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INTERFACE MIGRATION UNDER CHEMICAL INEQUILIBRIUM

8.1 GENERAL PHENOMENA

When a polycrystalline solid becomes chemically unstable at high temperatures, equilibration reactions occur in a reasonable time span to form a new solid solution in chemical equilibrium. Sometimes the equilibrating reactions do not occur by conventional lattice diffusion but with boundary migration accompanied by boundary diffusion, forming a new solid solution behind the migrating boundaries.³⁶⁻⁴⁰ This phenomenon is referred to as ‘Diffusion-Induced Grain-boundary Migration (DIGM)’ or ‘Chemically Induced Grain-boundary Migration (CIGM)’. When a liquid film migrates in a solid–liquid two-phase system with a liquid film between grains, the phenomenon is called ‘Diffusion-Induced (or Chemically Induced) Liquid Film Migration’ or, simply, ‘Liquid Film Migration (LFM)’. For both grain boundary and liquid film migration the term ‘Diffusion-Induced (or Chemically Induced) Interface Migration (DIIM or CIIM)’ is used. DIIM has been observed in a number of systems,⁴¹⁻⁵⁴ but is most common in systems with substitutional solute elements. Recently, however, a change in defect concentration has also been found to induce interface migration.^{52,53} Figure 8.1 is a typical microstructure of DIGM showing the position of grain boundaries before and after the migration. The original position of the migrating boundaries is revealed by a thermal etching before the migration.

DIIM is observed mostly when solute elements diffuse into or from the polycrystal and where the grain boundary or liquid film provides a rapid path for material transport. The interface migrates when the solutes go into or out of the bulk grain by lattice diffusion. In general, the interface area increases with interface migration. The interface migration occurs therefore when the driving force for DIIM is larger than the energy increase caused by the reduction in the radius of curvature of the migrating interface. Unlike the

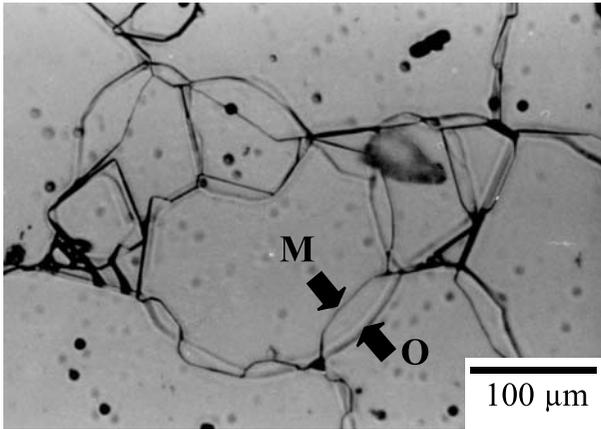


Figure 8.1. Diffusion-induced grain boundary migration in Al_2O_3 . A sintered Al_2O_3 polycrystal annealed at 1600°C for 2 h in Fe_2O_3 vapour-containing air. Arrows with 'O' and 'M', respectively, indicate positions of grain boundaries before and after annealing.

conventionally considered solid solution formation by lattice diffusion and the consequent symmetric distribution of solutes across the interface, DIIM involves the formation of a new solid solution with an asymmetric distribution of solute atoms by interface migration and lattice diffusion at the interface.

Figure 8.2 schematically shows the solute concentration profile across the moving boundary during DIIM caused by solute addition. The chemical potential of the solute in the migrated region is essentially the same as that at the boundary. The solute concentration in front of the moving boundary in the receding grain decreases drastically from the surface of the grain. A solution of macroscopic diffusion equations for a boundary migrating at velocity v_b shows that a solute diffusion zone of thickness of about D_l/v_b exists in front of the migrating boundary.⁵⁵ The thin diffusion layer formed at the surface of the grain in shrinkage is coherent with the bulk. On the other hand, when the thickness of the migration layer is greater than a critical value, the migration layer becomes incoherent with the growing grain forming misfit dislocations, as shown in an example in Figure 8.3.⁵⁶ The transition from coherency to incoherency of the migration layer is similar to that of the precipitates in a precipitation process.

