

KINETICS OF DISCONTINUOUS PRECIPITATION IN A Zn-2 at.% Ag ALLOY

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(Revised June 22, 1993)Introduction

Formation of a precipitate phase (β) and a solute depleted matrix phase (α) behind a migrating boundary advancing into a supersaturated matrix phase (α_0) is called discontinuous precipitation (DP) [1]. The precipitation is characterized by discontinuous changes in orientation and composition between the matrix phases (α_0/α) across the migrating boundary, called the reaction front (RF), which provides a short-circuit path of solute transport [1-3]. Analysis of the steady state DP reaction kinetics provides a convenient and reliable method of grain boundary chemical diffusivity ($s\delta D_b$) measurement in systems which undergo DP [3]. This approach has already been applied in a number of binary systems like Zn-Al [4], Cu-In [5], Ni-Sn [6], Al-Zn [7], etc. DP in the Zn-Ag system has recently been reported by Manna et al. [8]. The present report involves kinetic studies of DP and determination of Arrhenius parameters of grain boundary chemical diffusion of Ag in a Zn-2at.%Ag alloy.

Experimental

The Zn-2at.%Ag alloy was prepared from high purity materials by vacuum induction melting. The 8 mm diameter cast ingot was homogenized at 688K for two weeks and quenched in water at room temperature. The isothermal treatments for DP were carried out in the temperature (T) range of 353-433K for varying lengths of time (t) followed by water quenching. Morphology and growth kinetics of DP were studied through both optical and scanning electron microscopy. The specimens for microscopic studies were carefully prepared by mechanical polishing and etching with a solution of 1 ml HNO₃ and 1 ml CH₃COOH in 98 ml distilled water. In order to normalize the variations due to difference in growth orientation of the precipitate colonies with respect to the plane of observation, the true colony width (w) was determined from the average colony width (\bar{w}) obtained from 20-30 independent measurements as follows [9] :

$$w = (\pi/4) \bar{w} \quad (1)$$

Since the morphology of β is mostly of rod type, similar normalization for obtaining the true inter-rod spacing (λ) is not warranted. An average of 15-25 independent measurements of the repeat distance of β was taken as λ .

Results and Discussion

Morphology

Figure 1 presents a typical microstructure showing a DP colony formed during isothermal precipitation at 353K for 450h. Precipitation in the present alloy appears to be confined to the discontinuous mode in the temperature range studied. It is interesting to note that the absence of continuous/matrix precipitation in the Zn rich Zn-Ag alloy is in direct contrast to the extensive matrix precipitation even at room temperature in the Zn rich Zn-Al system [4,10]. Extensive metallographic studies reveal that β rods maintain a statistically constant λ within the DP colonies under isothermal growth conditions. However, orientation of β may change within the same colony, perhaps, to accommodate the probable change in the direction of RF migration (Fig.1).

Kinetics

Figure 2 shows the variation of w as a function of t at different T . The close fit of the respective set of data points for each T within the time period studied to a straight line equation allows determination of the isothermal RF velocity, $v = (dw/dt)_T$, by suitable regression analysis. Figure 3 reveals the dependence of v on T . λ also records a similar increase as a function of increasing T (Fig. 4). It is known that DP may occur up to a maximum T (below the equilibrium solvus, T_{sv}), above which the available chemical driving force is inadequate to support creation of α/β interfaces and migration of the RF [11]. Theoretically, $1/\lambda = 0$ signifies infinite repeat distance of the β phase in a DP colony or cessation of the DP reaction. Extrapolation of $1/\lambda$ to $1/\lambda = 0$ in Fig. 4 intersects the temperature axis at $T_{DP} = 500K$, where T_{DP} is the highest temperature above which DP should cease [12]. It is interesting to note that the T_{DP} (= 500K) is marginally below the T_{sv} (= 523K) for the present alloy.

