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DISCONTINUOUS PRECIPITATION AND COARSENING IN Al-Zn ALLOYS

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ABSTRACT

Lamellar discontinuous precipitate (DP) formd in Al-Zn alloys containing 30, 40, 59 at.%Zn by isothermal aging has been observed for further decomposition by discontinuous coarsening (DC) into a coarser Lamellar structure of the same phases (a + b) with further aging. The interlamellar spacing and the rate of growth vary as a function of temperature and the results have been analyzed on the basis of the Ptermann and Hornbogen theories of discontinuous precipitation and coarsening which suggests that the cell boundary diffusion is the rate controlling factor in the Al-Zn system.

1. INTRODUCTION

Isothermally aged Al-Zn solid solution containing from 10 to 29 at.%Zn been observed to decompose by discontinuous precipitation (DP) into lammelar structures of a and b phases which far from their equilibrium compositions [1-3].

In alloys containing from 12.2 to 38.0 at.%Zn, the discontinuous reaction was observed to occur simultaneously with the general precipitation of Geniuer-Preston zone (GPZ), the metastable rhomobohedral R-phase or the face centered cubic a-phase [1-5].

A second cellular or discontinuous coarsening reaction (DC) has been oberved in some of the above studies to decompose the lammelar product of the discontinuous precipitation reaction [3,4 and 6].

In the present study, the growth kinetics of this second cellular or discontinuous coarsening reaction have been studied in an aluminum containing 30, 40 and 59 at.%Zn alloy with the object for determining the rate controlling process.

In addition, the growth kinetics of the first cellular reaciton have been restudied because the kinetics of the second reaction depend on those of the first.

2. EXPERIMENTAL DETAILS

2.1 Materials

The ingots pf Al-Zn alloys were prepard by arc melting from 99.99 wt.%Al and 99.9995 wt.%Zn in argon atmosphere. The ingots were homogenized at 360°C for 21 days, in Duran glass capsules under a vacuum of 10^{-3} Pa and then quenched in an ice-salt-methanol mixuture (-15 to -20°C). The length and diameter of the specimen which are used approximately 5 mm and 100 mm respectively.

2.2. Heat Treatment

The discontinuous reaction treatments were performed in two types of mixed salt bathes, nitric acid system (NaNO2 and KNO3) and chloric acid system (BaCl2, KCl and NaCl) in range of temperature 50 to 680°C. Aging treatments shorter than 10 hours were carried out in these salt bathes, and for the longer aging time in a quartz tube under high vacuum annealed in horizontal furnace.

2.3. Microscopic Testing

For light microscopic observations, the aged specimens were prepared by wet grinding, prepolishing and "Miniment" polishing through 3 µm and 1 µm diamond paste using a "Nylon" polishing cloth. The Al-Zn alloys were etched with a solution of 322.5% HNO3 in distilled water at etching temperature ranging from 40 to 60°C and etching time 30 seconds.

3. RESULTS AND DISCUSSION

3.1. Morphological Analysis

The morophologies of the discontinuous precipitation which are produced during the reaction are visible as shown in Fig. 1, a-e. The supersaturated a-phase in all three alloys was observed to decompose rapidly by a discontinuous precipitation reaction at the aging temperatures into a lamellar mixture of aluminum rich FCC "a" and Zn rich "b" phases.

In the alloys which have high Zn percentage the formation of Geniuer preston zone (GPZ) does not stop the discontinuous precipitation as happen in aluminum with low concentration of Zinc [5].

3.2 THE GROWTH KINETICS

3.2.1. Discontinuous precipitation reaction

Fig. 2 shows that the growth rates of the reaction fronts for discontinuous precipitation which obtained from the slopes of w' -t plots, where t is the aging time w is the mean seam width. For determination of the mean seam width about 30 individual w' values [3] were used:

$$w = \Pi w' / 4 \qquad (1)$$

The growth rate for discontinuous precipitation with v_1 initially increases by two orders of magnitude with an increase in aging temperature from 50°C to 250°C and then decreases typical "C-curve" behaviour.