8.2 DRIVING FORCE OF DIFFUSION-INDUCED INTERFACE MIGRATION (DIIM)

After the observation of DIGM and LFM in the 1970s,^{41–43} several models and mechanisms were proposed for the driving force of the phenomena.^{36–38} Among them, the coherency strain model of Hillert⁵⁷ is now widely supported by some critical experiments of Yoon and others.^{45,46,50–53}

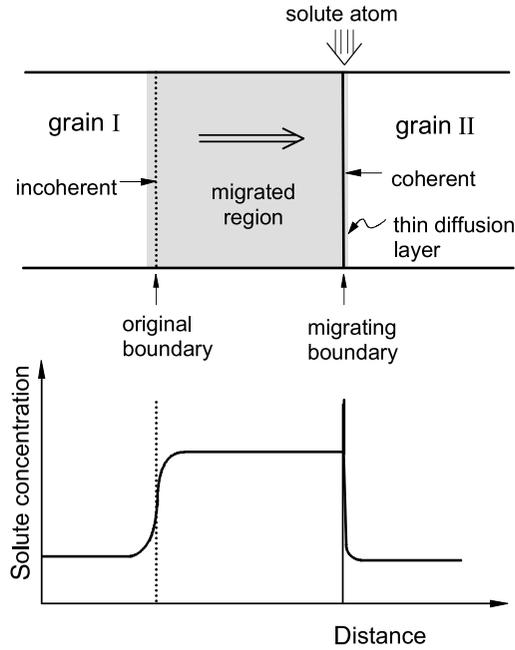


Figure 8.2. Schematic profile of solute concentration during diffusion-induced interface migration.

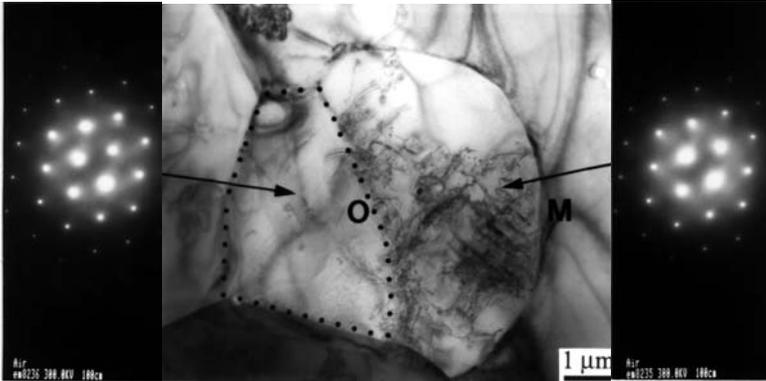


Figure 8.3. TEM micrograph showing misfit dislocations formed in a DIGM region in a $99\text{Al}_2\text{O}_3\text{-1Fe}_2\text{O}_3(\text{wt}\%)$ sample sintered at 1600°C in $95\text{N}_2\text{-5H}_2$ and then annealed at 1500°C in air. 'O' and 'M', respectively, indicate positions of grain boundaries before and after DIGM.⁵⁶ The diffraction patterns are from the original grain (left) and from the migrated region (right) with a $[0001]$ axis.

