruded alloy specimens had been previously aged for a period in excess of 2 years at ambient temperature.

The isothermal holding was carried out at 170 and 140 °C respectively. X-ray diffraction (XRD) identification, scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA) techniques were applied for investigation of decomposition of the phases involved and microstructural change during ageing at 170 and 140 °C. A X-ray diffractometer with nickel filtered CuK_α radiation was employed scanning on flat specimens at a speed of 1 deg/min within a 2θ range from 35° to 47° to obtain characteristic X-ray diffraction peaks. Standard metallographic examination was carried out in a scanning microscope using back-scattered SEM image to receive visible atomic number contrast.

3. Results and discussion
3.1. Decomposition of Zn-rich η'_E and ε phases
It was observed that the extruded alloy consisted of Al-rich α phase and Zn-rich η'_E and ε phases before isothermal holding, as shown in the X-ray diffractograms of the extruded eutectoid Zn-Al based alloy at various stages of ageing at 170 and 140 °C respectively (Figs 1 and 2). Both supersaturated Al-rich α'_s and Zn-rich β'_s phase decomposed during extrusion at 250 °C and appeared as fine and coarse lamellar structures, as shown in the back-scattered SEM images (Fig. 3). The η'_E and ε phases particles formed in the interdendritic region of the original cast eutectoid Zn-Al based alloy.

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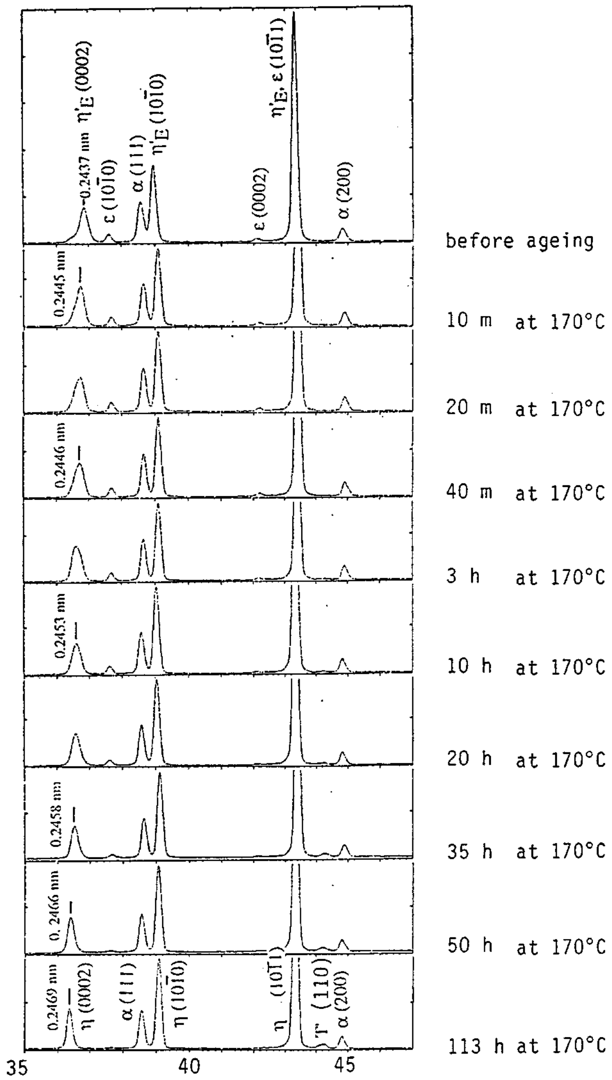


Figure 1 X-ray diffractograms of the extruded eutectoid Zn-Al alloy after various stages of ageing at 170 °C.

