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Exothermic reaction in eutectoid Zn–Al based alloys

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Abstract

Both solution treated and quench-aged eutectoid Zn–Al based alloys (ZnAl20Cu3Si2 and ZnAl22Cu2 in wt.%) were studied by differential scanning calorimeter (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. An exothermic phenomenon was observed at the early stage of ageing. Similar behavior was also found for the cast eutectoid Zn–Al alloy. The activation energy for the exothermic phenomenon was calculated, which was in a good agreement with that derived from X-ray diffraction examination for the decomposition of the supersaturated β'_s phase in the eutectoid Zn–Al based alloy. It is concluded that the decomposition of the β'_s phase is an exothermic solid state reaction in the eutectoid Zn–Al based alloys.

Keywords: Zn–Al alloys; Exothermic reaction; Scanning electron microscopy

1. Introduction

A characteristic of the Zn–Al binary alloy phase diagram is the existence of broad single solid phase fields (α and β) with fcc crystal structure, as shown in Fig. 1 [1,2]. Even when the Zn content is up to 96%, a fcc β phase is still found in the alloy. With the addition of a small amount of some third elements in this single phase solid with a wide span of composition range, various potential industrial Zn–Al based alloys have been developed [3,4].

The fcc β phase is an unstable supersaturated β'_s phase at ambient temperature. The ageing characteristic of the decomposition of this fcc β'_s phase is important for the phase transformation of the Zn–Al based alloys because more than 70% zinc rich ε and η are formed during the decomposition of the β'_s phase at the early stage of ageing [5,6]. It was also reported that external stress induced microstructural change from a coarse lamellar structure to a fine grain structure played an important role for improved mechanical properties such as the plastic deformation behavior. The coarse lamellar structure is derived from the decomposition of the supersaturated Zn-rich β'_s phase [7–11]. Therefore the decomposition of the β'_s phase has become an interesting research topic recently [12].

In this paper, more results on the exothermic phenomenon in relation with the decomposition of the supersaturated β'_s phase are reported.

2. Experimental procedure

Both solution treated and quench-aged eutectoid Zn–Al based alloys were studied by Differential scanning calorimeter (DSC), X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques.

The eutectoid Zn–Al based alloy (ZnAl22Cu2 in wt.%) cylinder specimen of 7 mm diameter and 1.5 mm thickness was solution treated at 350°C for 4 days and then quenched into ice water. The specimen was put into the specimen holder inside a differential scanning calorimeter (DSC-2800, TA Instruments) immediately after quenching. The heat flow was automatically recorded during isothermal ageing at various temperatures, 30, 45, 50 and 75°C.

Two solution treated eutectoid Zn–Al based alloys (ZnAl20Cu3Si2 and ZnAl22Cu2 in wt.%) were quenched into ice water. The as quenched specimens and the aged specimens were examined by a Philips

