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Complex microstructural changes in as-cast eutectoid Zn–Al alloy

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Phase transformations and microstructural changes of an as-cast eutectoid Zn–Al alloy ($ZnAl_{22}Cu_2$) were investigated during isothermal holding. The typical dendritic structures consisted of α'_s phase as a core with the edge of decomposed β'_s phase and decomposed η'_s in the interdendritic regions. A series of complex phase transformations was observed. Both decompositions of β'_s and η'_s were determined at an early stage of ageing and a four-phase transformation, $\alpha_f + \varepsilon \rightarrow T' + \eta$, was observed at the boundaries of α_f phase and the ε phase, instead of clearly observed at the boundaries of ε phase, in a solution-treated Zn–Al alloy during prolonged ageing.

1. Introduction

The phase transformations and structural changes in eutectoid alloys have been under investigation as a fundamental topic for many years. In the last decades, the phase transformations and structural changes of Zn–Al alloy have been studied in greater detail, because its superplasticity is recognized as having considerable application in the metal-forming industry.

As a part of the systematical investigation of phase transformation in Zn–Al based alloys, phase transformations of the supersaturated phases in solution-treated Zn–Al alloy have been well investigated during the isothermal processes [1–12]. Three stages of phase transformations were observed during the ageing processes, as follows.

1. Decomposition of the supersaturated zinc-rich fcc, β'_s phase at early stage of ageing

$$\beta'_s \rightarrow \alpha'_T + \varepsilon + \eta \qquad (1)$$

2. Decomposition of the metastable phase aluminium-rich fcc, α'_T

$$\begin{array}{l} \alpha'_T \rightarrow GPZ \rightarrow \alpha''_m \rightarrow \alpha'_m \rightarrow \eta \\ \qquad\qquad\quad \searrow \alpha'' \rightarrow \alpha' \rightarrow \alpha_f \end{array} \qquad (2)$$

3. Decomposition of ε phase in a four-phase transformation

$$\alpha_f + \varepsilon \rightarrow T' + \eta \qquad (3)$$

These three decompositions were in good correlation with the equilibrium phase relationships, i.e.

$$\beta + \varepsilon \rightleftharpoons \alpha + \eta \quad \text{at} \sim 276\,^\circ C \qquad (4)$$

$$\alpha + \varepsilon \rightleftharpoons T' + \eta \quad \text{at } 268\,^\circ C \qquad (5)$$

and the compositional change of aluminium in α phase at 275 °C, to the same phase at 268 °C [1, 13, 14].

In the present work, we were particularly interested in the decompositions of the supersaturated phases (α'_s, β'_s, and η'_s) in a chilled as-cast eutectoid Zn–Al alloy ($ZnAl_{22}Cu_2$) during isothermal holding. Much more complicated phase transformations are examined in the as-cast Zn–Al alloy. This may be of importance in understanding the mechanism of the superplasticity of the alloy.

2. Experimental procedure

The nominal composition of the Zn–Al alloy is Zn–22Al–2Cu (wt %). The alloy was induction melted from aluminium, zinc and copper (99.9% purity) and degassed with a commercial degasser, then poured at 600 °C into a preheated steel mould. The solidified ingots were chilled after 1 min air-cooling in the mould by water-spray cooling.

The chilled as-cast ingots were quickly cut into pieces with different sides for X-ray diffraction examinations and observations by both optical and scanning microscopies during ageing at 90.4 and 150 °C. Special care was taken during X-ray diffraction examination in the early stage of ageing. A nickel filter and copper radiation were applied within the diffraction 2θ angle range from 35°–48° in order to obtain the characteristic X-ray diffraction. A Jeol STEM and electron probe microanalysis (EPMA) were applied for determining the compositions of the phases of the alloy.

