Fundamentals of Mass Transport at Migrating Grain Boundaries (Part II)

3. Discontinuous coarsening

Discontinuous coarsening reaction (DC) occurs in an advanced stage of aging in all systems in which the DP reaction is initially observed. The process starts at first at the primary grain boundaries, then at the impingement of various cells. Figure 11(a) is a typical example of the coarsened structure of the α and β lamellae which nucleated at the impingement of various cells. The thickness of the α_{DC} lamellae is 3 times larger than that for α_{DP} but there are also examples [25] showing that the coarsening factor can be as large as 9.





Fig. 11. (a) TEM micrograph showing the results of a discontinuous coarsening reaction at the impingement of two different areas of the primary discontinuous precipitates. Examples of solute concentration profiles taken (b) across the α_{DP}/α_{DC} boundary and (c) across the α_{DC} lamella. Al-22 at.% Zn aged at 450 K for 350 h.

The microchemical analysis within the products of discontinuous coarsening. show (Fig. 11(b)) that the step-like change across the α_{DP}/α_{DC} reaction front is preserved during DC, providing convincing proof of the discontinuous behavior of the reaction. A flat solute concentration profile across the α lamella after the DP reaction would indicate that the driving force for the DC reaction is solely the change in the interfacial free energy of the lamellar structure. However, this is rather an idealized case as the solute profile within the α lamellae is commonly observed after the DP reaction confirming a chemical contribution to the overall driving force of the DC reaction. A representative example of an EDX analysis performed across an α lamella is presented in Fig. 11(c). The solute distribution is rather flat and corresponds to the equilibrium state.

However, further processes are also possible. They are called secondary or ternary discontinuous coarsening reactions [14, 25, 31]. For example, two kinds of DC were observed in the Co-13 at.% Al alloy [25], which were named DC I and DC II. DC I. (Fig. 12a) is characterised by an approximately 3-4 times larger thickness of the α lamellae, while DC II (Fig. 13a) showed almost a 9-fold difference in the thickness of the primary and secondary α lamellae. The results of the EDX analyses across the migrating front of the DC reaction (Figs. 12b and 12b) also suggested that the $\alpha_{DP}/\alpha_{DC I}$ and $\alpha_{DP}/\alpha_{DC II}$ boundaries were paths for fast diffusion of the solute atoms. The profile within the $\alpha_{DC I}$ lamella (Fig. 12c) still showed a maximum although not so well pronounced as it used to be in the primary α lamellae. On the other hand, the Al profile within the $\alpha_{DC \ II}$ lamella (Fig. 12c) was rather flat with the Al content corresponding to the equilibrium solvus line. The results obtained indicate that not only the tendency of the system to decrease its surface free energy by a decrease of total area of interfacial boundaries between the α and β lamellae, but also the excess of chemical free energy remaining after the DP reaction within the α lamellae (see Figs. 12c and 13c) were the driving force of DC I and DC II. All the excessive of chemical free energy is used up to create the α lamellae of the DC II reaction. As the thickness of the $\alpha_{DC \ II}$ lamella is twice as large as that of $\alpha_{DC \ I}$, a greater contribution to the total driving force originating from the surface term is expected.

One should mention that two kinds of DC reaction were also observed in other alloy systems but except for the nucleation of DC II at the reaction front of DP, the coarse lamellae developed also at the DC I front.



Fig. 12. (a) TEM micrograph showing the development of the DC I reaction in a Co-13at.% Al alloy aged for 20 days at 850 K. (b) Al profile taken across the $\alpha_{DP}/\alpha_{DC I}$ boundary. (c) Al profile taken across an $\alpha_{DC I}$ lamella.



Fig. 13. (a) TEM micrograph showing the development of DC II reaction in a Co-13at.% Al alloy aged for 20 days at 850 K. (b) Al profile taken across the $\alpha_{DP}/\alpha_{DC II}$ boundary. (c) Al profile taken across an $\alpha_{DC II}$ lamella.