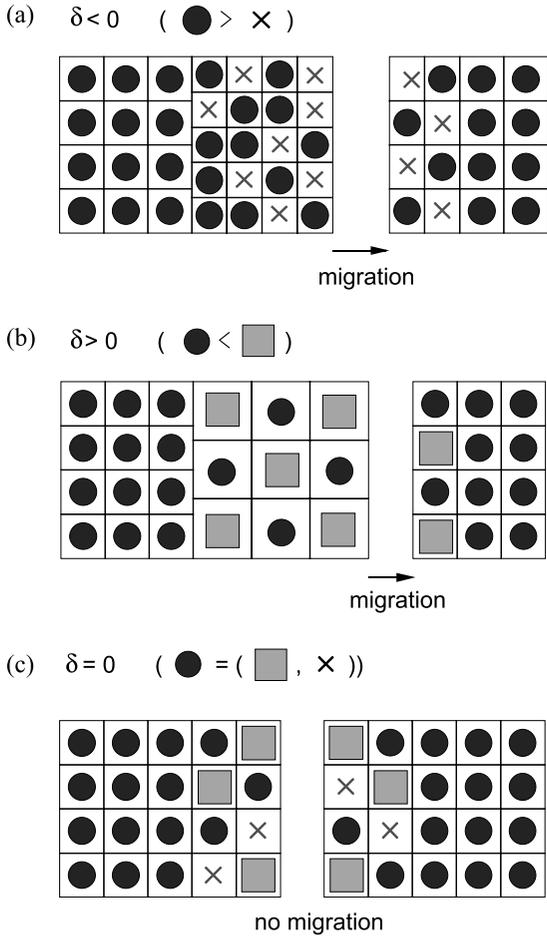


Figure 8.4. Coherency strain induced by diffusion of smaller (\times) or larger (\square) solute atoms than the host atoms (\bullet): (a) $\delta < 0$, (b) $\delta > 0$ and (c) $\delta = 0$.

Figure 8.4 shows schematically the coherency strain induced in a diffusional layer of solute atoms which are either smaller or larger than the solvent atoms. When the solute atoms move along the grain boundary (or a liquid film) and diffuse into the grains, a thin diffusional layer whose lattice parameter is different to that of the parent grain forms at the surface of the grain. If the layer is thin enough, it will be coherent with the parent grain, and a coherency strain energy is stored in the layer. The coherency strain energy E_c is expressed as

$$E_c = Y\varepsilon^2 \tag{8.1}$$

where Y is the coefficient of coherency strain energy and ε the coherency strain.^{58,59} For cubic systems, ε is isotropic irrespective of the solute element because solute atoms are dilational centres; however, it is, in general, anisotropic for non-cubic systems. On the other hand, Y varies with crystallographic orientation even in cubic systems because it is a combination of elastic stiffnesses. Therefore, the coherency strain energies stored in thin diffusional layers on the surfaces of two adjacent grains are initially different to each other for all crystal systems. Yoon *et al.*³⁹ suggested that the direction of DIIM is from the grain with low strain energy to that with high strain energy. Some investigations⁶⁰⁻⁶³ using single- and bi-crystals support this suggestion of DIIM direction.

As shown in Figures 8.4(a) and 8.4(b), coherency strain energy is stored in the thin diffusional layer when the solute atom is either smaller (Figure 8.4(a)) or larger (Figure 8.4(b)) than the host atom. However, when two kinds of solutes whose sizes are smaller and larger, respectively, are added at the same time, the lattice parameter of the new solid solution can become equal to that of the parent phase (lattice matching) at a specific addition ratio of the two solute species (Figure 8.4(c)). In this case, no strain energy is stored in the diffusion layer and therefore no DIIM is expected to occur. The formation of a new solid solution occurs only by lattice diffusion and its rate is a few orders of magnitude smaller than that found for DIIM. The idea of lattice matching was experimentally confirmed in the Mo-Ni-Co-Sn system, as shown in Figure 8.5.⁴⁵ This experimental result demonstrates, in turn, that the driving

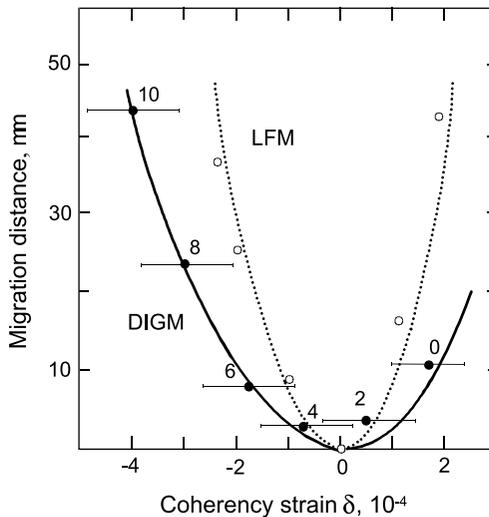


Figure 8.5. Observed variation of the average migration distance for DIGM and LFM with estimated δ in Mo-Ni specimens heat treated at 1460°C for 2 h after embedding in Mo-Ni-Co-Sn liquids of varying Co/Sn ratio.⁴⁵

force for DIIM is not the chemical free energy of mixing but the coherency strain energy stored in a thin diffusional layer. Such an experimental demonstration has also been made in some ceramic systems.^{50,51,53}