Estimation of Driving Force

The driving force in terms of the Gibbs free energy change (ΔG) in a precipitation reaction with negligible strain energy change is given by :

$$\Delta G = \Delta G_1 + \Delta G_2 \quad (2)$$

where, ΔG_1 and ΔG_2 represent the chemical and interfacial contributions, respectively. Since free energies of formation and activity coefficients of the concerned phases are not available in the literature, ΔG_1 may be calculated using the ideal solution model [13] as follows :

$$\Delta G_1 = - RT [X_0 \ln (X_0/X_1) + (1-X_0) \ln \{(1-X_0)/(1-X_1)\}] \quad (3)$$

where, X_0 and X_1 represent the respective solute contents in α_0 and α phases obtained from the relevant phase diagram [14] and R is the universal gas constant. In view of the relatively low initial solute concentration (2at.%), slow reaction kinetics and close proximity of T_{DP} and T_{sv} , it may be reasonable to assume that the solute contents in the product phases of α and β reach the concentrations indicated by the respective equilibrium solvus curves following DP. In fact, the supplementary investigation of lattice parameter measurement by X-ray diffraction has indicated that solute content in the α phase does not differ from the respective equilibrium solid solubility data.

Assuming hexagonal packing of the precipitate rods in the Zn rich matrix, the interfacial free energy contribution (ΔG_2) may be expressed as follows [15] :

$$\Delta G_2 = 3.8 \left\{ (X_0 - X_1) / (X_2 - X_1) \right\}^{0.5} (V_m \gamma / \lambda) \quad (4)$$

where, X_2 refers to the equilibrium solute content in the β phase, γ is the interfacial energy per unit area of the α/β boundary and V_m denotes the molar volume of the α_0 phase. Since γ for the Zn-Ag system is not available in the literature and the grain boundary specific energy of pure Zn is 340 mJ/m² at 573K [16], it may be reasonable to assume that $\gamma = 280$ mJ/m² at 573 K with $d\gamma/dT = -0.1$ mJ/m²-K for the Zn-2 at.% Ag alloy (considering a decrease in γ due to alloying). V_m value for α_0 in the present alloy has been calculated to be 9.10×10^{-6} m³/mol. Thus, the overall change in Gibbs free energy per mole (ΔG) may be calculated through equation (2) obtaining ΔG_1 and ΔG_2 contributions as per equations (3) and (4), respectively. Table 1 presents the calculated values of ΔG_1 and ΔG_2 with the concerned solute content values used.

TABLE 1 : Thermodynamic Data for Driving Force Estimation.

T (K)	X_1	X_2	$-\Delta G_1$ (J/mol)	γ (mJ/m ²)	ΔG_2 (J/mol)
353	0.0030	0.126	61.79	302	0.96
373	0.0045	0.126	44.75	300	0.77
393	0.0065	0.126	29.59	298	0.68
413	0.0085	0.126	19.47	296	0.51
433	0.0105	0.126	12.34	294	0.35

Grain Boundary Diffusivity

Since the earliest approach of Zener [17] to quantify the growth kinetics of a moving boundary reaction, several analytical models [18-24] have been proposed to estimate the grain boundary diffusivity triple product ($s\delta D_b$) through kinetic analysis of DP utilizing the experimentally determined parameters of v and λ . Williams-Butler [1] and Gust [2] have reviewed the scope of application and relative merits of these analytical models. Several of these models [19-22] necessitate the metastable solvus data for the α phase to calculate a relevant thermodynamic function. Unfortunately, neither the metastable solvus curve for the Zn-Ag system is reported in the literature nor does the X-ray diffraction analysis evidence a measurable residual solute supersaturation in the α phase following DP in the present alloy. Further, the Aaronson-Liu model [23] is essentially an extension of the Turnbull model [18] and yields very similar results. Therefore, kinetic analyses in the present study to calculate $s\delta D_b$ have been carried out only through the models of Turnbull [18] and Petermann-Hornbogen [24].

According to Turnbull [18] :

$$s\delta D_b = [X_0 / (X_0 - X_1)] v \lambda^2 \quad (5)$$

where, s = segregation factor [25], δ = thickness of the RF and D_b = grain boundary chemical diffusivity. X_1 may be obtained from the relevant equilibrium phase diagram. It may be noted that the Turnbull model considers the chemical contribution in terms of solute concentration gradient to be the

sole driving force for DP [18].

Petermann-Hornbogen [24] express the growth kinetics as :

$$s\delta D_b = RT v \lambda^2 / [8(-\Delta G)] \quad (6)$$

where, ΔG is the overall driving force to be obtained from equations (2) through (4). Table 2 summarizes the kinetic data of DP in the temperature range studied.

TABLE 2 : Kinetic Data on DP and Grain Boundary Diffusivity Calculation.

