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

1. Introduction

Grain boundaries (**GBs**) are highly disordered, as compared to the adjacent grains, and only a few atomic distances in thickness. They provide a much more open medium for the atomic movements than the adjoining grains. Diffusion at GBs, being orders of magnitude faster than that through the bulk of crystal, plays a key role in a large number of metallurgical and technological processes associated with the production of advanced metallic and ceramic materials used in the electronic, energetic and nuclear industry. On the other hand, diffusion at GBs widely appear during service of various devices. One can mention, the liquation phenomenon in austenitic steel at elevated temperatures [1], diffusion and GBs migration at materials subjected to irradiation [2] and within Fe-Zn coatings applied in the automotive industry in order to protect against corrosion [3]. Also the factors leading to the electromigration and subsequent degradation of electronic interconnections are closely related to the diffusion and GBs migration [4].

Therefore, the understanding the mechanism and kinetics of diffusion at GBs has been a challenge for many years. However, most of the information gathered so far has been from experiments on stationary GBs [5-7]. Much less attention has been paid to the diffusion at GBs accompanied with simultaneous GB migration, which better reflects the real circumstances during service of the materials. For example, the concentration gradient created is larger small and all the effects, associated with the interaction of diffusing atoms with each other and with the deviation of the GB solid solutions from the ideal state, cannot be neglected.

The most representative examples of the phenomena involving simultaneous diffusion at GBs and their migration are discontinuous solid state phase transformations during which the formation of a new phase is heterogeneous and limited to a migrating reaction front [8-12]. The reaction front, separating the transformation products from the parent phase, is a high angle grain boundary which serves as a path of rapid diffusion. The name „discontinuous" originates from the discontinuous or very sharp change in the chemical composition as well as crystal orientation between the parent phase and the matrix of the reaction products across the RF, whereas the crystal structures of the parent phase and matrix of the product phases are the same.

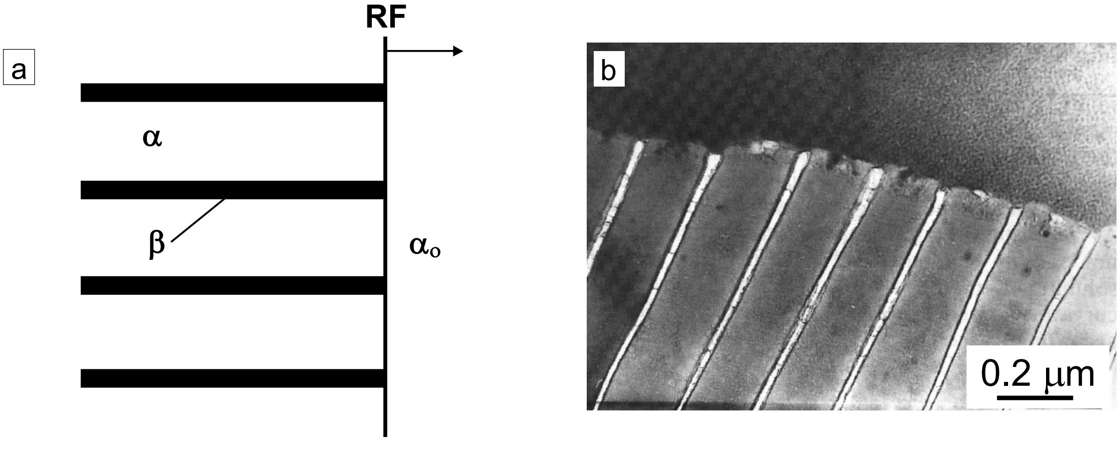

Fig. 1. (a) Schematic representation of discontinuous precipitation. Arrow indicates the direction of reaction front (RF) movement. (b) TEM micrograph showing discontinuous precipitation in the Al-22 at.% Zn alloy aged at 450 K for 10 min [13].

Four basic types of the discontinuous reactions can be distinguished:

- Discontinuous precipitation (DP);
- Discontinuous coarsening (DC);
- Discontinuous dissolution (DD);
- Diffusion-induced grain boundary migration (DIGM).

The discontinuous precipitation reaction (Fig. 1) takes place during aging of a sample in the two-phase field of the phase diagram. Under these circumstances a supersaturated solid solution (α_o) decomposes into a usually lamellar structure of a new solute-rich phase (β) and a solute-depleted initial phase (α) with the same crystal structure as α_o according to the scheme: $\alpha_o \rightarrow \alpha + \beta$. However, the equilibrium state is not reached in the transformation products as manifested by the presence of a solute concentration profile across the α lamellae. This excess of solute is diminished or even removed owing to the discontinuous coarsening (DC) reaction.