The strain energy in a diffusional layer can also vary with external pressure in the case of DIGM.⁶⁴ When an external pressure is applied to a sample, the boundary parallel to the pressure is in compression while that perpendicular to it is in tension. Therefore, if a pressure is applied to a sample where the DIGM is the result of compressive coherency strain energy, the compressive strain energy in the coherent layer parallel to the applied pressure is higher than that present without applied pressure while the compressive strain energy in the layer perpendicular to the applied pressure is lower. The result of these strain energy changes is a faster and slower migration of the boundaries parallel and perpendicular, respectively, to the compression direction.⁶⁴ Such a dependency of DIGM on external pressure also supports the view that the coherency strain energy is the driving force for DIIM.

8.3 QUANTITATIVE ANALYSIS OF DIIM

When the lattice parameters of two different phases, either bulk or thin layer on a bulk material, are different and their interface coherent, an elastic deformation of the two phases is inevitable and therefore coherency strain energy is produced. Such a coherency problem at the interface is a factor in many metallurgical and ceramic processes, such as precipitation, spinodal decomposition, thin film growth, heat treatment and interface migration. The coherency strain energy varies with crystallographic orientation, following Eq. (8.1). Cahn⁵⁸ and Hilliard⁵⁹ independently derived equations of the coherency strain energy in isotropic and cubic systems. However, a general equation of coherency strain energy applicable to any crystal system can be obtained through the transformation strain problem treated by Eshelby.⁶⁵ Hay⁶⁶ and Lee and Kang⁶⁷ have also derived general equations which can be applicable to all crystal systems. All three equations give the same result and any one of them can be used to calculate the coherency strain energy.

In the case of DIIM the coherency strain energy stored in a thin diffusional coherent layer is expressed as⁶⁷

$$E_c = \frac{1}{2} [C_{ijkl}\varepsilon_{kl}\varepsilon_{ij} - (\sigma_{1'1'}\varepsilon_{1'1'} + 2\sigma_{1'3'}\varepsilon_{1'3'} + 2\sigma_{1'2'}\varepsilon_{1'2'})] \quad (8.2)$$

Here C_{ijkl} is the elastic stiffness of the diffusion layer, ε_{ij} the elastic strain due to the formation of a new solid solution, and $\sigma_{i'j'}$ and $\varepsilon_{i'j'}$, respectively, the stress and strain relaxed in the direction perpendicular to the surface of the diffusion layer.

Figure 8.6⁶² shows the calculated coherency strain energy map (CSEM) of rhombohedral Al_2O_3 with Fe_2O_3 as a solute from Eq. (8.2). In this figure the maximum coherency strain energy appears on the (0001) C plane in terms of the

