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Early stages of phase transformation in quenched zinc–aluminum based alloys

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Abstract

X-ray diffraction, optical and electron microscopic techniques were used to investigate the early stages of ageing in supersaturated Zn–Al based quaternary alloys. Discontinuous precipitation was observed to occur by means of a cellular reaction in both monotectoid and eutectoid Zn–Al based alloys. The cellular reaction was correlated with an equilibrium phase transformation that took place at about 276°C.

Keywords: Phase transformation; Zinc–aluminum based alloys; X-ray diffraction

1. Introduction

There is a great deal of interest in the decomposition of Zn–Al based alloys, in which the general pattern has been summarized [1–5] as follows: the supersaturated solid solution phase α'_s forms G.P. zones, then the rhombohedral transitional phase α''_m, which transforms into an f.c.c. phase α'_m and finally into zinc (η).

In recent work [6–9], discontinuous precipitation was observed at various stages of ageing, but the formation of G.P. zones was considered to be the first stage of the decomposition in most cases. The initial decomposition of the supersaturated solid solutions in both monotectoid and eutectoid Zn–Al binary alloys has been investigated in detail, and two stages of decomposition were reported to occur after the formation of G.P. zones. In the first stage, an f.c.c. metastable phase (α'_1) was formed by discontinuous precipitation. This zinc-rich f.c.c. phase then decomposed in the second stage with the formation of the equilibrium phase η and α, the latter being almost pure aluminum. The first product of the discontinuous precipitation was suggested to be the extension of the equilibrium monotectoid reaction at 340°C, shown as the extended line "a" in Fig. 1, [6,7].

In the present work, an investigation of the early stages of ageing in Zn–Al–Cu–Si alloys with monotectoid and eutectoid compositions was carried out, and the decomposition reactions were correlated with recently established equilibrium phase relationships [10,11].

2. Experimental

Zn–Al–Cu–Si alloys were prepared from high purity materials by air-melting in an induction furnace. Cylindrical ingots weighing 500 g were made by casting into mild steel moulds preheated to 250°C. The compositions of the alloys are shown in Table 1. Specimens of 12 mm diameter by 4 mm thickness were cut from the ingots, solution treated at 350°C, and then quenched and aged to provide the thermodynamic and kinetic conditions for the phase transformation [10].

Ageing was carried out in air or water at 21°C, 50°C, 70°C, 100°C, 150°C, and 170°C, with the temperature maintained to ±1°C. The ageing times were counted from the moment when the specimens reached the bath temperature.

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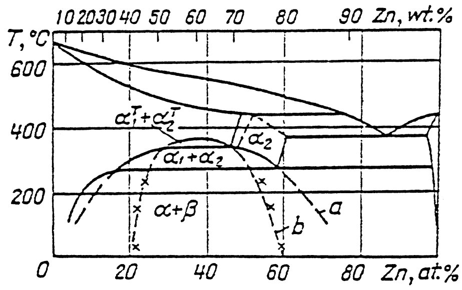


Fig. 1. Zinc–aluminum binary phase diagram showing metastable diagrams according to [6].

Table 1
Compositions of the alloys (wt%)

	Zn	Al	Cu	Si
Al–Zn_{60}–Cu_3–Si_2	61.1	33.0	3.4	2.6
Al–Zn_{75}–Cu_3–Si_2	75.0	19.4	3.1	1.4

X-ray diffraction was carried out on flat samples using nickel-filtered Cu Kα radiation in a Phillips diffractometer operated at 40 kV. The diffractometer was repeatedly scanned through a range of 35–48° 2θ at a speed of 1°/min and the peak intensity data was recorded automatically by computer, with simultaneous display of the intensity trace on a chart recorder.

Standard metallographic preparation techniques were used for light microscopy. For TEM studies, foils were prepared by a disk-jet technique and studied in a Jeol 100B electron microscope.

3. Results

The X-ray diffraction patterns from alloy Al–Zn_{60}–Cu_3–Si_2 during ageing at 70°C are shown in Fig. 2(a). After ageing for 90 min the diffraction peak of the supersaturated phase α'_s had decreased substantially from its early level, and this was accompanied by the appearance of three sets of new peaks, from α'_T, ε and η phases. The α'_T was an aluminum-rich metastable phase, the principle peak of which was only 0.3° to the low-angle side of the equivalent peak from the supersaturated phase α'_s. After 510 min, both the (2 0 0) and (1 1 1) peaks of α'_s had disappeared, leaving the peaks from α'_T, ε and η phases clearly visible. This transformation from α'_T to the product phases is shown in Fig. 2.