3. Results and discussion

3.1. Solidification of the eutectoid Zn–Al alloy

Aluminium-rich α'_s phase solidified first from the melt. The average composition of the α'_s is listed in Table I, determined using EPMA. In comparison with the average composition of α'_s phase in Zn–27% Al alloy

TABLE I Average compositions of α'_s phase in Zn–27% Al and eutectoid Zn–Al alloys

	Al	Zn	Cu
Eutectoid Zn–Al alloy	33.3	64.9	1.8
Zn–27% Al	54.9	43.5	1.6

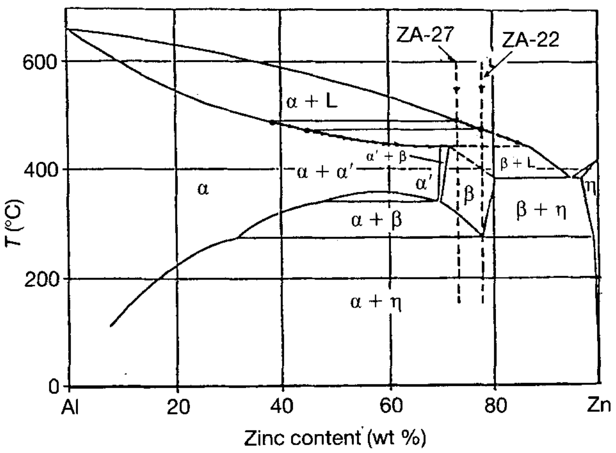

Figure 1 Phase diagram of the Al–Zn system.

listed in Table I [16], α'_s in the Zn–Al alloy contained more zinc, which is in accordance with the Zn–Al based alloy phase diagram, shown in Fig. 1 [15].

With continued solidification, the composition of α'_s phase around the first solidified α'_s phase gradually changed to the composition of β'_s phase, close to the solidus line α + L/α and the compositions of the melt changed along the liquidus line L/α + L to the zinc-rich side, according to the Zn–Al phase diagram, shown in Fig. 1. The η'_s phase finally solidified in the interdendritic regions to complete the whole solidification of the Zn–Al alloy. According to the X-ray diffraction identification, both α'_s and β'_s had fcc crystal structure, and η'_s had hcp crystal structure.

3.2. Chilled as-cast state of the eutectoid Zn–Al alloy

The alloy was water-chilled within 1 min after complete solidification. According to the X-ray diffraction test, there were three phases (α'_s, β'_s and η'_s) in the chilled as-cast eutectoid Zn–Al alloy, as shown in Fig. 2. The diffraction peaks of α'_s and β'_s appeared overlapped on the X-ray diffractograms due to the close composition of the two phases. The typical dendritic structures consisted of α'_s phase as a core with the edge of β'_s phase, and decomposed η'_s phase in the interdendritic region, shown in Figs 3 and 4. There were no clear phase boundaries between α'_s and β'_s phases observed on the optical and SEM observations.

Within the interdendritic region of η'_s phase, ε phase particles were observed both on optical and SEM observations indicating that η'_s phase was unstable even at room temperature and decomposed during specimen preparation and observation.