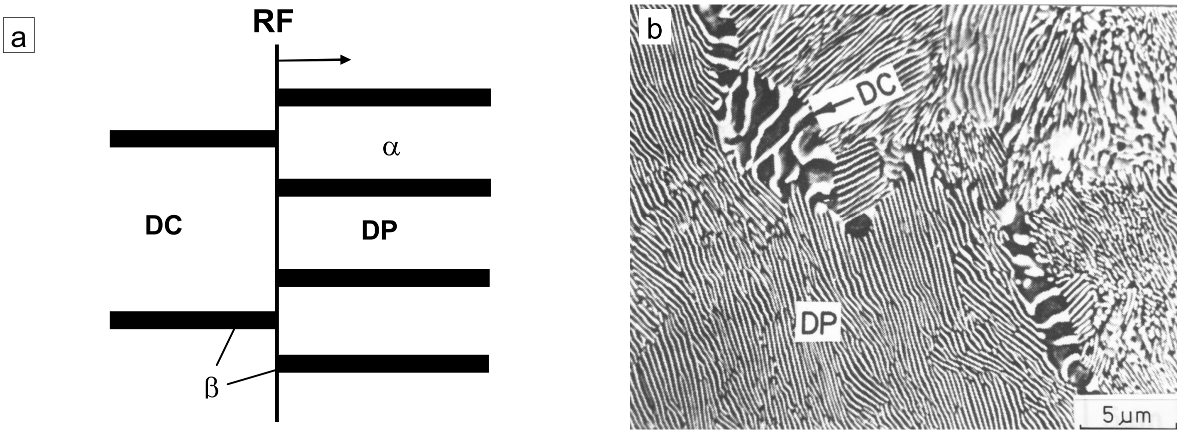

Fig. 2. (a) Schematic representation of discontinuous coarsening. Arrow indicates the direction of reaction front (RF) movement. (b) SEM micrograph showing DP and DC reactions in Al-39.3 at.% Zn aged at 523 K for 1 hour [14].

Discontinuous coarsening (Fig. 2) is a reaction during which a fine-lamellar structure is transformed into a coarser one containing the same α and β phases according to the reaction: $(\alpha + \beta)_{\text{fine}} \rightarrow (\alpha + \beta)_{\text{coarse}}$

On the other hand, annealing of the DP products close to the solvus temperature results in a recession of the reaction front of the former DP cell leading to a one-phase structure according to the scheme: $\alpha + \beta \rightarrow \alpha_{\sim}$ The process results in the formation of an inhomogeneous $\alpha_{\sim}$ solid solution manifested by the so-called „ghost image" of the previous positions of the β lamellae at which a maximum value of the solute content is expected.