The X-ray diffraction patterns from the same alloy aged at 100°C are shown in Fig. 2(b), and reveal the same sequence of changes. The decomposition of α'_s started earlier and was well advanced after 3.5 min. The decomposition was complete after 12 min.

On ageing at 150°C, again the same changes were revealed by the diffraction examination, Fig. 2(c) shows the changes in the diffraction peaks.

The other alloy of near-eutectoid composition, Al–Zn_{75}–Cu_3–Si_2, was aged at 100°C, 150°C, and 170°C. Fig. 3(a) shows the X-ray traces for 100°C ageing, and the first four curves show the decomposition of the high-temperature phase (which although structurally identical to α'_s is now called β'_s as its zinc content is much greater). The β'_s phase transformed into α'_T, ε and η phases after 1 min at this temperature, and even in the as-quenched condition partial decomposition of the supersaturated phase had occurred.

Fig. 4 is an optical micrograph of this as-quenched alloy and shows discontinuous precipitation at the grain boundaries. After 0.5 min at 100°C, this had developed to greater extent, Fig. 5.

Ageing at 150°C produced the same phase transformations, Fig. 3(b), but at earlier times. The first stage, i.e., the decomposition of β'_s phase to α'_T, ε and η phases, for example, was completed in only 10 s.

Using the positions of the (2 0 0) peaks from the supersaturated phases and the phase formed after long periods at low temperatures as a calibration, it was calculated that the approximate zinc content of the α'_T phase was 32.5%.

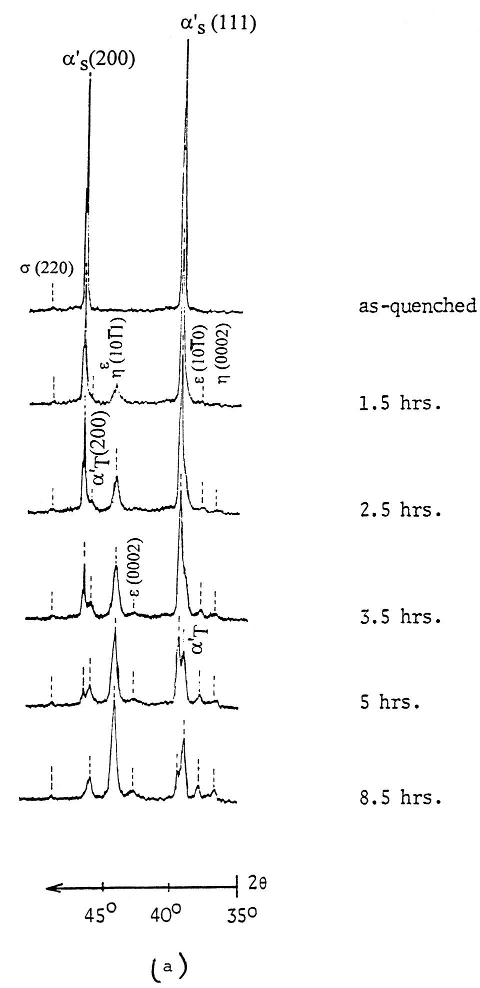


Fig. 2. X-ray diffraction patterns from Al–Zn_{60}–Cu_3–Si_2 alloy on ageing for different times: (a) 70°C; (b) 100°C; (c) 150°C.