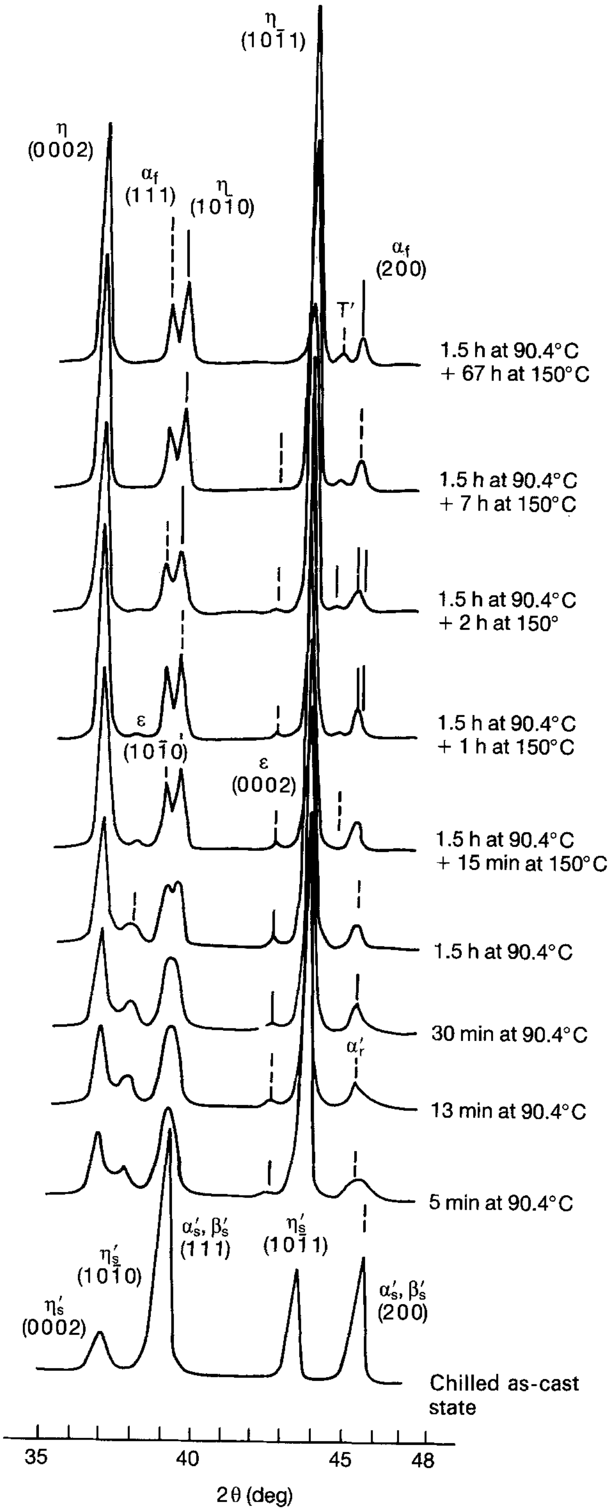

Figure 2 X-ray diffractograms of the chilled as-cast eutectoid Zn–Al alloy ($ZnAl_{22}Cu_2$) during ageing.

According to the identification of the phases, the lattice parameters of the supersaturated hcp η'_s phase in the chilled as-cast alloy were as follows: $a_0 = 0.2668$ nm, $c_0 = 0.4842$ nm, $c_0/a_0 = 1.8148$.

3.3. Ageing characteristics

The chilled as-cast Zn–Al alloy was then aged at 90.4 and 150 °C. It was observed that both β'_s and η'_s phases decomposed after 5 min ageing at 90.4 °C into the three phases α'_s, ε and η, respectively. Both peaks of β'_s

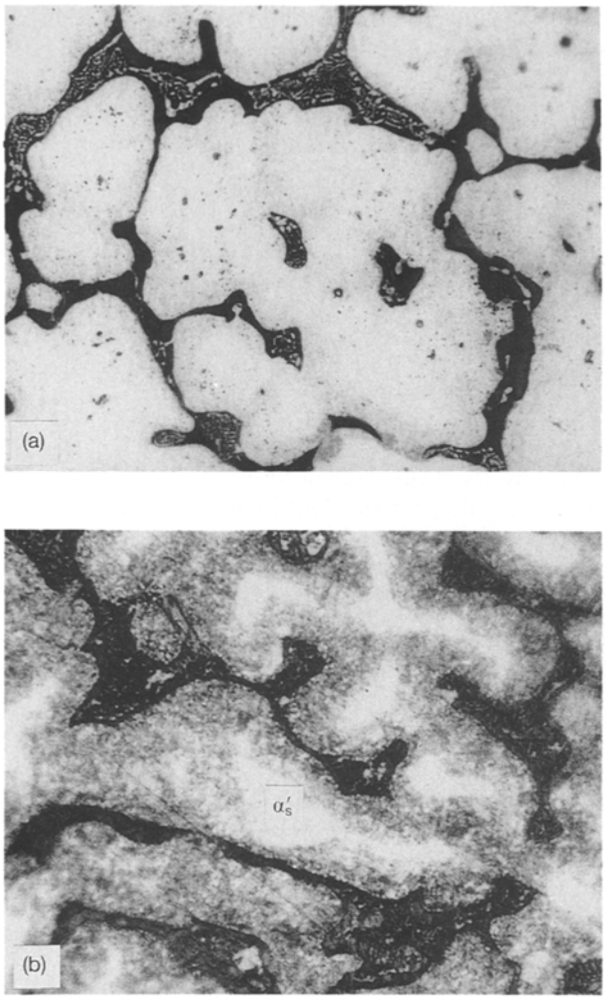

Figure 3 Optical micrographs of as-cast eutectoid Zn–Al alloy: (a) chilled as-cast state; (b) after 30 s ageing at 90.4 °C.