In general, the maximum of growth rate for discontinuous precipitation reaction is occuring at:

$$T_{max} = 0.89\ T_{sv} \qquad (2)$$

The behaviour of the growth rate curve is similar to the behaviour observed for Al-22, 28.4 at.%Zn [3], Ni-In and Co-Al [2]. The mean values (λ') of the lamellar spacing are determined from 10-15 individual values using an equation analogous to eq. 1. The lamellar spacings of the discontiuous precipitation reaction cells are

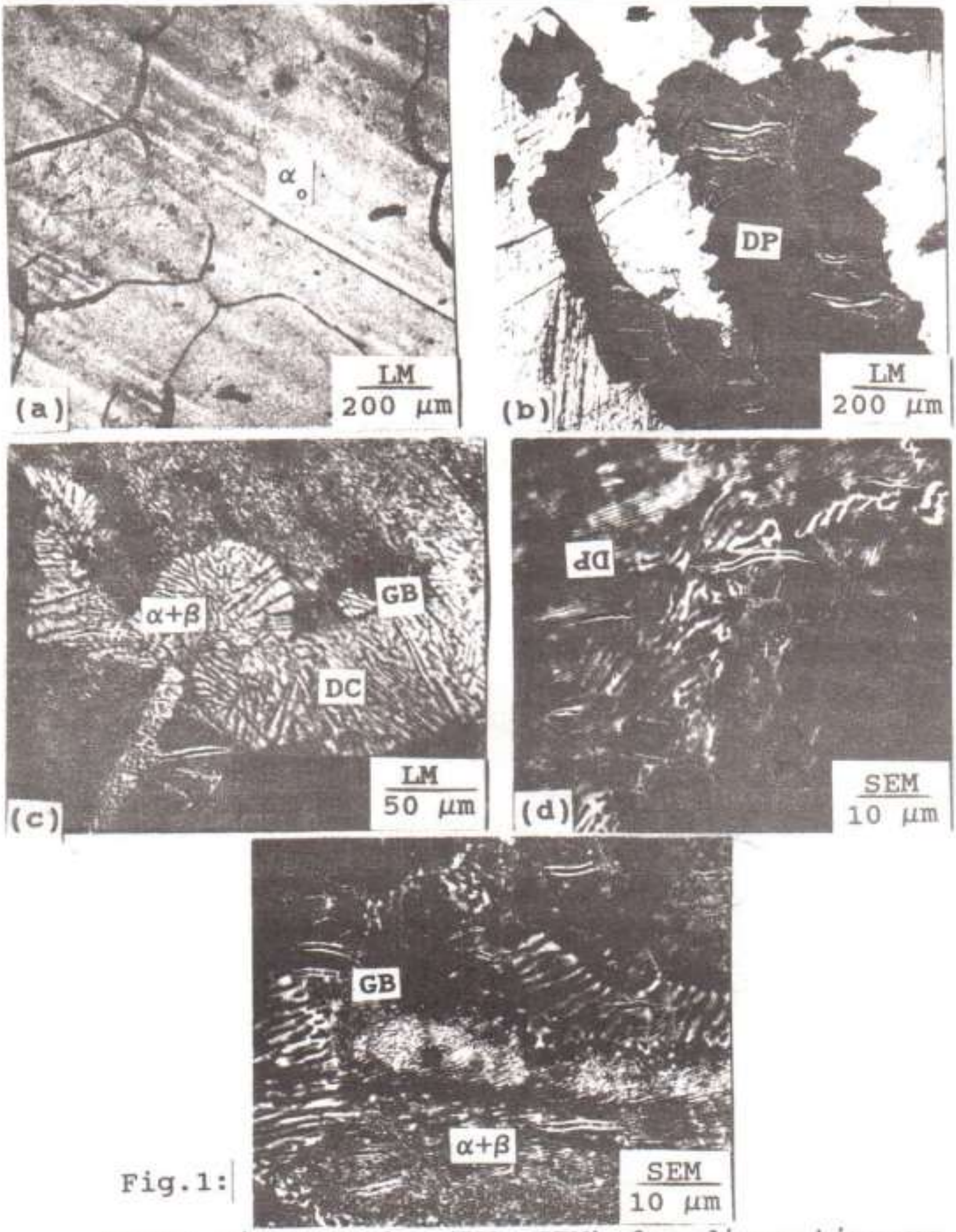

Fig.1: Photo micrographs (LM, SEM) for discontinuous reactions in Al-Zn alloys :