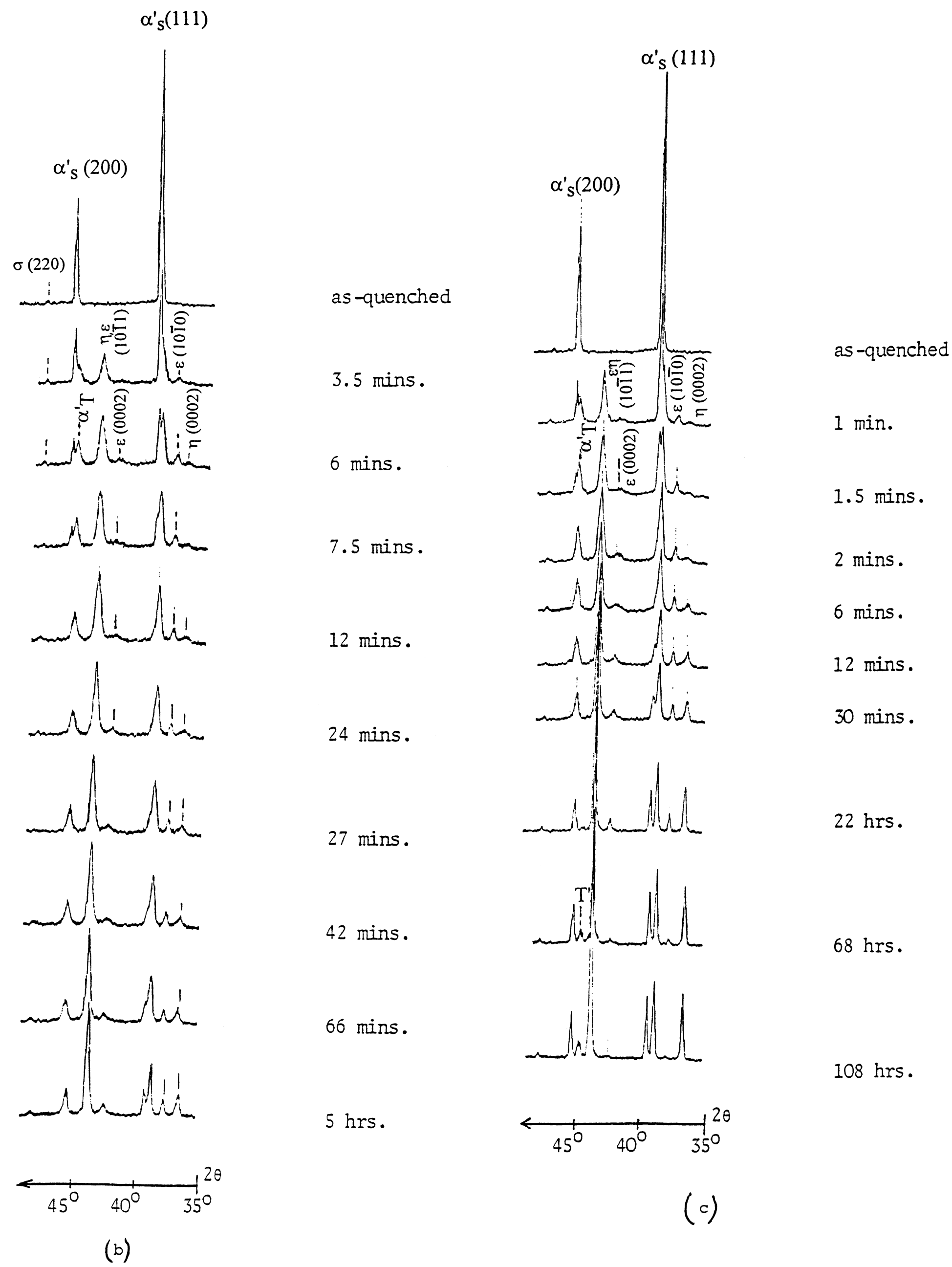


Fig. 2. (*Continued*)

Quantitative transformation curves for the phases in both alloys aged at 100°C, 150°C and 170°C were calculated using the integrated intensities of selected diffraction peaks. Fig. 6 showing such curves for monotectoid alloy aged at 150°C. Figs. 7 and 8 show similar curves for the eutectoid alloy aged at 100°C and 170°C, respectively. Overlapping of the peaks from the β'_s phase with those from the α'_T phase made it impossible to calculate the fractional transformation of the former with a reasonable degree of accuracy at particular times of ageing, dashed lines having been used in these figures where the positions of the lines are imprecise.

Transmission electron microscopy was carried out with special care on samples aged for upto 10 min at 100°C. The lamellar structure was not observed until after 1.5 min. After 2 min both the lamellar structure and a two-phase structure of equi-axed grains was obtained. After 8.5 min two different modes of decomposition were seen, as shown in the micrograph of Fig. 9(a). Discontinuous cellular products formed on one side of high-angle grain boundaries, and general precipitates in the matrix on the other. The electron-diffraction pattern from the cellular side is shown in Fig. 9(b). Trace analysis indicated a possible growth direction for the α'_T lamellae of $\langle 1\ 1\ 1 \rangle$.