T (K)	λ (μm)	$(10^{-7} \dot{\gamma}_2 \text{ m/s})$	$X_0/(X_0-X_1)$	$s\delta D_b^{(a)}$ (m^3/s)	$-\Delta G$ (J/mol)	$s\delta D_b^{(b)}$ (m^3/s)
353	4.06	8.3	1.18	1.61×10^{-22}	60.83	8.27×10^{-22}
373	4.81	30.5	1.29	9.10×10^{-22}	43.98	6.21×10^{-21}
393	5.07	36.1	1.48	1.37×10^{-21}	28.91	1.30×10^{-20}
413	6.30	41.6	1.74	2.87×10^{-21}	18.96	3.73×10^{-20}
433	8.40	58.3	2.10	8.66×10^{-21}	11.99	1.54×10^{-19}

[Note : $s\delta D_b^{(a)}$ = using equation (5) and $s\delta D_b^{(b)}$ = using equation (6)]

Figure 5 shows the Arrhenius plot of $s\delta D_b$ calculated according to the models of Turnbull [18] and Petermann-Hornbogen [24], using equations (5) and (6), respectively. The activation energy (Q) values determined from the slopes of the straight lines fitted to the respective set of data points obtained by equations (5) and (6) are 58.3 and 78.2 kJ/mol. Table 3 compares the Q values obtained in the present study with the relevant data reported in the literature. The higher Q value calculated for the present alloy containing 2at.%Ag in comparison to that for the Zn-4at.%Ag alloy [8] (as per the analytical model by Petermann-Hornbogen [24]) may be attributed to the lower initial solute content and, hence, a smaller chemical driving force for the DP reaction. However, the Q values calculated for the present alloys compare well with those for grain boundary self diffusion in Zn [26]. Finally, it is relevant to note that the Q values for grain boundary chemical diffusion are considerably lower than the average Q for volume diffusion of Ag in the Zn-Ag system [27] (cf. Table 3).

Table 3 : Comparison of Activation Energy Values of Diffusion (in kJ/mol).

Grain boundary diffusion		Volume diffusion	
Chemical diffusion		Self diffusion	Impurity tracer diffusion
Zn-2Ag (*)	Zn-4Ag [8]	Zn in Zn [26]	Ag in Zn-Ag [27]
58.3 ^(a)	78.2 ^(b)	61.1	112.0

(*) present study, (a) = using equation (5), (b) = using equation (6)

Summary

The Zn-2at.%Ag alloy undergoes a discontinuous mode of precipitation in the temperature range of 353-433K. The rod like precipitate phase in the DP colony maintains a statistically constant distance of separation under isothermal conditions of precipitation. The DP reaction in the present alloy is predicted to cease at $T_{DP} = 500\text{K}$, which is marginally below its equilibrium solvus. Finally, detailed kinetic analysis of DP yields the

Arrhenius equations of grain boundary chemical diffusion of Ag for the Zn-2at.%Ag alloy as follows :

$$s\delta D_b^{(a)} = 8.71 \times 10^{-14} \exp [-0.7024 \times 10^4 / T(K)] \text{ m}^3/\text{s}$$

$$s\delta D_b^{(b)} = 3.71 \times 10^{-10} \exp [-0.9422 \times 10^4 / T(K)] \text{ m}^3/\text{s}$$

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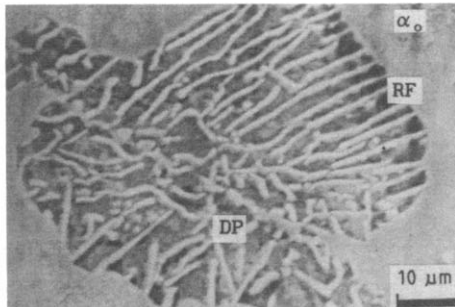


FIG.1
A typical scanning electron micrograph showing a DP colony separated from the α_0 matrix by the RF during isothermal precipitation at 353K for 450h.