a) Al- 30Zn, t = 120 sec., T = 50 °C.
b) Al- 40Zn, t = 600 sec., T = 100 °C.
c) Al- 59Zn, t = 45 min. , T = 150 °C.
d) Al- 30Zn, t = 20 min. , T = 250 °C.
e) Al- 40Zn, t = 30 min. , T = 125 °C.

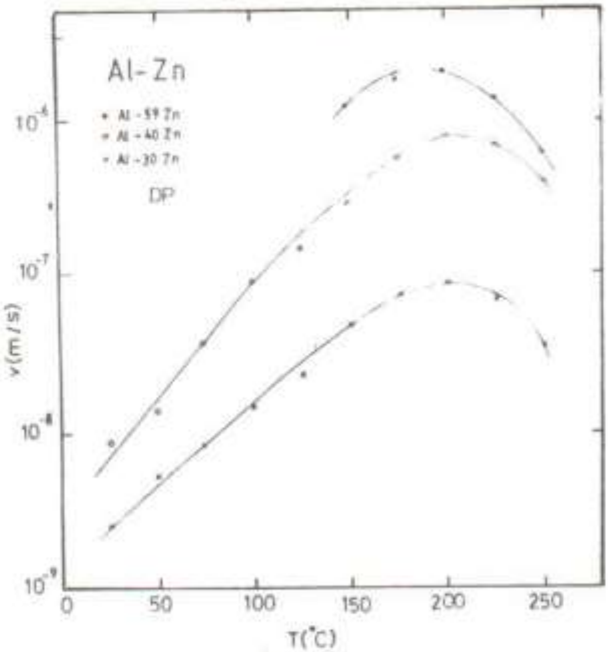

Fig.2:

The cell growth rate for discontinuous Precipitation reaction against aging temperatures in Al-containing 30, 40 and 59 at.%Zn alloys.

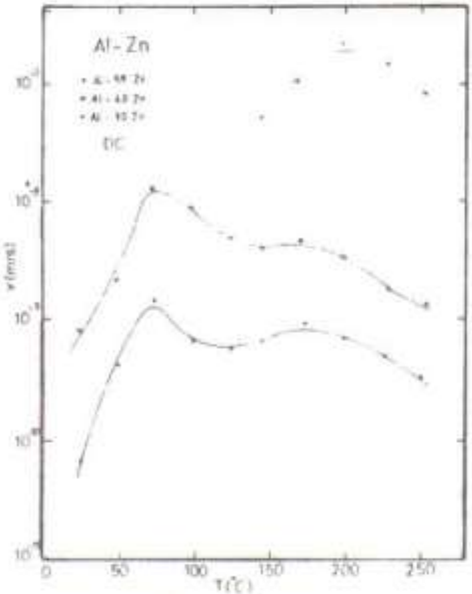

Fig.3:

The cell growth rate for discontinuous coarsening reaction against aging temperatures in Al-containing 30, 40 and 59 at.%Zn alloys.

observed to increase monotonically with increasing aging temperature as shown in fig. 4.

3.2.2. Discontinuous coarsening reaction

At all aging temperature studies (25-250°C) the fine lamellar structure produced by discontinuous precipitation is tranformed into a coarse lamellar structure by a discontinuous coarsening reaction. The discontinuous coarsening cells are shown in Fig. 1-b. The secondary reaction front separating the coarse lamellar strucutre form the fine one can be clearly seen. The reactions were observed to initiate at the grain boundaries by a boundary bowing mechanism [5] similar to that described by Fournelle and Clark [7] and to develop a steady state lamellar strcuture by branching of the lamellar as they grew into the discontinuous precipitatiaon reaction [8] as shown in Fig. 1-c.