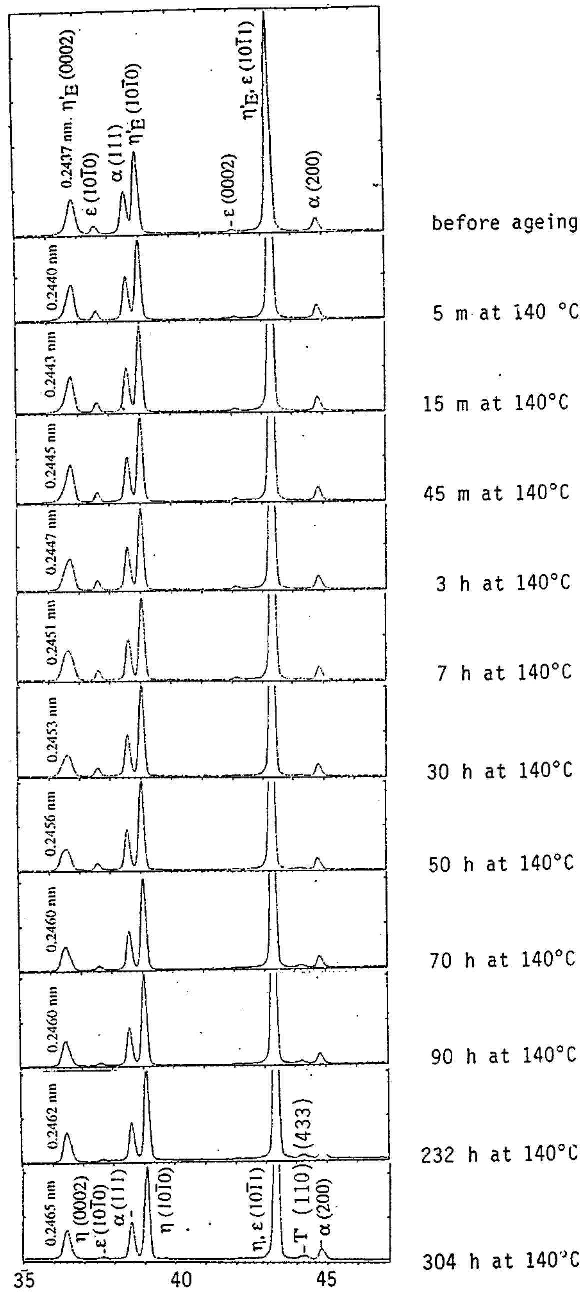


Figure 2 X-ray diffractograms of the extruded eutectoid Zn-Al alloy after various stages of ageing at 140 °C.

It was noticed that the d-spacing of the (0002) crystal planes of the Zn-rich η'_E phase in the extruded alloy was 0.2437 nm, accordingly $2\theta = 36.8^\circ$ before ageing.

After 10 min ageing at 170 °C, the (0002) diffraction peak of the η'_E phase shifted to the lower 2θ angle, and the d-spacing of the crystal planes increased accordingly to 0.2445 nm. This (0002) diffraction peak shifted further and the d-spacing increased to 0.2446 nm. The shifting of the (0002) peak of the Zn-rich η'_E phase was reported to occur in the same alloy during tensile and creep deformation, and mechanical milling [4–7]. This is a characteristic of the decomposition of the Zn-rich η'_E phase. It was reported that the Zn- rich η'_E phase decomposed into three phase, i.e. $\eta'_E \rightarrow \eta + \alpha + T'$ [2]. The decomposition of the η'_E phase at the early stage of ageing was then followed by decomposition of the ε phase during prolonged ageing. As shown in Fig. 1, the diffraction intensity of the ε phase both from (1010) and (0002) planes decreased after 3 h ageing at 170 °C. With increasing ageing time the intensity of the ε phase further decreased, whilst the diffraction intensity of the T' phase from (110) (433) crystal planes increased. After 113 h ageing at 170 °C the diffraction peaks of the ε phase vanished in the X-ray diffractogams, and the T' phase was well developed. The relative X-ray diffraction intensity changes of the ε and T' phases during ageing at 170 °C are shown in Fig. 4a (here t is ageing time). It is well recognized that the decomposition of the ε phase takes place via a four-phase transformation, $\alpha + \varepsilon \rightarrow T' + \eta$, in the prolonged ageing, also occurs under external stress [3–11].

It was also noticed that the shifting of the (0002) diffraction peak of the η'_E phase occurred during the whole process of ageing at 170 °C. The diffraction angle (2θ) of the (0002) peak decreased finally to 36.42°, accordingly the d-spacing increased to 0.2469 nm. The lattice parameters "c" of the η'_E phase both before and after ageing at 170 °C were calculated as 0.4874 nm and 0.4938 nm respectively, as shown in Fig. 1.