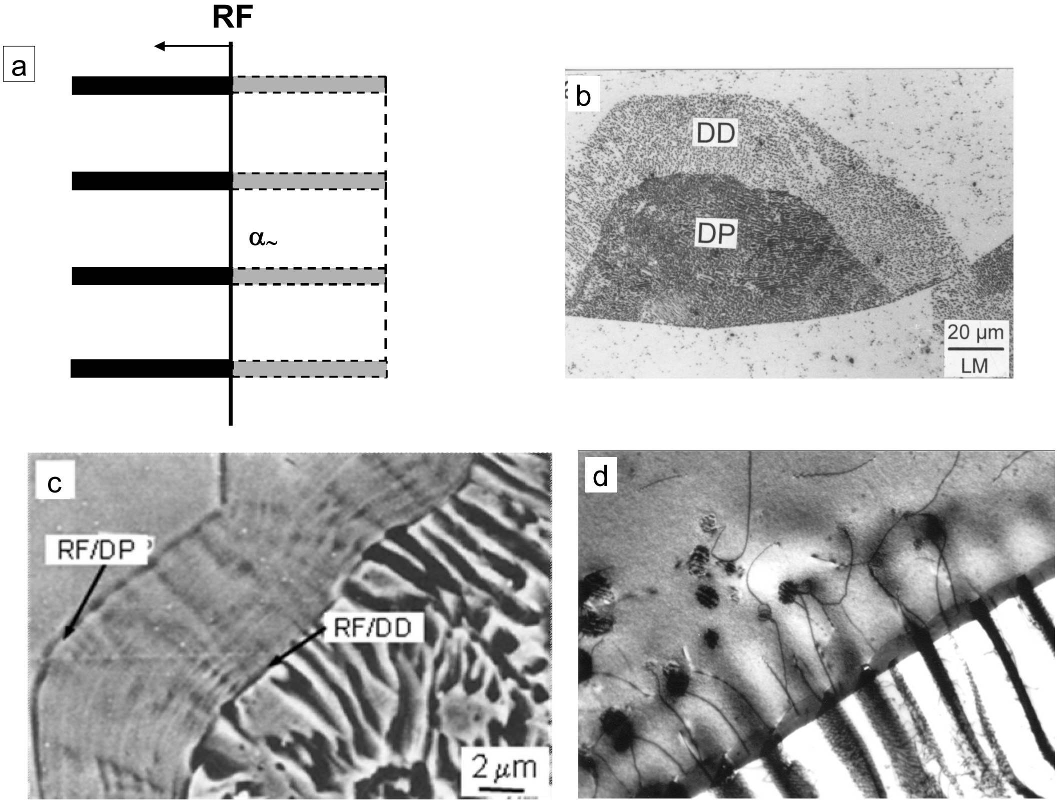

Fig. 3. (a) Schematic representation of discontinuous dissolution. Arrow indicates the direction of reaction front (RF) movement. (b) LM micrograph showing DD reaction in Mg-7.3 at.% Al alloy aged at 498 K and annealed at 625 K for 7 min [15]. (c) SEM micrograph showing DD reaction in Fe-13.5 at.% Zn aged at 723 K and subsequently annealed at 886 K [16]. (d) TEM micrograph showing DD reaction in Al-22 at.% Zn alloy aged at 448 K for 540 s and then annealed at 630 K for 1 s [17].

The diffusion-induced grain boundary migration (DIGM) (see Fig. 4 and 5) reaction is the phenomenon associated with the migration of grain boundary in a pure metal or a solid solution caused by the diffusion of solute atoms into or out of the material along the boundary [18-20]. In a consequence, the region behind the moving boundary is enriched or depleted with solute, which is manifested by so-called an alloyed or de-alloyed zone, respectively.

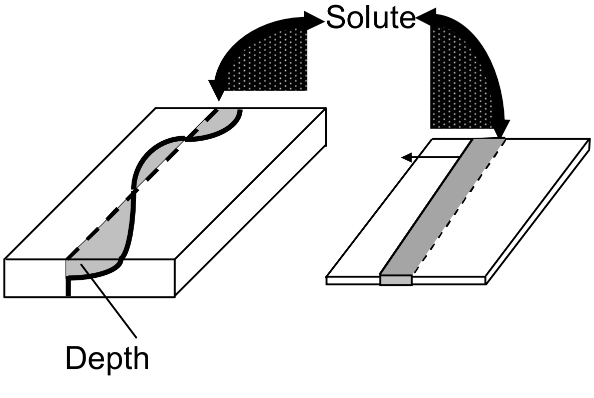

Fig. 4. Schematic representation of diffusion induced grain boundary migration. The direction of grain boundary movement is indicated by arrow. The dashed line shows the original position of grain boundary. The area in grey colour is alloyed or de-alloyed zone.