The growth rates for discontiuous coarsening were obtained from the slops of the mean width versus aging time. Fifteen individual measurements were made for each aging condition along the original grain boundary.

The cells growth rates are presented in Fig. 3. The discontinuous coarsening growth rates were about 10 to 100 times slower than those for the discontinuous pricipitation. The growth rates for discontinuous coarsening do not exhibit smooth "C-curve" behaviour. There is a decrase in the growth rate at temperatures ranging from 75 to 165°C. This is similar to the behaviour observed for discontinuous coarsening cells in Al-Zn [3]. Ni-Sn [9] and Cu-Be [10]. Because discontinuous coarsening reaction growth rate depends on the the lamellar spacing and phase compositions of the discontinuous precipitation reaction, there is probably no simple explanation of this behaviour.

The lammellar spacings determined for the coarsening cell are shown in Fig. 4. The coarsening ratio, λ_2 / λ_p, is also graphically represented in these curves (Fig. 4).

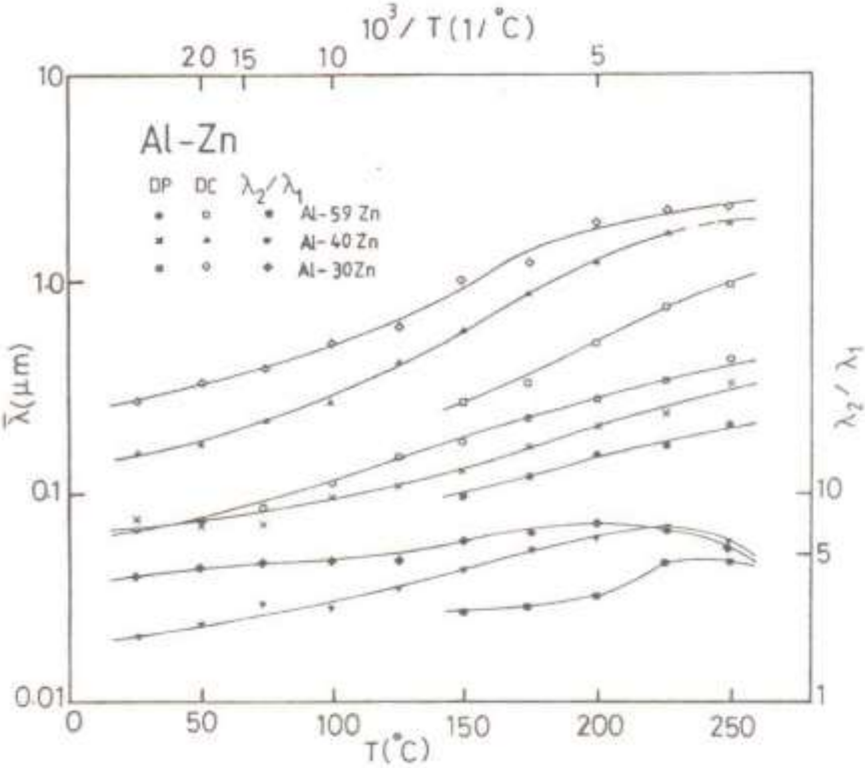

Fig.4: Mean interlamellar spacing of discontinuous precipitation and discontinuous coarsening against aging temperatures in Al-containing 30, 40 and 59 at.%Zn alloys.

The average concentration values x_1 and x_2 of the α-phase lamellar produced by discontinuous precipitation or discontinuous coarsing were interpolated by the present paper from the experimental values produced by Haltgreen [11]. Arrhenius plot of the equilibrium concentration is shown in Fig. 5. The equilibrium concentration values, X_e were taken from the latest version of the phase diagram [12].