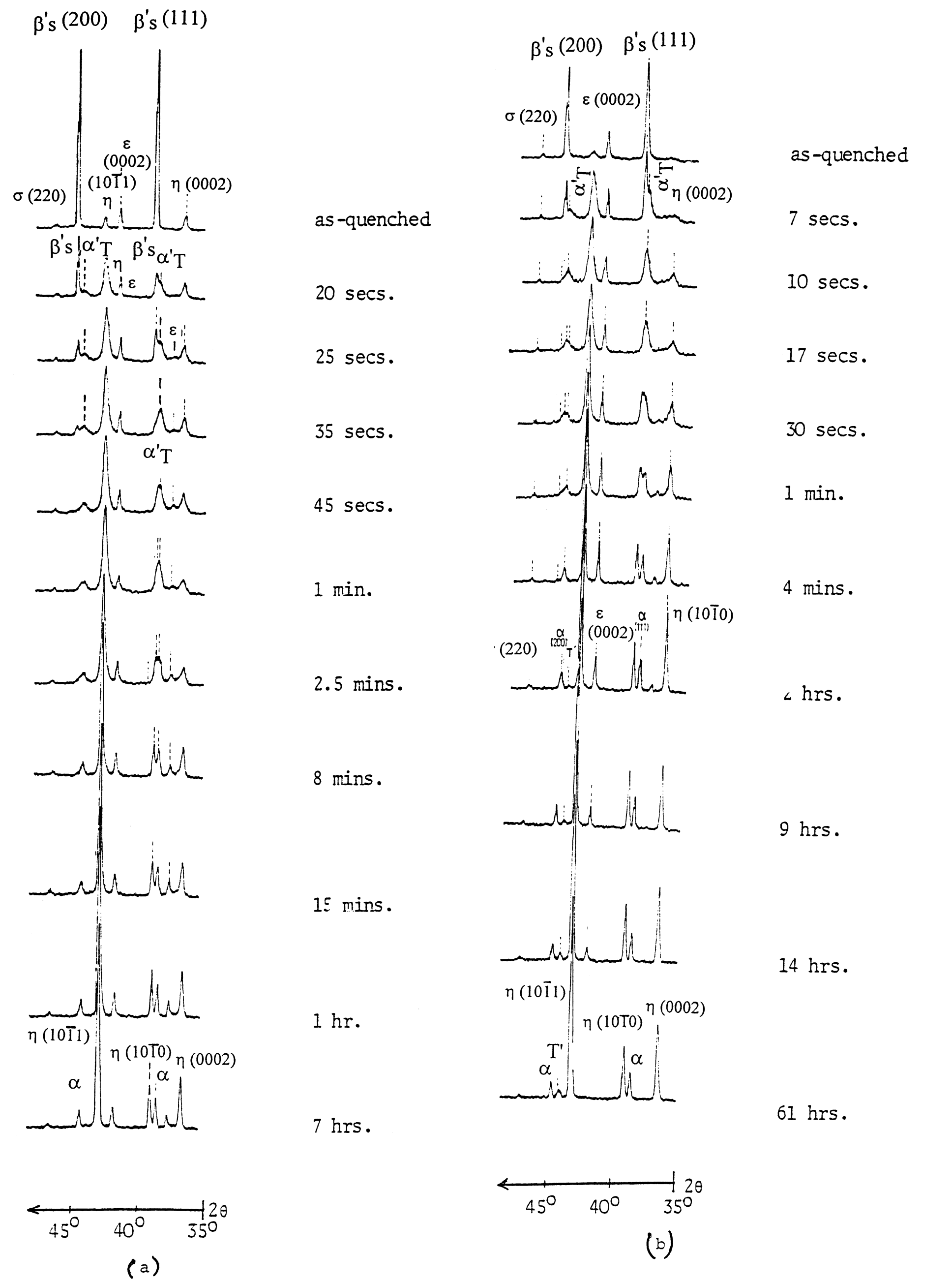


Fig. 3. X-ray diffraction patterns from Al–Zn_{75}–Cu_3–Si_2 alloy on ageing for different times: (a) 100°C; (b) 150°C.

4. Discussion

The X-ray diffraction peaks from the supersaturated α'_s and β'_s phases reduced with ageing time, whilst the peaks from α'_T phase of lower zinc content appeared separately at lower Bragg angles, together with peaks from the ε and η phases. This early stage of transformation was observed in all of the X-ray diffraction patterns from both alloys at the ageing temperatures used, see Figs. 2 and 3. Amongst these, Fig. 2(a) and (b) and Fig. 3(a) showed clearly the first stage transformation in the low-zinc alloy on ageing at 70°C and 100°C, and in the higher-zinc alloy on ageing at 100°C.

Examination of Figs. 6–8 shows that they all exhibit the same essential features. There was an initial rapid increase in zinc (η) and the metastable ε phase, followed by a more gradual increase in both over a comparatively long period of time. Finally the ε phase was replaced by T′ phase and simultaneously the formation of zinc was completed. The eutectoid-based alloy shows the initial rapid increase in zinc, followed by a second rapid increase after a while, to an even more marked degree.