A similar phase transformation sequences was observed in the specimens aged at 140 °C, as shown in Fig. 2. The (0002) diffraction peak of the η'_E phase

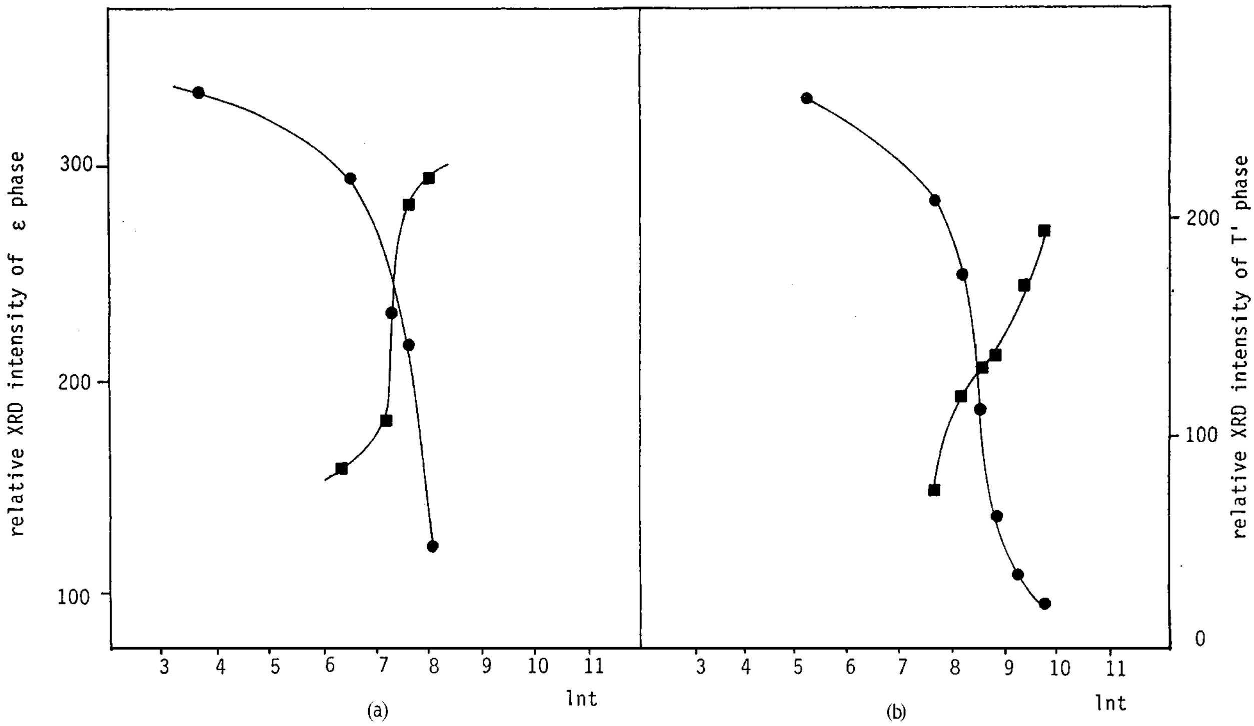
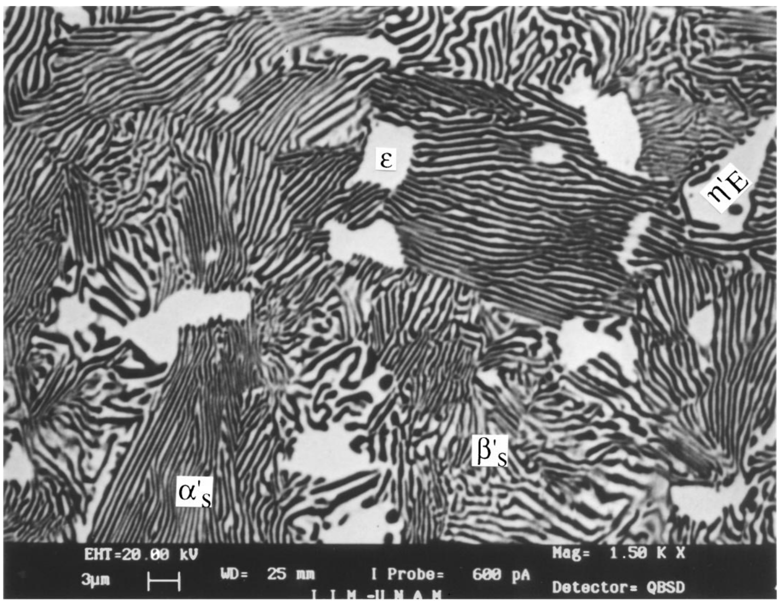


Figure 3 The relative X-ray diffraction (XRD) intensity changes of ε and T' phases during ageing at 170 °C (a) and 140 °C (b). ● from (10$\bar{1}$0) planes of the ε phase; ■ from (433) planes of the T' phase.