and η'_s decreased in height, accompanying the formation and growth of three sets of peaks of α'_T, ε and η phases. The lattice parameters of the ε and η phases decomposed from η'_s and β'_s were determined as follows. ε phase: $a_0 = 0.2767$ nm; $c_0 = 0.4289$ nm; $c_0/a_0 = 1.55$. η phase: $a_0 = 0.2671$ nm; $c_0 = 0.4946$ nm; $c_0/a_0 = 1.852$. This indicates that both β'_s and η'_s phase decomposed in the Reactions 1 and 7

$$\beta'_s \rightarrow \alpha'_T + \varepsilon + \eta \qquad (1)$$

$$\eta'_s \rightarrow \alpha'_T + \varepsilon + \eta \qquad (7)$$

It was observed that the decomposition of η'_s occurred at a very early stage of ageing (after 3 s ageing at 90.4 °C), which will be discussed in a separate paper. This might be the reason why it is very difficult to observe the single-phase η'_s interdendritic regions on optical and scanning electron micrographs.

The decomposition of β'_s was clearly observed after ageing at 90.4 °C for 30 s, shown in Figs 3b and 4b, as was determined in previous investigations on the Zn–Al based alloys [1–12].

The first stage of phase transformation, i.e. decompositions of β'_s and η'_s phases, was completed after about 30 min ageing at 90.4 °C, as shown in the X-ray diffractograms (Fig. 2). Both β'_s and η'_s have almost disappeared from the X-ray diffractograms.