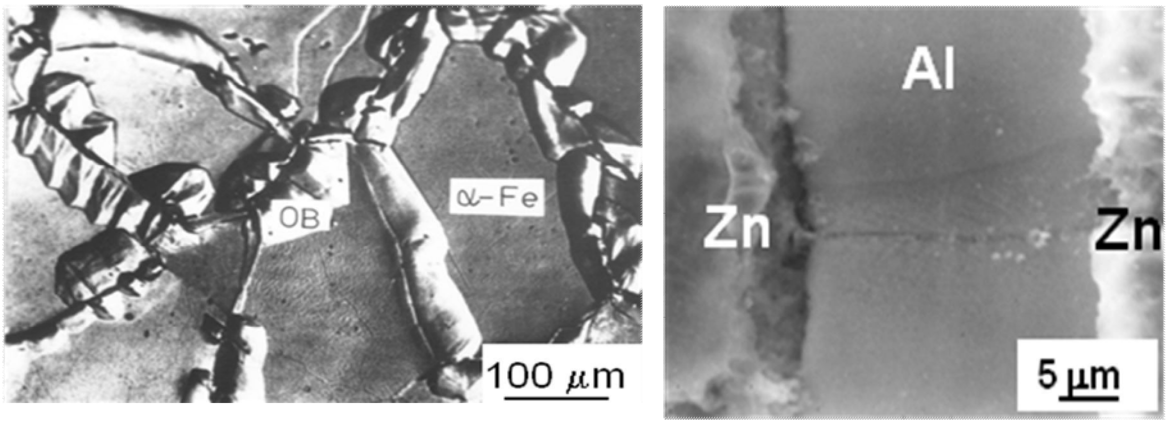

Fig. 5. a) DIGM process in a-iron sample alloyed with zinc from external source for 4 hours at 873 K [18], b) Cross-sectional view of DIGM process in Al sample covered with zinc and annealed at 455 K for 10 days [21].

2. Discontinuous Precipitation

The DP reaction starts at the high angle grain boundaries of alloy. There are two main mechanisms of the β lamella formation. The first mechanism involves the nucleation of lens-shape solute-rich precipitates, then GB bowing between them (Fig. 6a). With time the bowing boundary continues to migrate forming a trail of precipitates, which acts as a sink for the solute atoms along the advancing interface (Fig. 6b).

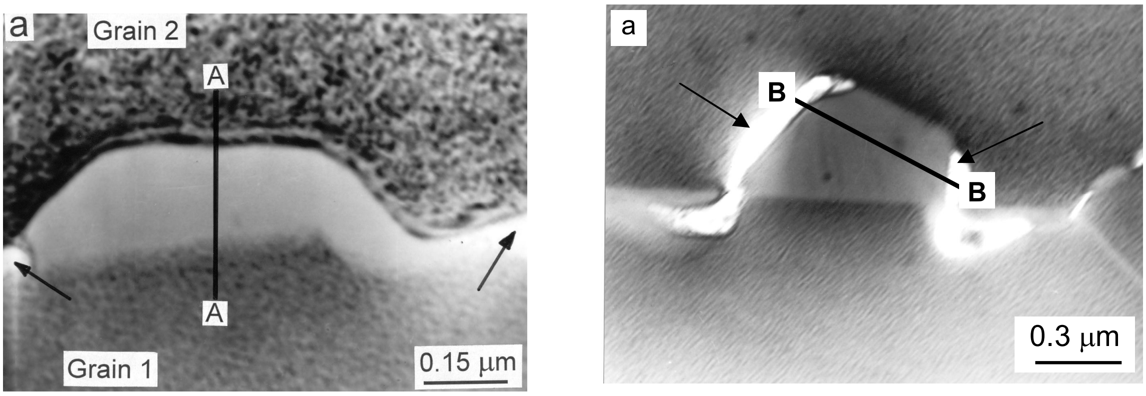

Fig. 6. (a) TEM micrograph of Al-22 at.% Zn aged at 450 K for 1 min (arrows indicate β precursor precipitates), TEM micrograph of Al-22 at.% Zn aged at 450 K for 3 min (arrows indicate β lamellae)

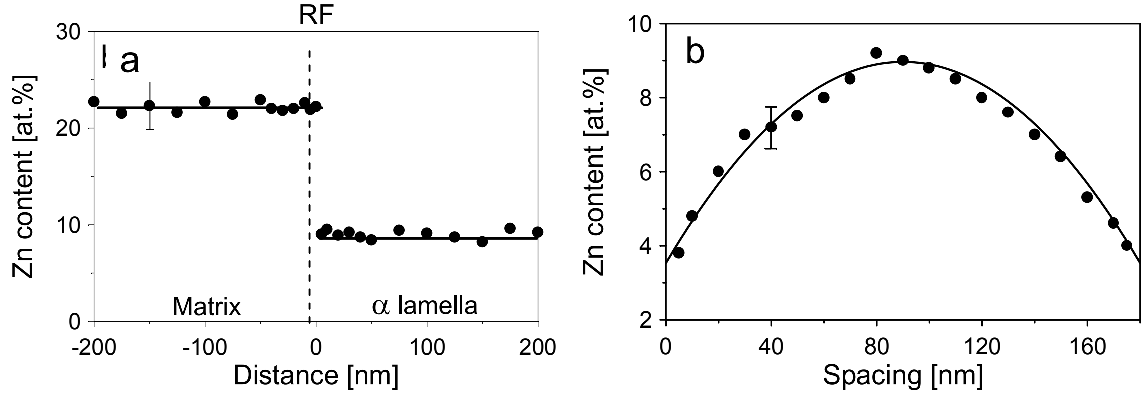

Fig. 7. Zn concentration profiles measured across moving RF (a) and across the a lamella in the Al-22 at.% Zn alloy aged at 450 K for 10 min shown in Fig.