(a)

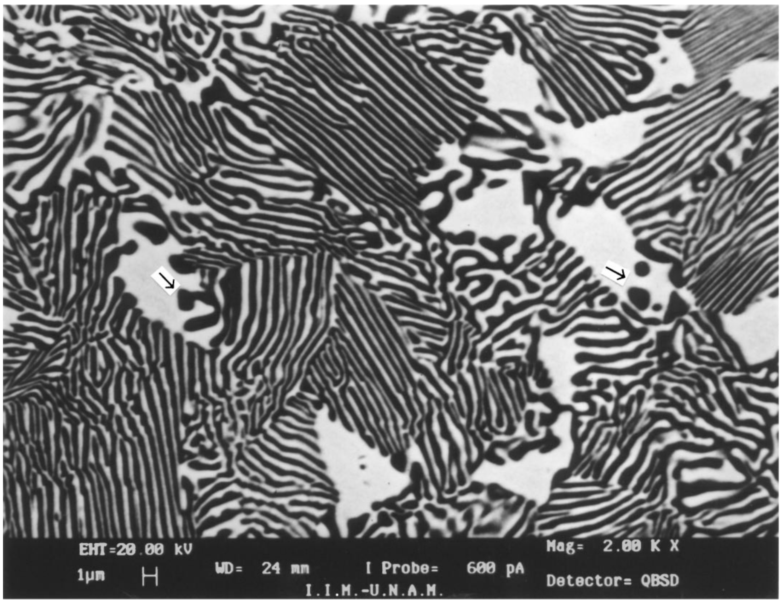
Figure 4 Scanning electron micrograph of the extruded eutectoid Zn-Al alloy (a) before ageing, and after ageing at 170 °C for 1 h (b), 10 h (c), and 50 h (d). → Precipitation of the η'_E phase; *→ precipitation of the ε phase. (*Continued*)

shifted to the lower 2θ, accordingly the d-spacing of the (0002) crystal planes increased, as labeled in Fig. 2. Also the relative changes of the X-ray diffraction intensity of ε and T' phases during prolonged ageing at 140 °C were observed, as shown in both Figs 2 and 4b. However the phase transformation rate at 140 °C was apparently lower than that at 170 °C. As shown in Figs 1 and 2, the X-ray diffraction peaks of the ε phase vanished after 113 h ageing at 170 °C, whist the (10$\bar{1}$0) X-ray diffraciton peak of the ε phase still exsisted after 304 h ageing at 140 °C.

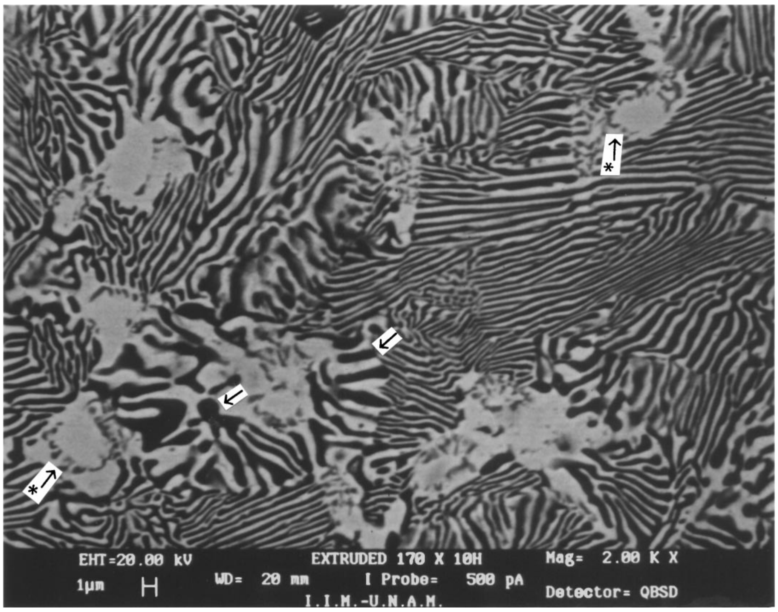
3.2. Microstructural characteristics

The above mentioned two stages of decomposition were clearly observed on scanning electron microscope. As shown in the back-scattered SEM images of the extruded eutectoid Zn-Al based alloy at various stages of ageing at 170 °C (Fig. 3), the microstructural evolution of the extruded eutectoid Zn-Al based alloy was characteristic of two kinds of decomposition of the Zn-rich η'_E and ε phases.