The growth kinetics of both the discontinuous precipition (DP) and discontitnous corseing reaction (DC) reactions were analyzed by calculating boundary diffusivities in the reaction fronts using the Petermann and Hornbogen theory [13], which assumes that the reactions are controlled by boundary diffusion of the alloy elements in the migrating reaction front, and comparing them with diffusivities in stationary boundaries. According to the Petermann and Hornbogen theory, the reaction front velocity v, the lammelar spacing λ, and the boundary diffusivity D_b are related according to the following equation:

$$V = \frac{8\, s\delta\, D_b\, \Delta F}{R\, T\, \lambda^2} \tag{3}$$

where s is the segregation factor, d is the reaction front width, R is the gas constant, T is the absolute temperature and ΔF is the free energy change during the reaction. For DP, ΔF is given by:

$$\Delta F_{DP} = \Delta G_{DP} + \frac{2\,\sigma\, V_m}{\lambda_{DP}} \tag{4}$$

where ΔG_{DP} is the chemical free energy change, σ is the α/β surface energy per unit area Vm is the molar volume. For DC, it is given by:

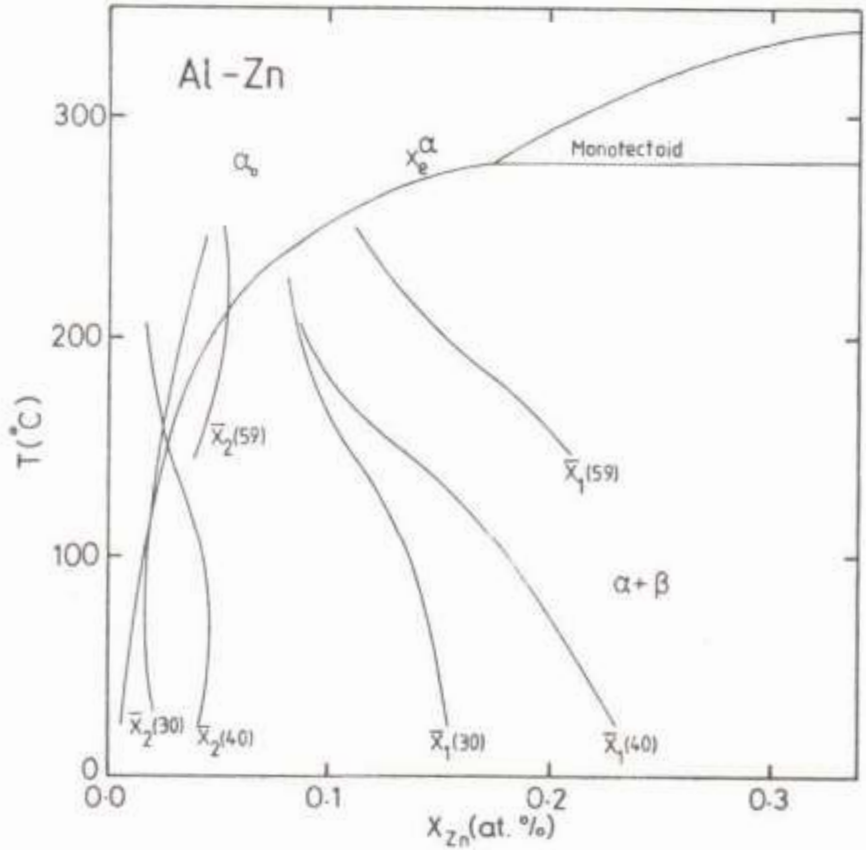

Fig.5:

The equilibrium concentration, X_e, and average concentration, $\overline{X}$, against the temperature for discontinuous precipitation and discontinuous coarsening reactions in Al-Zn alloys.

$$\Delta F_{DC} = \Delta G_{DC} + \frac{2\sigma V_m}{\lambda_{DC}} - \frac{2\sigma V_m}{\lambda_{DC}} \qquad (5)$$

The ΔG and σ values were calculated as described previously [4].