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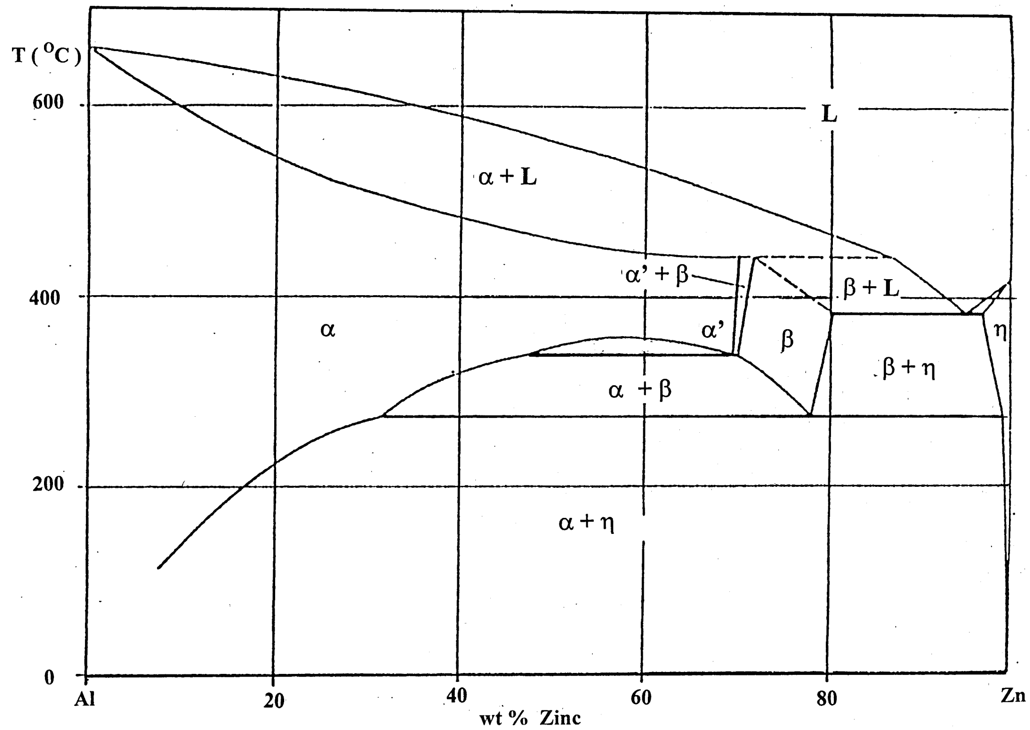

Fig. 1. Phase diagram of Al–Zn system.

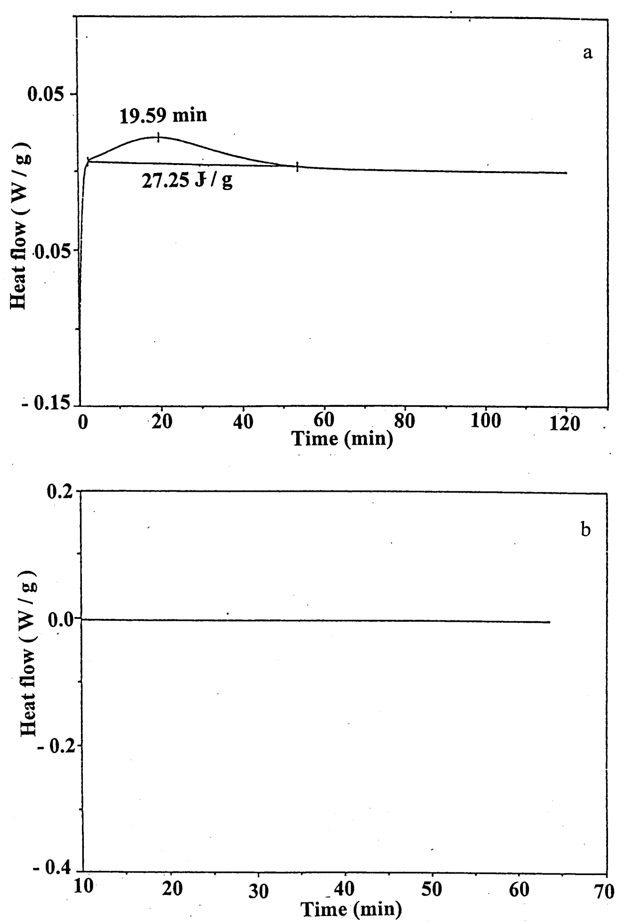

Fig. 2. Exothermic heat flow of the eutectoid alloy (ZnAl22Cu2) during quench-ageing at (a) 50°C and (b) 200°C.

X-ray diffractometer with Nickel filtered Cu-Kα radiation, scanning at a speed of 1° per min.

Back scatter scanning electron microscopy was applied for metallographic observation of the heat treated specimens to obtain atomic contrast of various phases.