The appearance of parallel alternating lamellae of the α and β phases accounts for the *steady state* morphology of the DP reaction. All the published examples of solute concentration profiles across the reaction front [22-26] confirm that the solute redistribution is limited to a region within 10 nm of the advancing grain boundary (Fig. 7a). On the other hand, a detailed analysis of the solute concentration profiles across the α lamella revealed that all the profiles possess a characteristic reverse „U“ shape (Fig. 7b) with maximum solute content much higher than that predicted by the equilibrium phase diagram [22-25, 27, 28]. The most frequently observed shape was the symmetrical one which is attributed to the so-called *regular type* of growth.

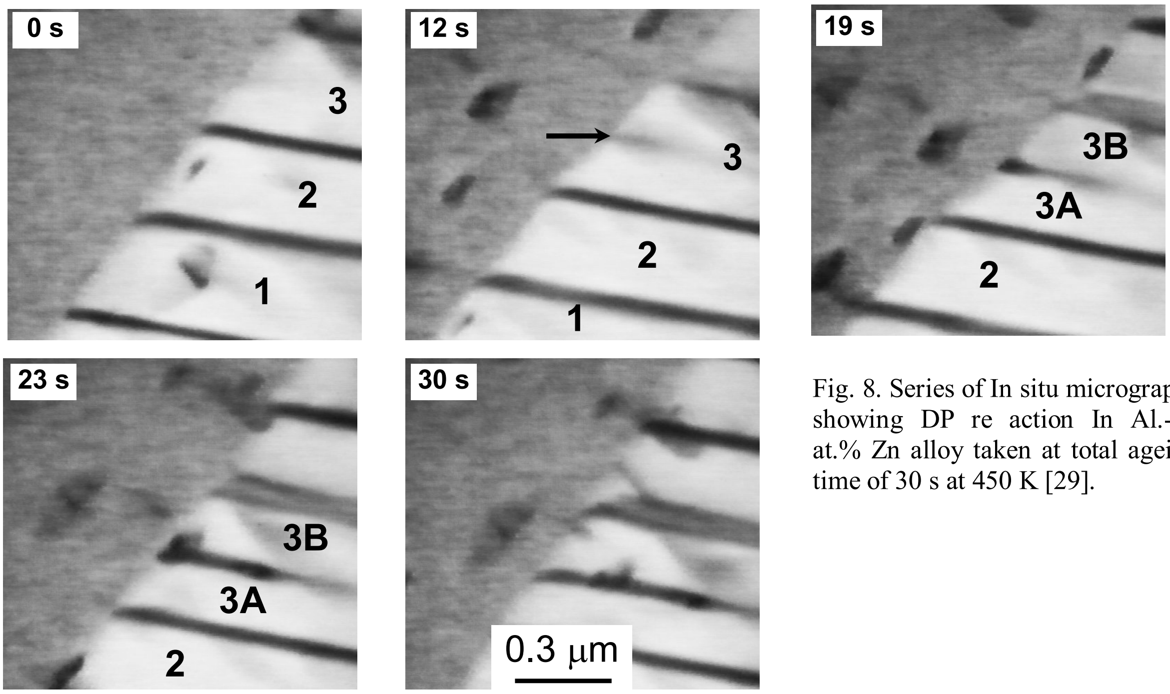

Fig. 8. Series of In situ micrographs showing DP reaction In Al.-22 at.% Zn alloy taken at total ageing time of 30 s at 450 K [29].

The occurrence of the DP reaction is influenced by various instabilities, which results in a so-called *irregular growth*. It seems that the system possesses some intrinsic capability to correct the local reaction front shape to balance the forces acting on it if the perturbation does not exceed a certain critical value. This sensitivity of the system may result in some asymmetry in the solute concentration profile across the α lamellae. If the critical value is exceeded, the asymmetry of the profile becomes larger leading to the well known phenomena of branching or re-nucleation of the β lamellae and a change in the growth direction. This is shown in Fig. 8 in a series of *in situ* micrographs. The thickness of lamella 3 increases beyond a critical value, so that the nucleation of a new β lamella (see arrow) becomes possible. In this way lamella 3 splits into parts 3A and 3B. The process results in a temporary reduction of the growth velocity of lamella 3. However, after a short time the cell front is again even.