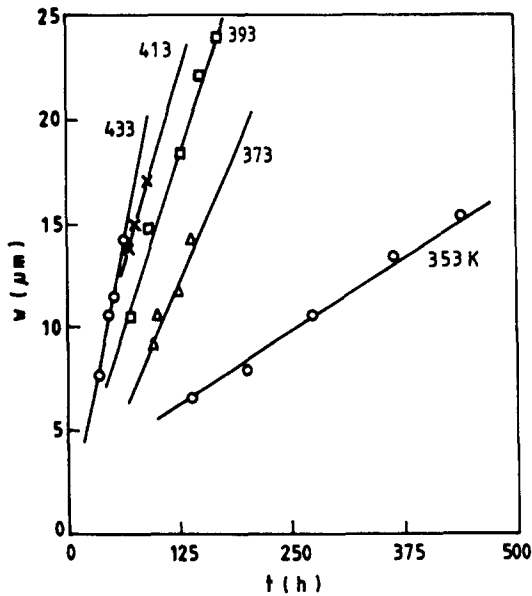


FIG. 2
Variation of DP seam width (w) as a function of time (t) at different temperatures.

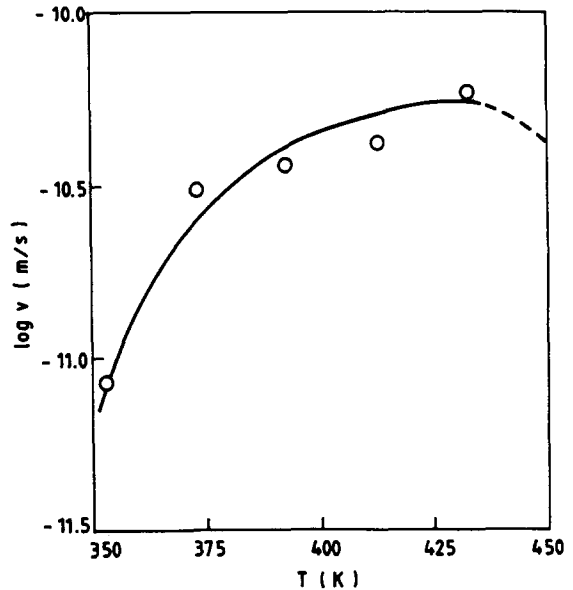


FIG. 3
Variation of the RF migration velocity (v) as a function of isothermal temperature (T).

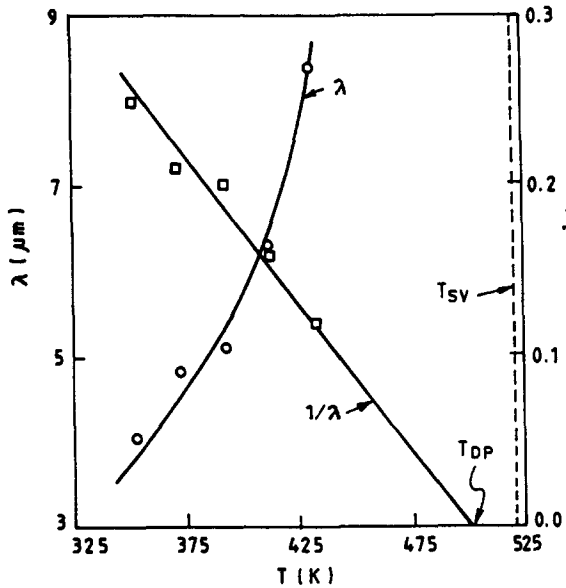


FIG. 4
Variation of precipitate-rod spacing (λ) and its reciprocal ($1/\lambda$) against temperature (T).

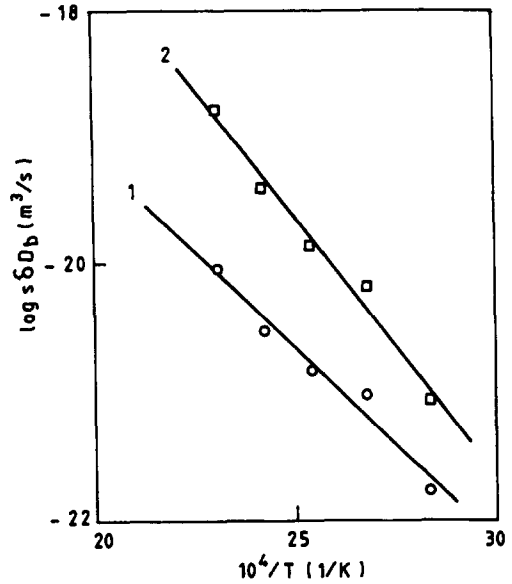


FIG. 5
Arrhenius plot of grain boundary chemical diffusivity triple product ($s\delta D_g$).