3. Results and discussion

3.1. Exothermic phenomenon in the eutectoid Zn–Al based alloys

The heat flow (W g^{-1}) during quench-ageing process at 50°C is shown in Fig. 2. An exothermic phenomenon was observed at the early stage of the ageing process

Table 1
Data for activation energy of exothermic reaction quench-ageing eutectoid Zn–Al based alloy

$\beta'_s \rightarrow \alpha'_T + \varepsilon + \eta$				
T°C	T°K	T°K^{-1} ($\times 10^{-3}$)	t(s)	ln t
30	303	3.30	5973	8.69
40	313	3.19	2089	7.64
50	323	3.10	1170	7.06
75	348	2.87	225	5.40
100*	373	2.68	45	3.80
150*	423	2.36	6	1.75
170*	443	2.25	2	0.65

* Data from X-ray diffraction.

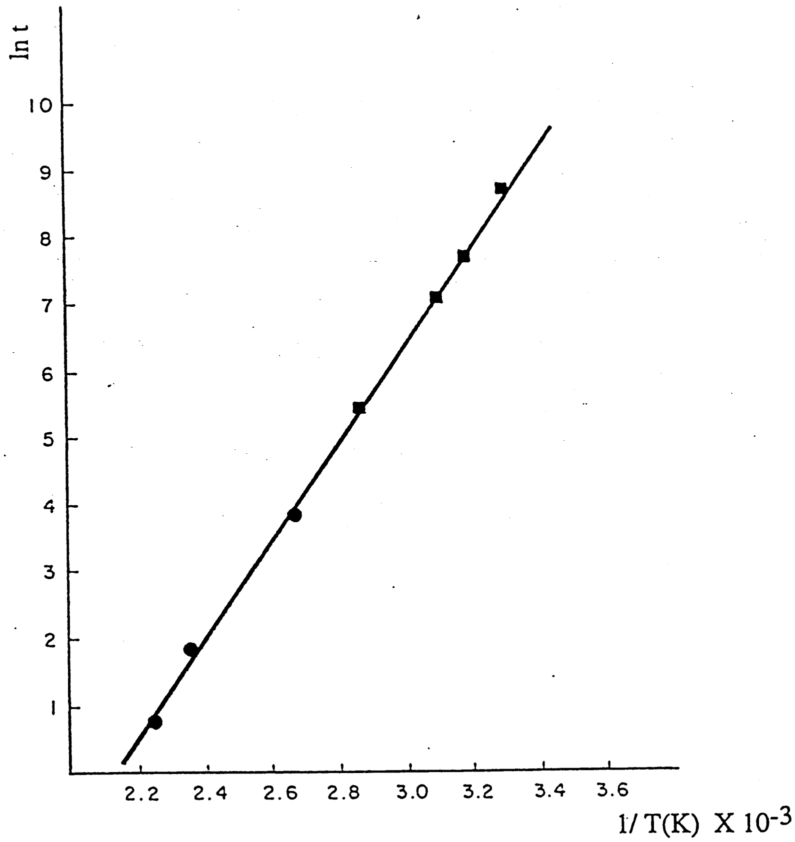

Fig. 3. Arrhenius plot for determination of activation energy of decomposition of β'_s phase in the eutectoid Zn–Al based alloy: ●, deduced from X-ray diffraction; and ■, deduced from exothermic measurements.

(Fig. 2a). A maximum exothermic rate was observed after ageing at 50°C for 19.5 min with an exothermic specific value of 27.5 J g^{-1}. After this early exothermic heat flow there was no exothermic phenomenon observed during subsequent prolonged ageing (Fig. 2b). The exothermic heat flow and the related ageing time for the maximum exothermic rates at 30, 45, 50 and 75°C are listed in the Table 1.

The logarithm of time to reach the maximum exothermic rate is plotted versus the related temperature of ageing, as shown in Fig. 3. By calculating the slope of the straight line in Fig. 3, the activation energy of the exothermic reaction is found to be 60.6 J mol^{-1}.

Similar exothermic phenomenon was observed in the cast eutectoid Zn–Al based alloy (ZnAl22Cu2). The effect of solidification cooling rate on the ageing characteristics was reported in a previous paper [13]. It was observed that the temperature of the as cast specimen slightly increased shortly after solidification with small heat flow arising, as shown in Fig. 4 [13].