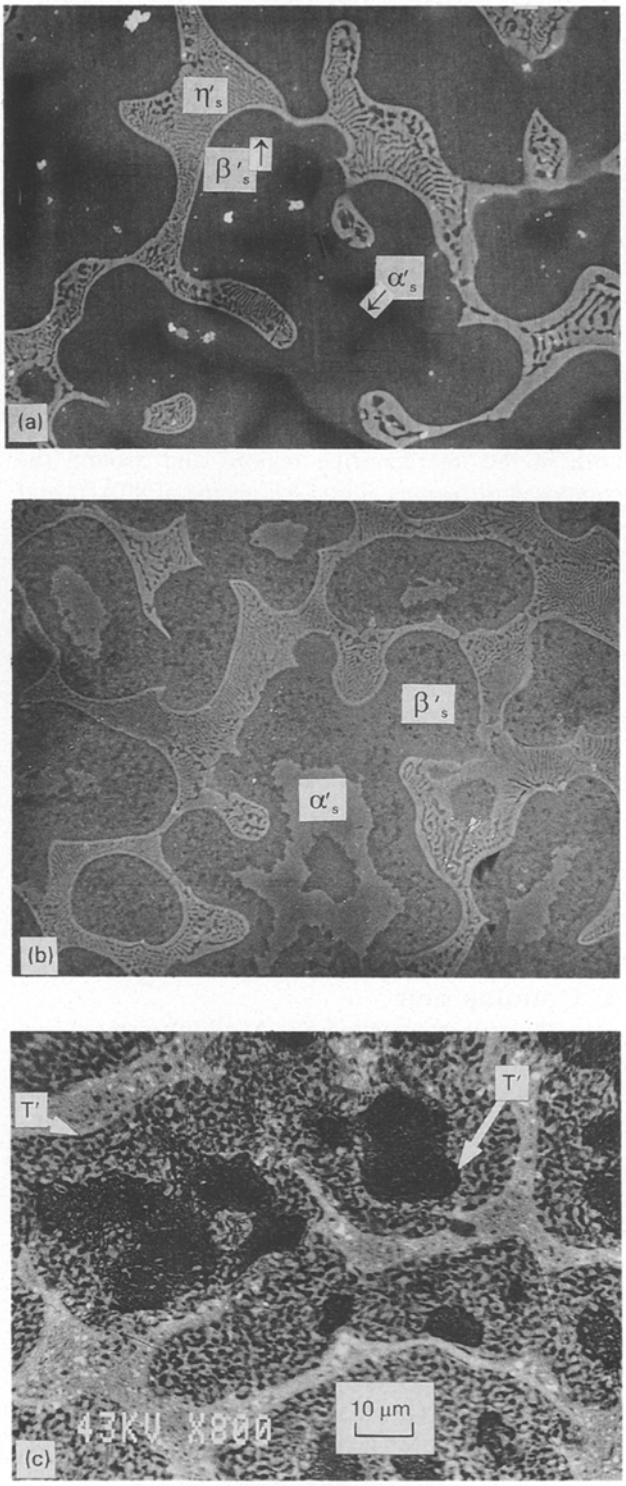

Figure 4 Scanning electron micrographs of as-cast eutectoid Zn–Al alloy: (a) chilled as-cast state; (b) after 30 s ageing at 90.4 °C; (c) after 1.5 h ageing at 90.4 °C and 67 h at 150 °C.

On further ageing, it was observed that the peaks of α'_T and α'_s shifted to the lower 2θ angles on the X-ray diffractogram, shown in Fig. 2. It was clear that the alloy had undertaken a spinodal decomposition, described by Reaction 2

$$\alpha'_T \rightarrow \text{GPZ} \rightarrow \alpha''_m \rightarrow \alpha'_m \rightarrow \eta$$
$$\searrow \alpha'' \rightarrow \alpha' \rightarrow \alpha_f \qquad (2)$$

as observed in previous investigations [1–12]. After prolonged ageing, it was observed that a four-phase transformation occurred as follows

$$\alpha_f + \varepsilon \rightarrow T' + \eta \quad (3)$$

On the X-ray diffractograms, shown in Fig. 2, T′ phase was observed at $2\theta = 44.4°$ after 1.5 h ageing at 90.4 °C and 15 min ageing at 150 °C. On further ageing at 150 °C, the diffraction peaks of ε phase apparently decreased in height, accompanied by an increase in diffraction peak height of T′ phase. After 1.5 h ageing at 90.4 °C and 7 h ageing at 150 °C, the diffraction peaks of ε phase vanished from the X-ray diffractograms and leaving a well-formed stable T′ phase peak.

On SEM observation, the T′ phase was observed both in the interdendritic regions and around the composed α'_s regions after 1.5 h ageing at 90.4 °C and 6.7 h at 150 °C, shown in Fig. 4c. Thus a four-phase transformation occurred at the boundaries of α_f and ε phase, instead of being clearly observed at the boundaries of ε phase in a solution-treated eutectoid Zn–Al alloy after prolonged ageing.

The observed dendritic structure of the as-cast eutectoid Zn–Al alloy was, in fact, the result of decompositions of various supersaturated phases. It consisted of fcc α'_s phase as the core, edged by decomposed β'_s, i.e. α'_T, ε and η phases, and the decomposed η′ phase in the interdendritic regions. Both decompositions of β'_s and η'_s were correlated to the equilibrium reaction $\beta + \varepsilon = \alpha + \eta$ at 276 °C.

4. Conclusions

1. The as-cast eutectoid Zn–Al alloy appeared as a typical dendritic structure consisting of the supersaturated α'_s phase as the core, edged by the decomposed β'_s and the decomposed η'_s in the interdendritic regions.

2. The supersaturated η'_s was determined in the chilled as-cast eutectoid Zn–Al alloy and identified to have hcp crystal structure and lattice parameters $a_0 = 0.2668$ nm, $c_0 = 0.4842$ nm, $c_0/a_0 = 1.8148$. It was unstable even at room temperature, and decomposed in early stages of ageing.

3. The phase transformations of the chilled as-cast eutectoid Zn–Al alloy consisted of decompositions of various supersaturated phases in the following steps:

(a) decomposition of β'_s and η'_s in the early stage of ageing, according to

$$\beta'_s \text{ (and } \eta'_s) \rightarrow \alpha'_T + \varepsilon + \eta$$

(b) decomposition of α'_T and α'_s, according to

$$\alpha'_T \text{ and } \alpha'_s \rightarrow \text{GPZ} \rightarrow \alpha''_m \rightarrow \alpha'_m \rightarrow \eta$$
$$\searrow \alpha'' \rightarrow \alpha' \rightarrow \alpha_f$$

(c) decomposition of ε phase, according to

$$\alpha_f + \varepsilon \rightarrow T' + \eta$$

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