The first stage represents the rapid formation of η and ε phases in both alloys and from the changes in the phase composition may be described by the reaction:

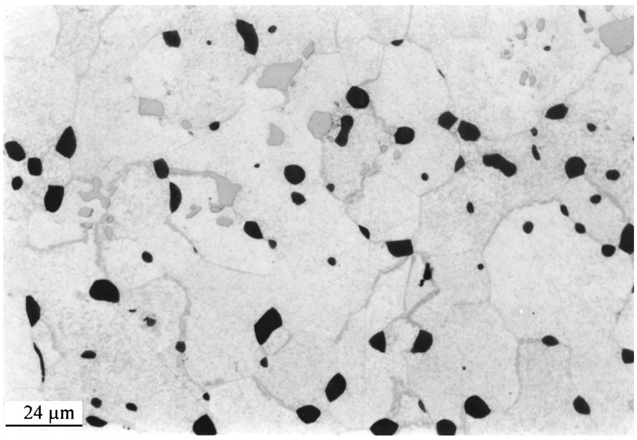


Fig. 4. Optical micrograph of Al–Zn_{75}–Cu_3–Si_2 alloy shortly after quenching.

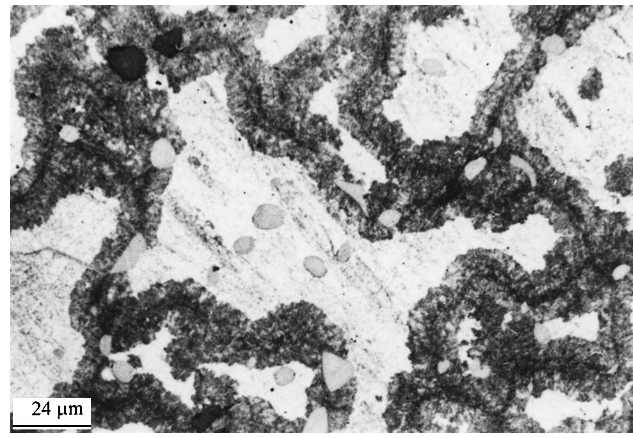


Fig. 5. Optical micrograph of Al–Zn_{75}–Cu_3–Si_2 alloy after quenching and ageing for 0.5 min at 100°C, showing the development of discontinuous precipitation at the grain boundaries.

$$\alpha'_{\mathrm{s}} \text{ (and } \beta'_{\mathrm{s}}) \rightarrow \alpha'_{\mathrm{T}} + \varepsilon + \eta$$

At the same time, optical and transmission electron microscopy showed that this transformation was the cellular reaction that occurred at the grain boundaries. In Figs. 6–8 it appeared that over 75% of the η phase, is formed by this reaction, the remainder resulting from the spinodal decomposition of the products in Stage II. Thus it appears that the nucleation and growth of cellular colonies in the supersaturated phases is a major mode of transformation, in agreement with Turnbull's observation [12].

Finally in Stage III the ε phase was replaced by another copper-rich phase, T′. Simultaneously the zinc content increases to its final amount, although this was sometimes not clear from the transformation diagram since the ε is only a minor phase compared to zinc, and thus the liberation of zinc from ε makes only a small contribution to the total zinc content. The phase reaction may be represented by an equation of the form:

$$\alpha + \varepsilon \rightarrow T' + \eta.$$

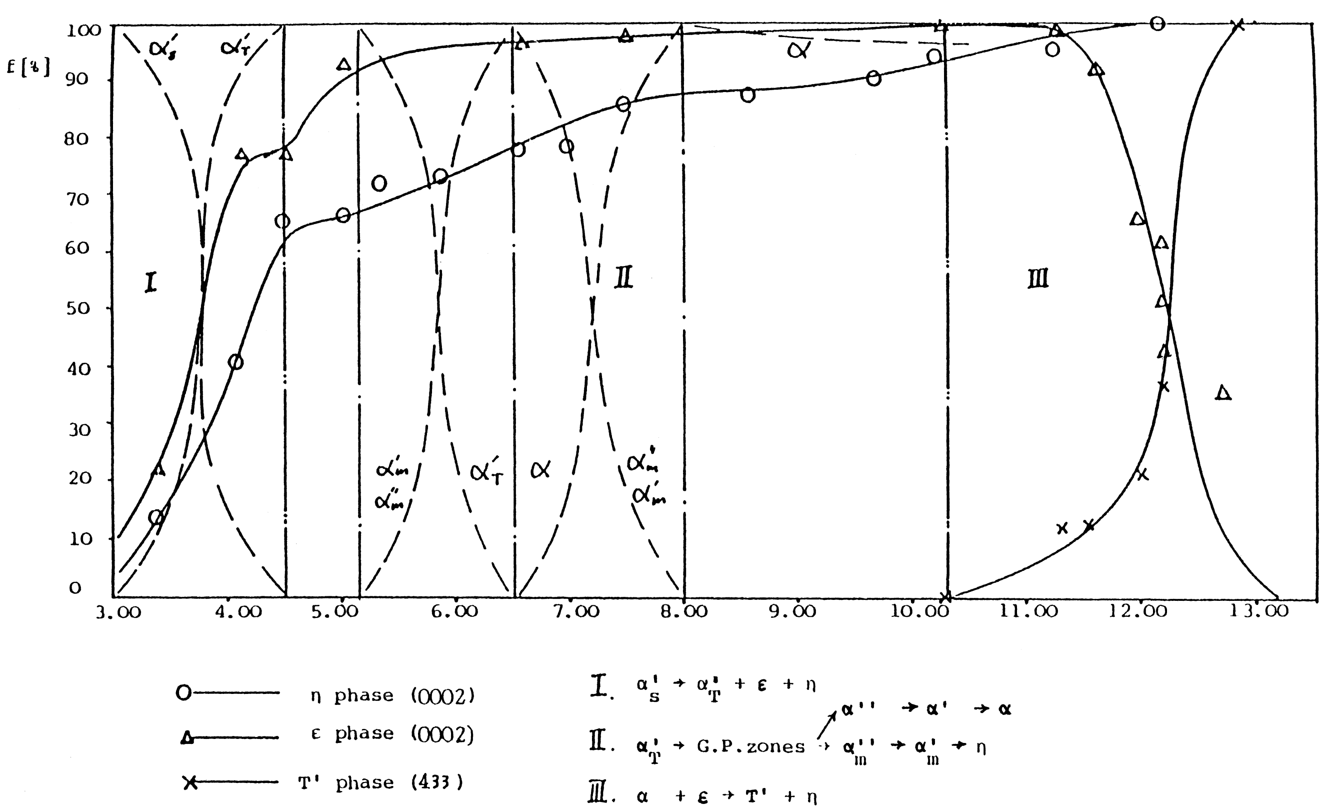


Fig. 6. Percentage transformation curves for the phases in the Al–Zn_{60}–Cu_3–Si_2 alloy aged at 150°C.

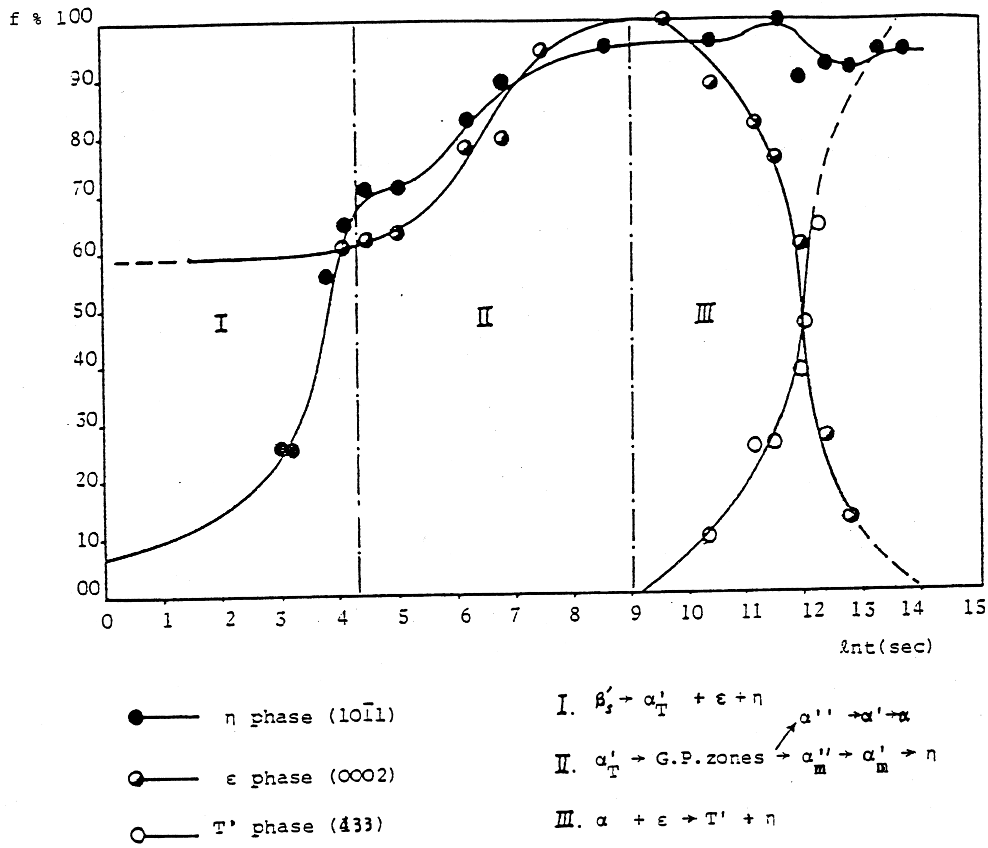


Fig. 7. Percentage transformation curves for the phases in the Al–Zn_{75}–Cu_3–Si_2 alloy aged at 100°C.