3.2. Decomposition of the supersaturated β'_s phase

In order to understand the exothermic phenomenon of the eutectoid alloy at the early stage of ageing, early decomposition of the supersaturated phases of the alloy was investigated during isothermal ageing by X-ray diffraction and microscopy techniques.

Shown in Fig. 5 are the characteristic X-ray diffractograms with 2θ angle ranging from 35 to 47° for both the as quenched and the aged specimens of the eutectoid Zn–Al based (ZnAl22Cu2). It was observed that there were only two phases, the β'_s phase and the ε phase in the as quenched specimen, as shown in Fig. 5a. The β'_s phase decomposed at the early stage of ageing. The X-ray diffraction intensity of the β'_s phase decreased, accompanying the formation of three phases α'_T, ε and η after quench and aged at room temperature for 16 min, as shown in Fig. 5b.

Both the as quenched and the aged specimens (ZnAl22Cu2) were examined on scanning electron microscopy using back scatter electron radiation. As shown in Fig. 6a, the matrix of the as quenched specimen is the supersaturated β'_s phase with grain size of 20–30 μm in diameter, where the Zinc rich ε compound (Zn_4Cu) appears as light contrast particles of 2–5 μm in diameter. The β'_s phase decomposed at the grain boundaries during quenching, as arrow pointed in Fig. 6a. The discontinuous precipitation was developed

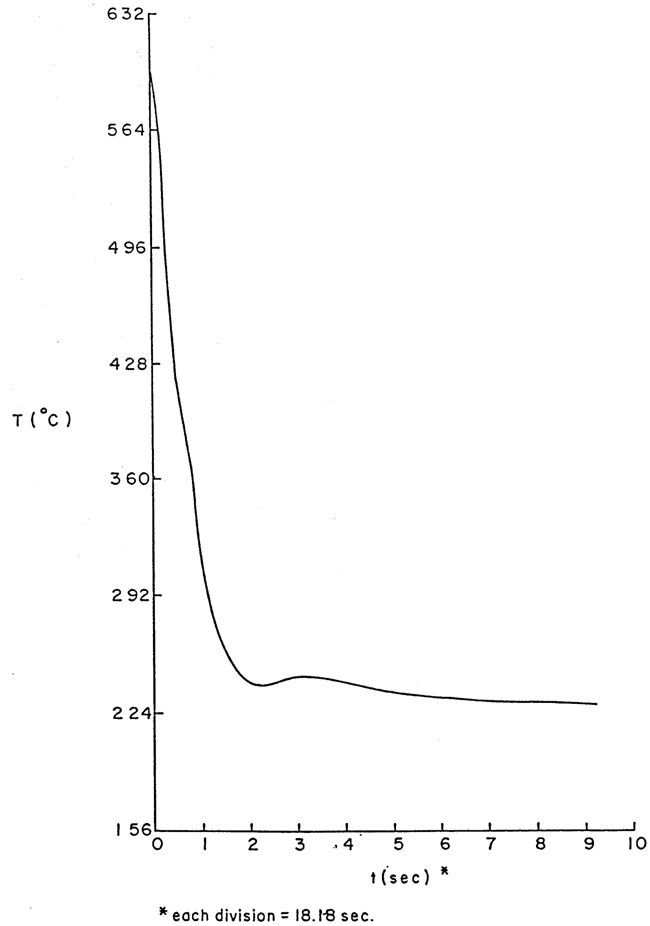

Fig. 4. Temperature variation of the as solidified specimen with time, showing slight exothermic heat flow shortly after solidification [13].