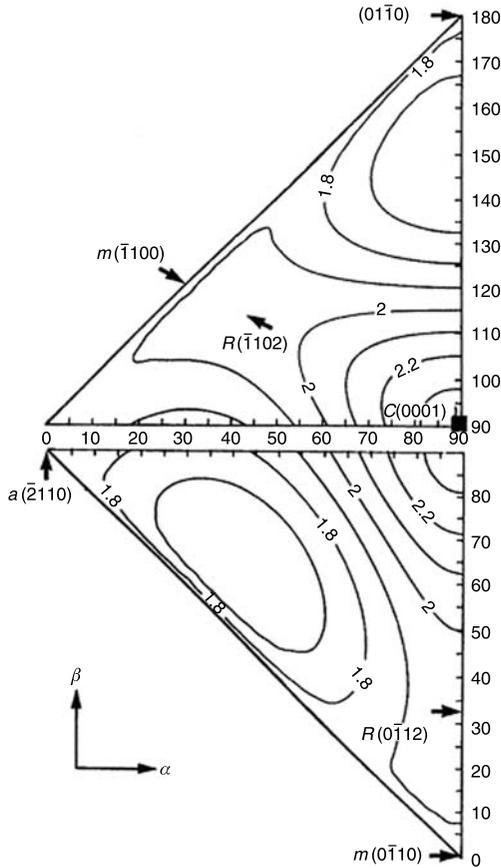


Figure 8.6. Coherent strain energy map (in MJ/m^3) of $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3(\text{Fe}_2\text{O}_3)$ for an Fe_2O_3 concentration of 5 mol% (with $\varepsilon_c/\varepsilon_a$ of 0.94) in a coherent diffusion zone.⁶² The axes represent the interplanar angles between the surface normal of the considered plane and those of an $a(-2110)$ plane (α) and an $m(0\bar{1}10)$ plane (β).

hexagonal coordination system and the minimum on the $(01\bar{1}2)_q$ plane. A series of experimental investigations^{61–63} using various single crystals and polycrystals have shown that the direction of DIIM was from the crystal with low E_c to that with high E_c , consistent with predictions based on the calculated CSEMs. When the difference in E_c between two crystals was not appreciable, a zigzag migration of the boundary was observed. This result may imply that in the case of inappreciable difference in E_c , local arrangement and diffusion of atoms can affect the migration direction. The change in curvature with local migration may also play a role in determining the migrating boundary shape.

The measured and estimated coherency strains in DIGM were in the range between 10^{-3} and 10^{-5} for metals as well as ceramics. However, since the

stiffness of ceramics is, in general, higher than that of metals, ceramics usually have higher coherency strain energy than metals. The variation in boundary velocity with solute concentration can be predicted by estimating the coherency strain energy provided that the boundary mobility is known. However, the boundary mobility is usually not a constant but varies with boundary orientation and type (faceted or rough).^{1,12-15,68,69} (See Section 9.2.1.) A recent investigation⁷⁰ showed that DIGM was suppressed in BaTiO₃ by a structural transition from rough to faceted. This result can be attributed to the considerable reduction of boundary mobility by the structural transition. Comparing LFM and DIGM, the velocity of LFM is higher than that of DIGM under the same driving force.^{45,52,71} This result may suggest that the mobility of a liquid film is higher than that of a grain boundary. The measured boundary velocity is dependent on the system, coherency strain, temperature, etc., but it is usually in the range between 1 $\mu\text{m/h}$ and 10 $\mu\text{m/h}$.

When the thickness of the front diffusion zone given by D_l/v_b increases to such a large value that coherency cannot be maintained, the diffusion layer becomes incoherent with the bulk (coherency breaking). For a cubic lattice the coherency strain at breaking $|\varepsilon_o|$ is expressed as⁴⁷

$$|\varepsilon_o| = \frac{bv_{bc}}{4\pi(1+\nu)D_l} \left(\ln \frac{D_l}{bv_{bc}} + 1 \right) \quad (8.3)$$

where ν is Poisson's ratio, b Burgers vector, and v_{bc} the critical boundary velocity for coherency breaking. When coherency breaking occurs, the boundary does not migrate any more and new solid solution forms only by lattice diffusion from the grain boundary into the bulk grains. This process is a few orders of magnitude slower than solution formation by boundary migration. As can be seen in Eq. (8.3), the occurrence or otherwise of coherency breaking is determined not only by lattice diffusivity but also by migration velocity which is in turn determined by coherency strain energy and boundary mobility.