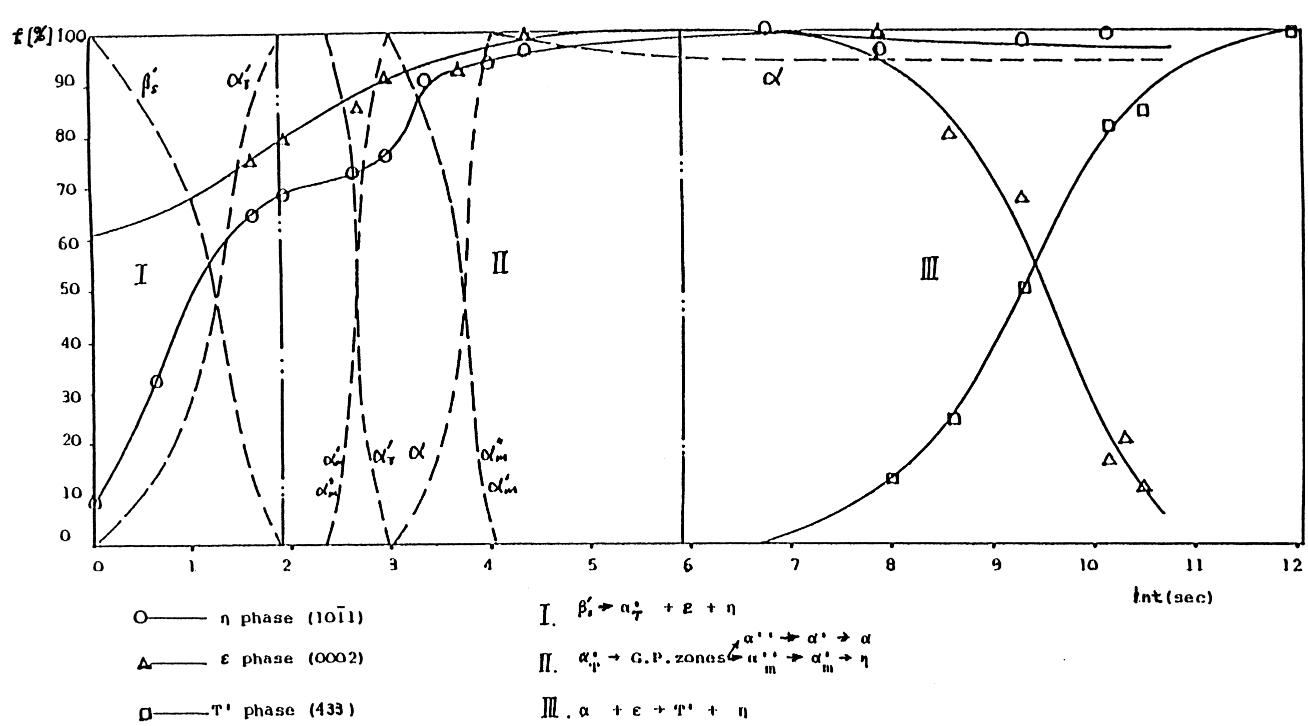
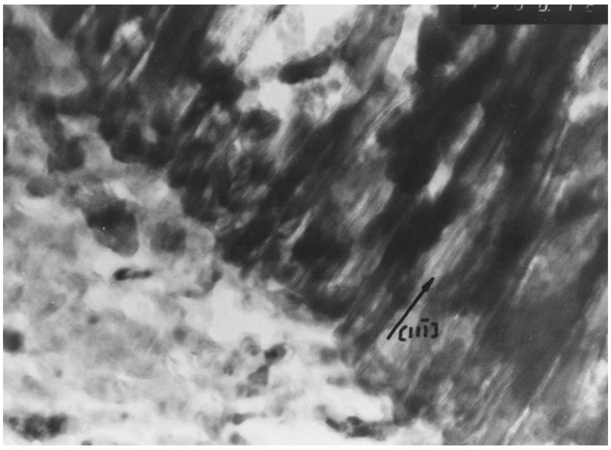
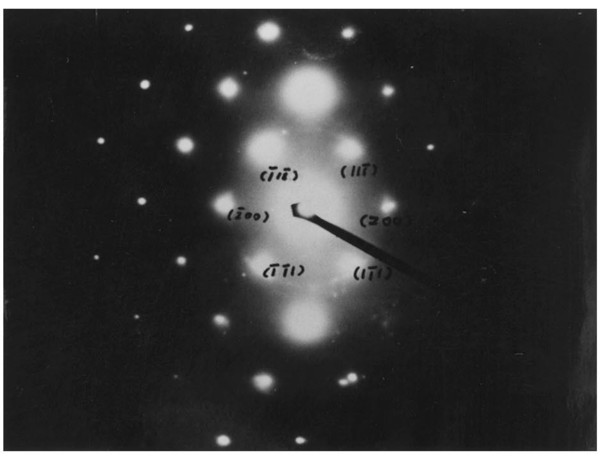