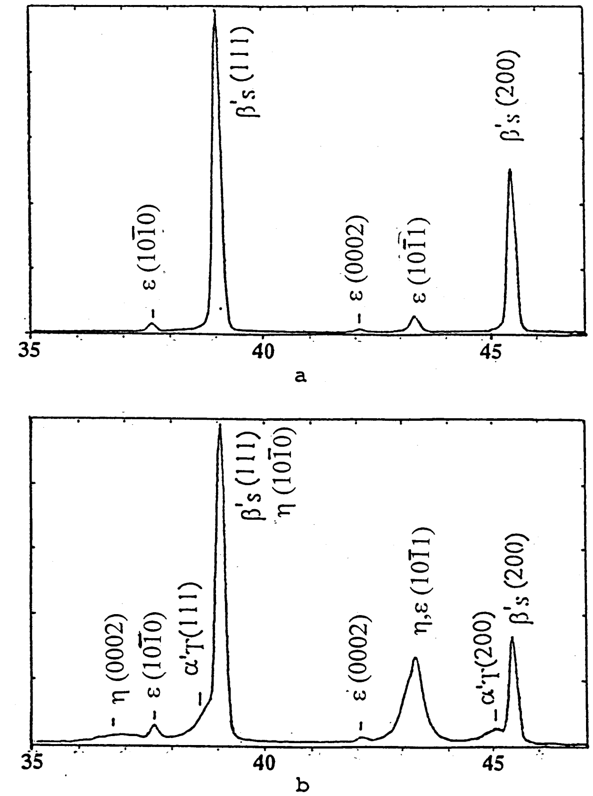

Fig. 5. X-ray diffractograms of the eutectoid Zn–Al based alloy specimens, as quenched (a) and after ageing at room temperature for 16 min (b).

along the grain boundaries in the β'_s phase after 10 and 20 min ageing at room temperature, shown in Fig. 6 (b,c), respectively. Compared with the variation of X-ray diffraction of the β'_s phase at the early stage of ageing, it is clear that this early precipitation belongs only to the decomposition of the supersaturated β'_s phase.

The X-ray diffractograms of the as quenched and the aged specimens (ZnAl20Cu3Si2) are shown in Fig. 7. Similar decomposition of the β'_s phase was observed. The X-ray diffraction peaks from the (111) and (200) crystal planes of the supersaturated β'_s phase decrease in intensity after 35 s ageing at 100°C, whilst the diffraction intensity of three phases α'_T, ε and η increase. It was reported that the β'_s phase decomposed in a way of discontinuous precipitation, $\beta'_s \rightarrow \alpha'_T + \varepsilon + \eta$ [6].

Based on the fractional transformation of the diffraction intensity of the phases in the eutectoid alloy (ZnAl20Cu3Si2), the logarithm of time to reach the maximum decomposition rate for the β'_s phase and the related temperature of ageing are also listed in Table 1 and plotted in Fig. 3. It is obvious that the results deduced from both the exothermic measurement and the X-ray diffraction determination of the decomposition of the β'_s phase are in good agreement. The small amount of silicon does not affect the phase transformation of the Zn–Al based alloys [5]. Therefore it is clear that the exothermic phenomenon in the solution treated eutectoid Zn–Al based alloy is directly related with only the decomposition of the β'_s phase at the early stage of ageing.

The decomposition of the supersaturated β'_s phase in the as cast eutectoid Zn–Al based alloy (ZnAl22Cu2) was also previously studied [13]. Shown in Fig. 8 is the X-ray diffractograms of the as cast eutectoid Zn–Al based alloy. It was found that when β'_s phase decomposed during solidification, a clear (200) diffraction peak of the α'_T phase appeared and was separated from the (200) diffraction peak of the β'_s phase in the cast-quenched specimen. The β'_s phase decomposed further at the early stage of ageing and the X-ray diffraction peaks of the β'_s phase disappeared after ageing at 90.4°C for 25 min. Obviously this decomposition of the β'_s phase is responsible for