4. Discontinuous dissolution

Annealing of a partially decomposed alloy at a temperature just below or slightly above the solvus line, results in dissolution of the DP product by the DD reaction. This is manifested by the backward migration of the reaction front of the DP reaction. Because the redistribution of the solute atoms behind the RF is apparently not complete, a characteristic "ghost" image of the former positions of the lamellar structure and the RF are visible (See Fig. 3c in Part I).

The observations at higher magnification performed on the TEM revealed clearly that the "ghost" image appears to be strictly related to the positions where the β phase lamellae have just been dissolved (see Fig. 3d in Part I)). One should note that such a "ghost" image is relatively difficult to be observed in the TEM because of the fact that usually a strong etching must be applied to reveal the ghost image in the samples for scanning electron and optical microscopy. The samples for TEM studies are electrolytically polished which does not facilitate the "ghost" image observation.

Figure 14 presents the evolution of the structure during *in situ* dissolution in an Al-22 at.% Zn alloy. Short time annealing at 550 K leads to the disappearance of single precipitates in the matrix as well as to a recession of the cell boundaries by a distance of approximately 1 μ m. The latter is a local process limited to the cells labelled 1 to 5 in Fig. 14 (a-c). There is no change of contrast behind the reaction front, which could be attributed to the variation of the solute content in this area. The next stage of the process is shown in Fig. 14c. A remarkable change in the contrast is visible ahead of cell 1. Such a fast dissolution of a b lamella is also observed in the cell areas labelled 2 and 3. This dissolution results in the formation of a new cell with a thickness of the a lamella twice as large as the previous one (Fig. 14d). Simultaneously, cell 1 recedes very fast leaving behind a "ghost" image at the initial position of the RF (see arrow in Fig. 14d). Further annealing (Fig. 14e-f) leads to a coalescence of the other b lamellae. At the same time, in the areas denoted A, B and C, the receding of cells begins as an abrupt change of the contrast at the matrix/ β lamella boundary.



Fig. 14. Sequence of micrographs showing an *in situ* dissolution at 550 K for 30 s. Al-22 at.% Zn alloy aged previously for up to 10 min at 450 K.

As it was already mentioned the interesting feature of the DD process is so-called "ghost image". Obviously the solute concentration in this area should be larger than the equilibrium value corresponding to the temperature at which DD takes place. The first direct measurements of the solute concentration just behind the tip of the β phase lamella were been per-

formed in an Al-22 at.% Zn alloy. They clearly revealed that the Zn-content can be as high as 42-47 at.% [32]. There was no pronounced dependence between the Zn content and the place of the DD initiation. This result was also predicted by the simulation [17] and also for other systems like: Ni-1.4 at.% In up to 4 at.% In [33], Mg-8 wt.% Al up to 16% Mg [34] and Ni-4 at.% Sn up to 6 at.% Sn [35].

References (continuation from part one)

- [31] S. Gupta, *Discontinuous coarsening of the cellular precipitate in a Ni-Sn alloy*, Scripta Metall. 20, (1986) 1323-1328.
- [32] P. Zięba, *Rola składu chemicznego w przemianach fazowych typu nieciągłego*, Zeszyty Naukowe Politechniki Śląskiej, Hutnictwo z. 51, Gliwice 1996, s. 68,
- [33] P. Zięba, D. Bradai, W. Gust, Prediction of Solute Concentration Profiles for Discontinuous Dissolution, Z. Metallkde 88 (1997) 425-428.
- [34] D. Bradai, P. Zięba, W. Gust, M. Hadi-Kanifi, On the Discontinuous Dissolution in Mg-8 wt.% Al Alloy, Practical Metallogr. 35 (1998) 673-680.
- [35] P. Zięba, W. Gust, Microanalytical Study of Discontinuous Precipitation and Dissolution in Ni-4 at.% Sn: Local and Global Characterization of the Reactions, Acta Mater. 47 (1999) 2641-2650.