8.4 MICROSTRUCTURAL CHARACTERISTICS OF DIIM AND ITS APPLICATION

In polycrystals, DIGM occurs either unidirectionally or in a corrugated manner and results in a variation in microstructure, as shown in Figures 8.1 and 8.7. During migration faceting of some boundaries sometimes appears (Figures 8.1 and 8.7(a)); the boundary faceting is related to a marked anisotropy of the boundary velocity in the shrinking grain.⁴⁹ (The observed parallelism in faceted boundaries (A to a, B to b(b'), C to c(c')) of a shrinking grain G in Figure 8.7(a) can be another experimental support for the coherency strain energy being the dominant driving force for DIGM.⁴⁹) Migration reversal is also observed, which is attributed to the coherency breaking of the

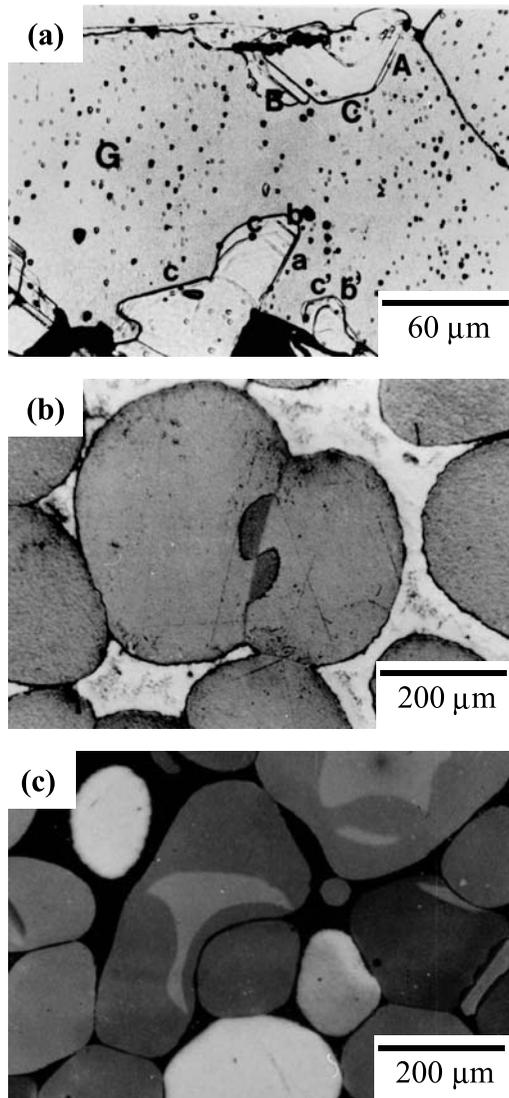


Figure 8.7. Various microstructures observed after DIIM: (a) faceted grain boundaries ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$),⁴⁹ (b) zigzag migration in Mo-Ni,⁷² and (c) migration reversal of liquid films in Mo-Ni.⁷³

front diffusion layer. In this case the boundary is at its original position but the regions of the new solid solution already formed remain within the grains, as in Figure 8.7(c).

When the difference in concentration between the parent phase and a new solid solution is high, diffusion-induced recrystallization (DIR—also called

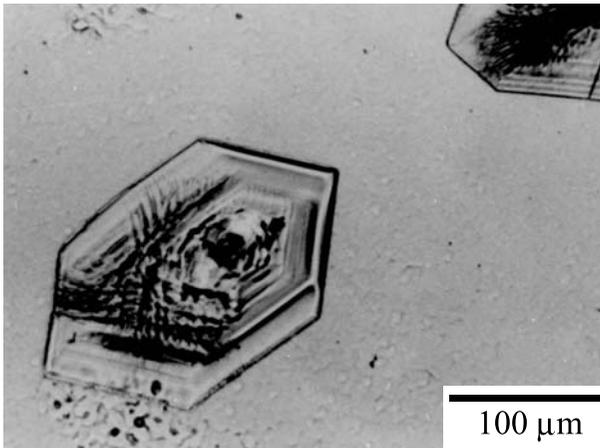


Figure 8.8. Diffusion-induced recrystallization in an Al_2O_3 single crystal by Fe_2O_3 .⁸⁰ The hexagonal grain is a recrystallized grain on an (0001) Al_2O_3 single crystal. Another recrystallized grain is also seen at the upper right corner of the figure.