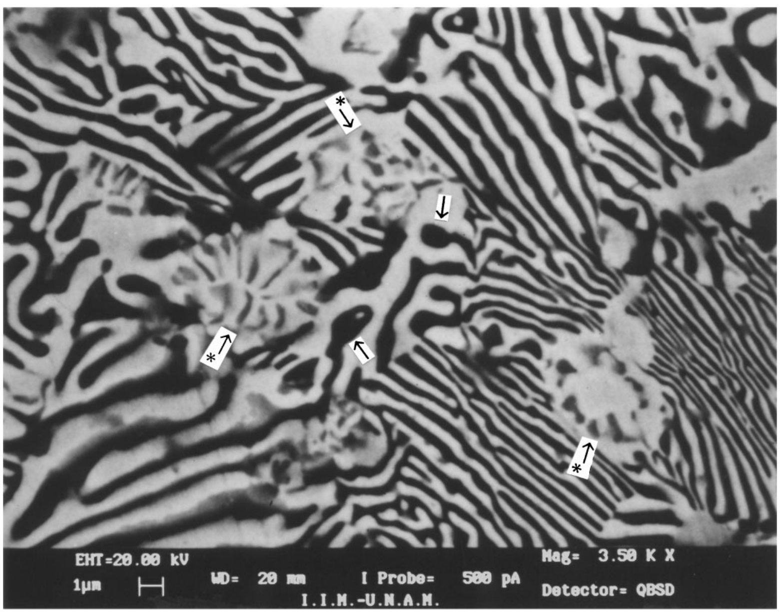
Before ageing the microstructure of the extruded eutectoid Zn-Al based alloy consisted of the light contrast



(b)