Fig. 6 shows the ($s\delta D_b$) values calculated from the experimental data using eq. (3) in comparison the data of Hässner [14] for Zn tracer diffusion in with statrionary grain boundries in Al-Zn alloys. As ca be seen, the sd Db valuesfor both DP and DC extrapolate into the values given by Håssner, thus, this indicates that both reactions are controlled by boundary diffusion in the reaction front. Like the Håssner diffusivities, those calcualted for the DP and DC reactions show a tendency to increase with increasing Zn content.

CONCLUSIONS

The following conclusions can be drawn from the present investigation:

1. The discontinuous precipitaiton cells get fromed at the large angle grain boundaries as well as within the grains.
2. The growth rates for discontinuous precipitation followed a "C-curve" behaviour while for discontinuous coarsening reaction did not achieve the "C-curve" behaviour.
3. The lamellar structure of the discontinuous precipitation reaction is decomposed at all aging temperatures by a second discontinuous reaction (DC) whose product has a coarser lamellar spacing.
4. The cell boundry diffusivities are two to three orders of magnitude higher than the grain boundary diffusivities of Zn Al in the temperature range from 200 to 300°C.
5. The grain boundary diffusivities determined on the basis of the model of Petermann and Hornbogen are in agree with the radio tracer measurement data in the Al-Zn system.

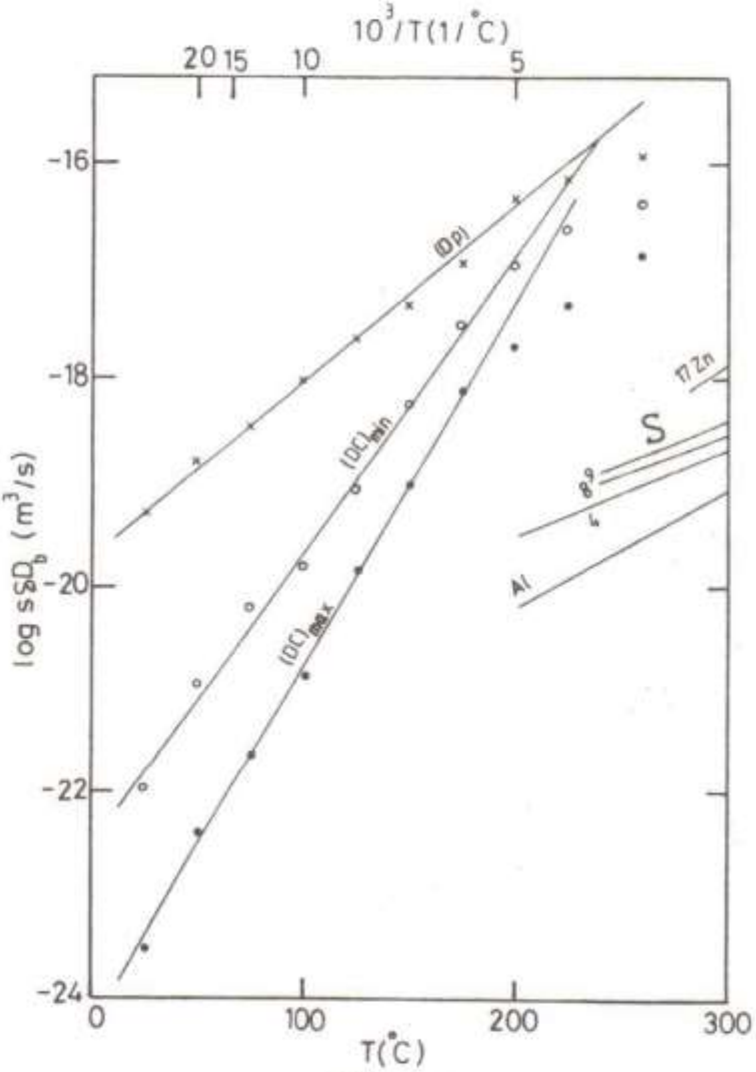

Fig.6:

Arrhenius plot of the $s\delta\ D_b$ values according to the theory of Petermann and Hornbogen for discontinuous precipitation in Al-30,40 and 59 at.%Zn alloys comparsion with literature data of the diffusion in stationary (S) grain boundaries.

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