The DP reaction is terminated in two cases. The first one is associated with formation of a precipitate-free zone ahead of the reaction front (Fig. 9a). It results from the fact that after a certain period the driving force of the growing front of the DP reaction is not large enough to extract solute atoms from the continuous precipitates in the matrix ahead of the reaction front. However, all the time, the RF will decrease its overall Gibbs energy. Because the average solute concentration in the α lamella is still much higher than the equilibrium value [30], it starts to consume any excess of solute atoms by backward migration until the Zn content within the precipitate-free zone is equal to the equilibrium value (Fig. 9b).

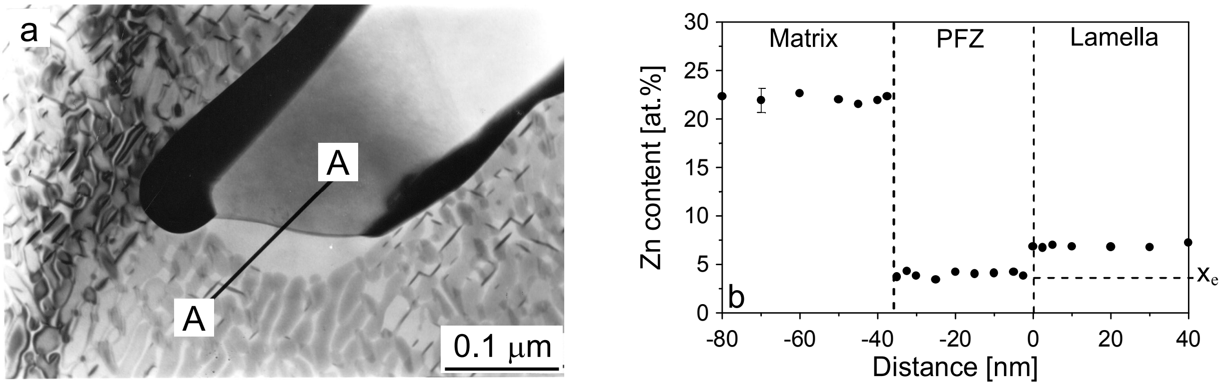

Fig. 9. (a) TEM micrograph of Al-22 at.% Zn aged at 450 K for 15 min. Formation of a precipitate-free zone (PFZ) preceding the stoppage of the DP reaction. (b) Corresponding EDX analysis made along the solid line in Fig. 9a.

The second case occurs after longer period of ageing due to impingement of the colonies growing from different parts of the original grain (Fig. 10), and the cell growth is stopped.

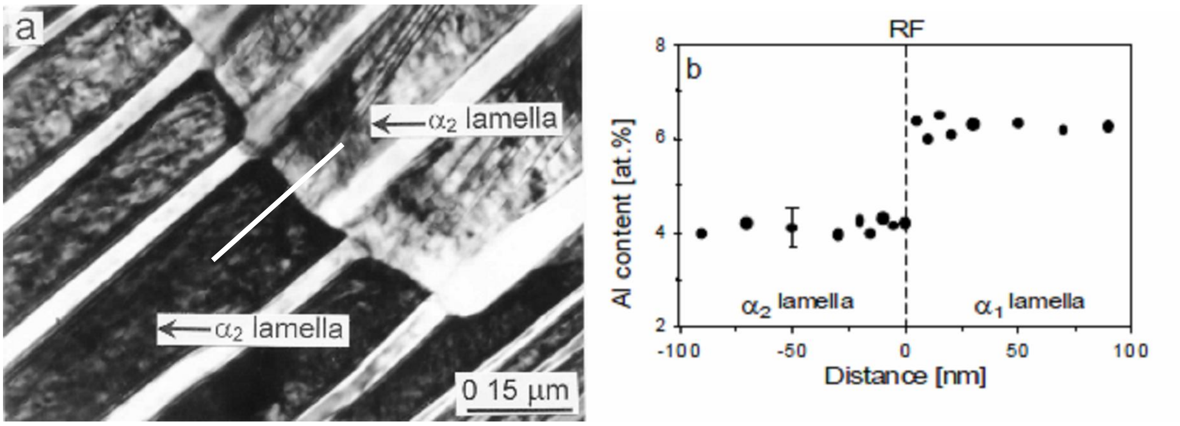

Fig. 10. (a) TEM micrograph of the impingement of two areas of cells in Co-13 at.% Al aged for 2 h at 800 K followed by 20 min at 950 K. (b) Corresponding EDX analysis made along solid line in Fig. 10a.

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