Fig. 8. Percentage transformation curves for the phases in the Al–Zn_{75}–Cu_3–Si_2 alloy aged at 170°C.



(a)



(b)

Fig. 9. Transmission electron micrograph of alloy Al–Zn_{60}–Cu_3–Si_2 aged at 100°C for 8.5 min (mag×13 000) and (b) the electron diffraction pattern from the cellular side in (a).

It is interesting to correlate these phase transformations with the equilibrium phase diagram for the system. In the binary Zn–Al diagram there is an eutectoid at 276°C, whereby the β phase decomposes into α and η, see Fig. 1. The introduction of copper and silicon modifies the phase relationships slightly in low-copper alloys. Murphy [12] had determined the solid-state transformations in ternary alloys containing copper, and it has been shown that the further introduction of small amounts of silicon produces only minor changes in the positions of phase fields compared with the ternary diagram [10]. In the Zn–Al–Cu–Si system at 350°C, the compositions corresponding to the two alloys examined here lie just inside the α' or β phase field, together with Si, which may be ignored for the present purposes. In binary alloys the β phase undergoes the eutectoid reaction at 275°C, and in the present low-copper alloys this also occurs, but the copper content is slightly in excess of the maximum solid solubility, so that at 270°C they lie in the $\alpha+\beta+\eta$ field. At 268°C the ε phase is replaced by the copper-rich T' phase by a four-phase transformation:

$$\alpha + \varepsilon \rightarrow T' + \eta,$$

so that ε may be regarded as a transitional copper-rich phase in both equilibrium cooling and quench-ageing transformations. Furthermore the cellular reaction in quench-aged alloys mimics the β phase eutectoid decomposition in equilibrium cooling, in that η and α'_{T} are formed.

5. Conclusions

1. It has been found that quenched monotectoid- and eutectoid-based zinc–aluminum alloys containing small amounts of copper and silicon show the same initial transformation on ageing.
2. The major part of the decomposition comes about by means of a cellular reaction, initiated at the grain boundaries, the products of which are similar to those produced under equilibrium cooling through the eutectoid transformation.
3. It is suggested that in zinc–aluminum based alloys the transitional phases formed on ageing at low temperatures are similar to those found at higher temperatures in the equilibrium system, and that the transformation reactions may also mimic those that take place at higher temperatures.

References

[1] M. Simerska, Y. Synecek, Acta. Met. 15 (1967) 223–230.
[2] G.J.C. Carpenter, R.D. Garwood, Met. Sci. 1 (1967) 202.
[3] K.G. Satyanarayana, K.-I. Mirano, Trans. Jpn. Inst. Met. 18 (1977) 403–411.
[4] R. Ciach, B. Dukiet-Zawadzka, J. Dutkiewcz, in: Proceedings of the 16th International H-T Conference Metals Soc., 1976, pp. 111–115.
[5] V.A. Toldin, G.V. Kleschev, D.V. Shimilov, A.I. Ahenkmen, Fiz. Met. i. Metall. 40(6) (1975) 1224–1226.
[6] V.A. Toldin, A.A. Burykin, G.V. Kleschev, Phys. Met. Metall. 17(1) (1981) 116–124.
[7] M. Vijayalakshmi, V. Seetharaman, V.S. Raghunathan, Mat. Sci. Eng. 52(1) (1982) 249–256.
[8] E. Hornbogen, M. Turwitt, Metall. 37(12) (1983) 1208–1211.
[9] Y.H. Zhu, T. Savaskan, S. Murphy, Mat. Res. Soc. Proc. 21 (1984) 835–840.
[10] Y.H. Zhu, Ph.D. Thesis, University of Aston, Birmingham, UK, 1983.
[11] D. Turnbull, Acta Met. 3 (1955) 55–63.
[12] S. Murphy, Zeit. Met. 71 (1980) 96–102.