

ABSTRACT

Discontinuous precipitation (DP) and coarsening (DC) are two model moving boundary reactions (MBRs) involving heterogeneous nucleation of precipitates on a migrating boundary, called the reaction front (RF), and concurrent migration of the latter. DP and DC bear similarities in transformation mechanism and kinetics with several important solid state MBRs, e.g. eutectoid transformations, recrystallization grain growth, etc. The studies on DP and related MBRs are warranted both for technological necessity as well as academic interest. Furthermore, steady state kinetic analysis of DP and DC may be utilized to determine grain boundary chemical diffusivity triple product ($s\delta D_b$) as a function of temperature. The present work concerns a detailed investigation into the reaction mechanism and kinetics of DP and DC, and determination of Arrhenius parameters of boundary chemical diffusion and mobility through an extensive isothermal kinetic analysis of the reactions in the present Zn-rich binary alloys. It may be pointed out that the occurrence of DP and DC in several of the present binary alloys has not been reported earlier. Moreover, the boundary chemical diffusivity data obtained in this study are not available in the literature.

Continuous precipitation (CP) accompanies DP in all the alloys except in Zn-2Ag. The CP products bear strict orientation relationship with the matrix and have considerable influence on the DP kinetics at higher temperatures or longer aging time. The DP and DC colonies comprise precipitate rods/lamellae maintaining a statistically constant repeat distance under a given steady state growth conditions. The constancy of inter-rod/lamellar spacing is maintained both by branching and re-nucleation near/on the RF. The RF-velocity in DP registers a typical 'C-curve' variation with temperatures with the maximum velocity occurring approximately between 0.8-0.9 of the concerned solvus temperatures. The predicted upper limit for the occurrence of

DP lies below the corresponding solvus temperatures indicating that a minimum chemical driving force is necessary for the RF-migration in DP.

While DP occurs in all the present alloys, DC is observed only in the Zn-4Ag alloys. The mechanisms for DC initiation and corresponding probable sites for the latter have been proposed. An extensive microstructural study has identified several aspects of the mechanism of DC including the orientation relationship between the lamellae in the primary and secondary colonies (and with respect to the RF), direction and mechanism of steady state growth of a DC colony, etc. The microstructures and growth kinetics indicate that the reaction mechanism in both the routines of DC (namely, DCI and DCII) are identical.

A detailed kinetic analysis of DP and DC using the experimentally determined kinetic parameters and analytically estimated driving force on the basis of the relevant kinetic models has enabled determination of $s\delta D_b$ in the temperature range studied. Arrhenius analysis of the $s\delta D_b$ data has yielded the activation energy values for boundary chemical diffusion in the present alloys. In addition, activation energy for boundary mobility has also been determined. These activation energy data are comparable to the grain boundary self diffusion in Zn, and significantly lower than that for the relevant volume diffusion. Therefore, it is concluded that DP and DC in the present alloys are boundary diffusion controlled moving boundary reactions.