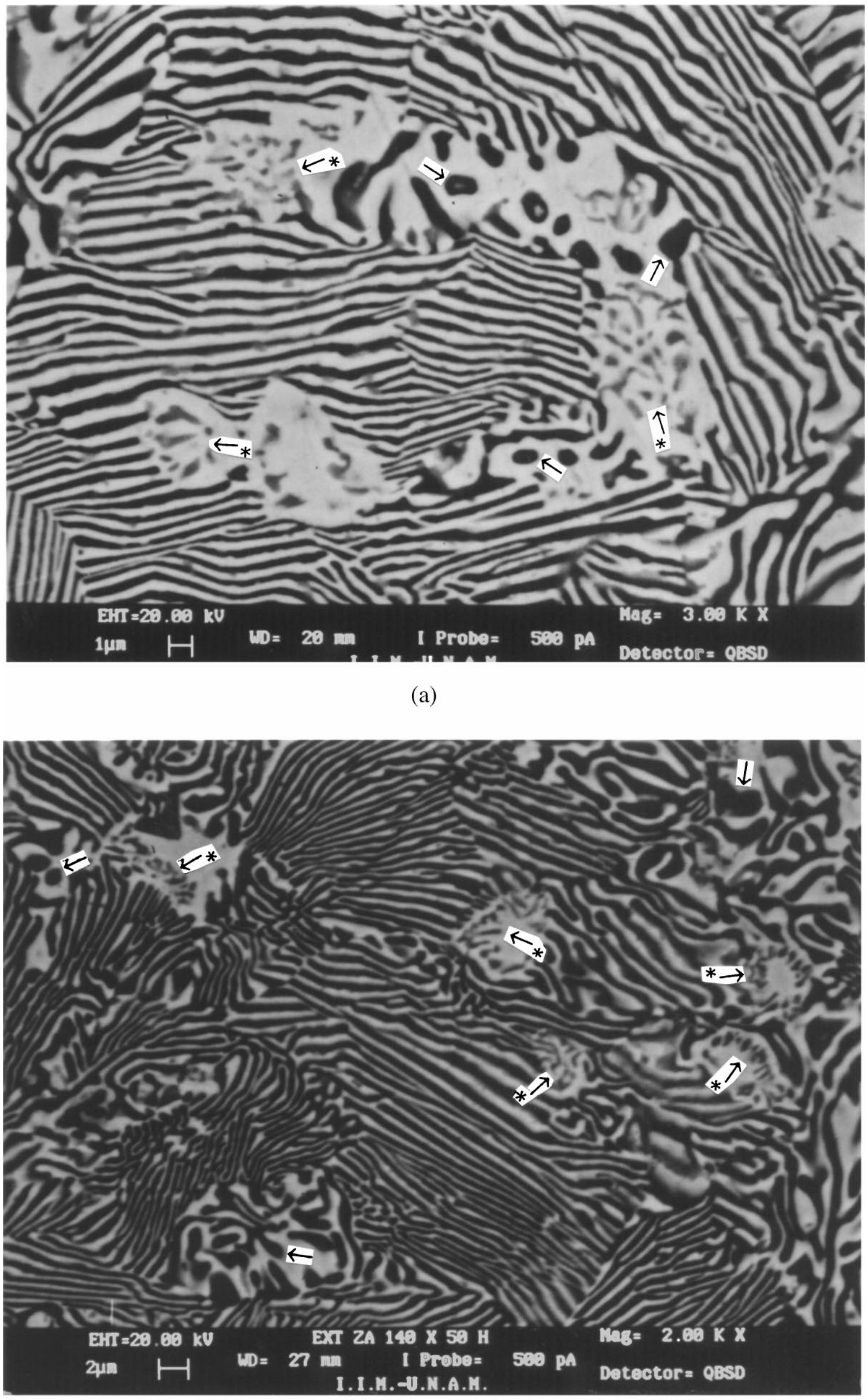


(c)



(d)

Figure 4 (*Continued*).



(a)

(b)

Figure 5 Back scatter SEM micrographs of the extruded eutectoid Zn-Al alloy after 50 h ageing at 170 °C (a) and 50 h ageing at 140 °C (b), showing two kinds of precipitates within the light contrast η'_E and ε phases. → Precipitation of the η'_E phase; *→ precipitation of the ε phase.

Zn-rich η'_E and ε particles and both fine and coarse lamellar structures, as shown in Fig. 3a. The η'_E phase and the intermetallic ε phase ($CuZn_4$) were identified by electron probe micro-analysis and labeled respectively in Fig. 3a. The fine and coarse lamellar structures were derived from supersaturated α'_s and β'_s phases in the cast eutectoid alloy respectively, which are also labeled by "α'_s" and "β'_s" in Fig. 3a.

After 1 h ageing at 170 °C, darker-imaged precipitates formed in the light contrast η'_E phase, as the arrow "→" pointing in the back-scattered SEM image (Fig. 3b). As previous work reported, the decomposition of the Zn-rich η'_E phase took place in a discontinuous precipitation, $\eta'_E \rightarrow \eta + \alpha + T'$ [2], where the Al-rich α phase appeared as the darker-imaged particle precipitates. After 10 h aging at 170 °C, the decomposition of the η'_E phase developed, as shown in Fig. 3c. At the same time the gray-imaged precipitates were observed in the light contrast ε phase, as indicated by the arrow "*→" in Fig. 3c. It is recognized that the decomposition of the ε phase occurred in a form of four-phase transformation, $\alpha + \varepsilon \rightarrow T' + \eta$ [3–11]. The ε phase reacted with the Al-rich α phase to form T' and η phases. As one of the products of the decomposition of the ε

phase, i.e. four-phase transformation, the T' phase appeared as the gray-imaged precipitates. The α phase was observed as the darker-imaged precipitates in the back scatter SEM image because of a higher content of Al in the α phase than the T' phase. A distictive atomic contrast between these two precipitates is shown in Fig. 4c. The gray-imaged precipitates, i.e. T' phase, were well developed after 50 h ageing at 170 °C, as shown in Fig. 3d.

As previous work reported, the Zn-rich η'_s and ε phases solidified finally in intendendritic region in the cast eutectoid Zn-Al based alloy [3]. During extrusion, the metastable η'_s transformed into η'_E. There was no great difference in atomic contrast between the η'_E and ε phases. Both appeared in light contrast image in the back scatter SEM image. However it was distinctive after isothermal holding. After 50 h ageing at 170 °C and 50 h ageing at 140 °C, the two kinds of discontinuous precipitates within the light contrast η'_E and ε phases were indicated by arrows "→" and "*→" in Fig. 5a and b respectively. This appears as a microstructural characteristics of the decomposition of the η'_E and ε phases.

4. Conclusions

The two Zn-rich phases η'_E and ε in the extruded eutectoid Zn-Al based alloy decompose sequentially during ageing at 170 and 140 °C. The decomposition of the η'_E phase occurs as a discontinuous precipitation at the early stage of ageing, while the decomposition of the ε phase takes place in a four phase transformation: $\alpha + \varepsilon \rightarrow T' + \eta$ in the prolonged ageing. Typical morphologies of the two kinds of decomposition of the Zn rich phases η'_E and ε are distinctive in back-scatter SEM image. The darker-imaged α phase precipitates and the gray-imaged T' phase precipitates stand for the decomposition of η'_E and ε phases respectively.

Acknowledgements

The authors would like to thank Atonio Caballero and Jose Guzman for their assistance in the experimental work.

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Received 28 July 1998
and accepted 8 February 1999