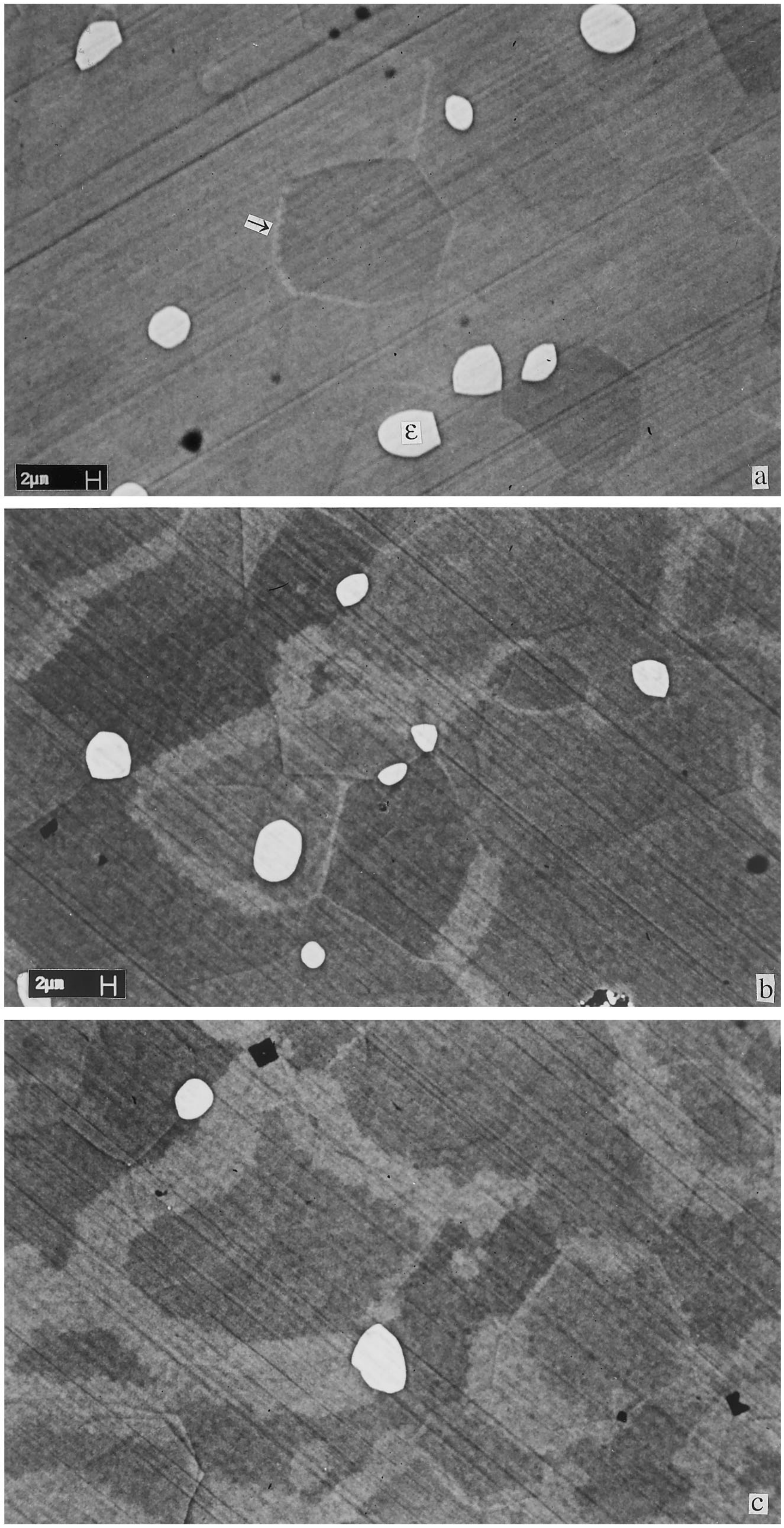

Fig. 6. Back scatter S.E.M. photos of the eutectoid Zn–Al based alloy specimens, as quenched (a) and after ageing at room temperature for 10 min (b) and 20 min (c).