chemically induced recrystallization (CIR)) can occur,^{48,49,74–80} as shown in Figure 8.8. Several mechanisms have been proposed for the recrystallization under chemical inequilibrium.^{74–77} In some recent investigations on TiC ⁷⁸ and Al_2O_3 ,^{79,80} it was revealed that DIR occurs through a process similar to the recrystallization of plastically deformed materials involving the formation of many dislocations within a new solid solution, polygonization and formation of new grain boundaries. The growth of recrystallized grains, however, was observed to occur by DIGM.⁸⁰

DIGM sometimes can promote grain growth or abnormal grain growth in polycrystals.^{54,70,81} Recently, Lee *et al.*⁵⁴ showed that grain growth was enhanced by DIGM under a local inhomogeneity in chemical composition. In this case the driving force for grain growth was suggested to be the sum of the coherency strain energy for DIGM and the capillary energy due to the grain boundary curvature of the grains. Figure 8.9 shows the estimated coherency strain energy and capillary energy as a function of the radius of grain boundary curvature in BaTiO_3 (PbTiO_3). The figure suggests that coherency energy dominates unless the radius of grain boundary curvature is smaller than a few tenths of a micron. Since the curvature radius is larger than the grain radius, the grain size must be smaller than the curvature value for the capillary energy to become comparable to the coherency strain energy.

During the sintering of mixed powder compacts, alloying and sintering proceed simultaneously. Since the usual sintering temperatures of materials are much lower than their melting temperatures, alloying of elemental powders can be achieved by DIGM rather than by lattice diffusion. The alloying is then much faster than expected even for coarse powders. When a liquid phase is

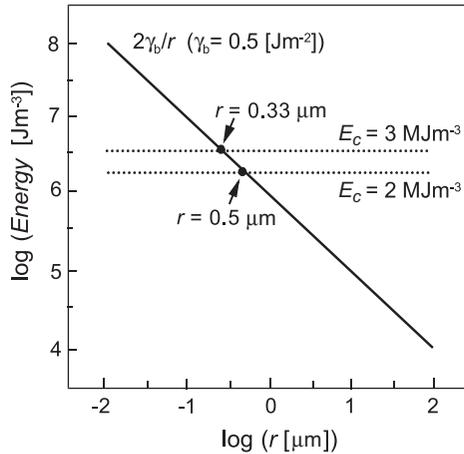


Figure 8.9. Comparison between capillary energy ($2\gamma_b/r$, r : the average radius of grain boundary curvature) and calculated coherency strain energies stored in a $(\text{Ba}_{0.8}\text{Pb}_{0.2})\text{TiO}_3$ layer on BaTiO_3 . Specific grain boundary energy is assumed to be 0.5 J/m^2 .⁵⁴

present, sometimes the alloying results in fast formation of a core/shell structure.⁸² The results of Lee *et al.*⁵⁴ suggest that the growth of solid particles can occur extensively by DIGM at the early stage of sintering, which suppresses densification. It also suggests that any chemical inhomogeneity has to be minimized in order to prevent extensive grain growth and hence improve sinterability of mixed powder compacts.

The effect of DIIM on physical properties is expected to be considerable because DIIM can drastically change the microstructure. Some recent investigations show considerable effects of DIIM on mechanical and dielectric properties in Al_2O_3 ,⁵⁶ $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$,⁸³ and SrTiO_3 -based⁸⁴ materials. In the case of $\text{Al}_2\text{O}_3(\text{Fe}_2\text{O}_3)$,⁵⁶ DIGM at the surface region which resulted in the formation of many misfit dislocations in the migration layer and the corrugation of grain boundaries changed the fracture mode of the surface region from intergranular to transgranular and considerably improved the cyclic properties. Unlike the case of alumina, suppression of DIGM and LFM remarkably improved the dielectric properties of SrTiO_3 -based boundary layer capacitors,^{52,84,85} which consist of oxidized layers between conductive SrTiO_3 grains. The improvement of dielectric properties was due to the minimization of the thickness of the oxidized dielectric layer through suppression of the migration according to the scheme shown in Figure 8.4(c). These two examples of migration enhancement and suppression for improving mechanical and dielectric properties may be typical ones. At this stage, however, investigations on the effect of DIIM on physical properties are very limited and it would be useful to study the effect of DIIM in other systems.