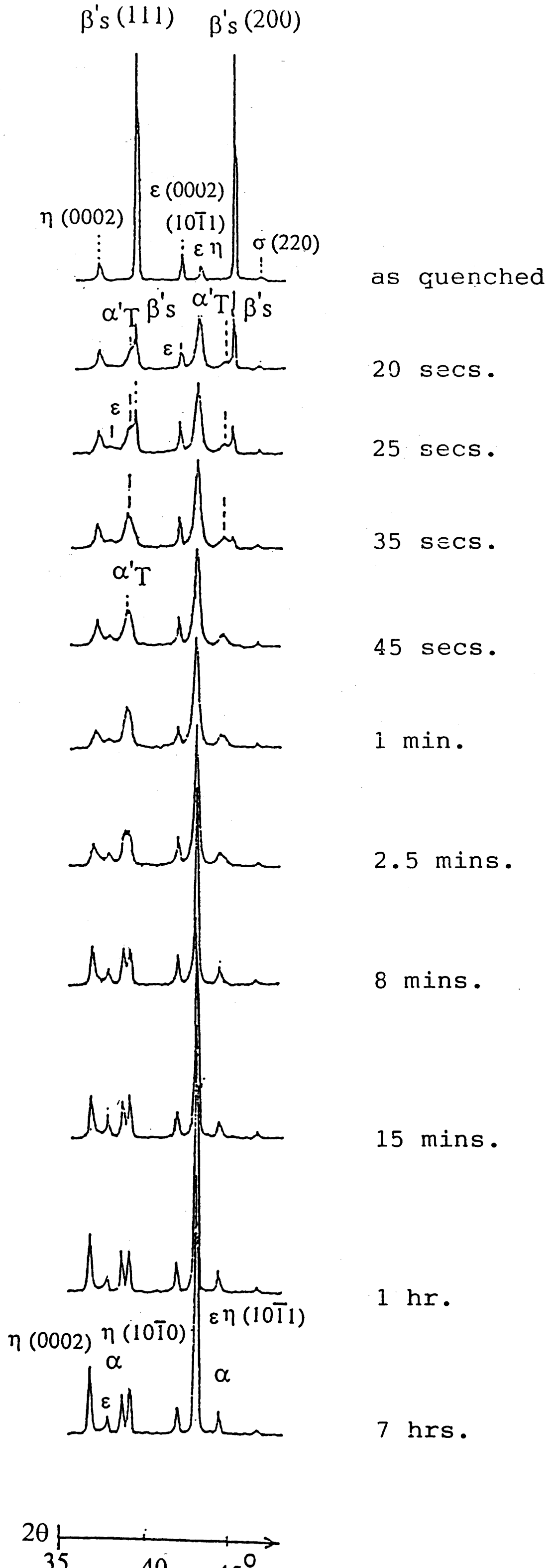

Fig. 7. X-ray diffractograms of the eutectoid Zn–Al based alloy (ZnAl20Cu3Si2) aged at 100°C.

the exothermic phenomenon in the cast eutectoid Zn–Al alloy, appearing as small peaks of the heat flow, as shown in Fig. 4 [13].

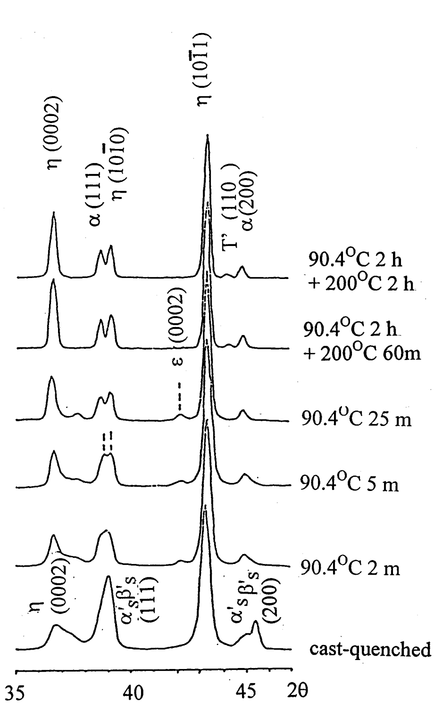

Fig. 8. X-ray diffractograms of the as cast eutectoid Zn–Al based alloy (ZnAl22Cu2), cast-quenched and during ageing.

4. Conclusions

The exothermic phenomena during ageing were observed in both the solution treated and the cast eutectoid Zn–Al based alloys. They are directly related with the decomposition of the β'_s phase at the early stage of ageing. It is concluded that the decomposition of the β'_s phase is an exothermic solid state reaction in the eutectoid Zn–Al based alloys. The activation energy of the exothermic reaction is 60.6 J mol^{-1}.

Acknowledgements

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