Preface

Grain boundaries and interfaces are generally diffusion short circuits; consequently, the major part of material transport will occur by grain-boundary/interface diffusion in nanomaterials where a large amount of atoms can lie on grain or interphase boundaries (about 50% for d=5 nm and 20% for d=10 nm; d is the grain size). The development of nanolayered materials and bulk nano-materials, prepared e.g. by compaction of nanocrystalline powders, by severe plastic deformation or by deposition of thin films and multilayers, is now raising the question of how the overall mass transport changes as the microstructural scale (at least in one direction) is reduced to nanometre dimensions.

In the first chapter of this book (by Suzuki and Mishin) our present knowledge on the grain boundary (GB) diffusion mechanisms is summarized. Besides enlightening the background of the well known semi-empirical relation (the ratio of the activation energies for GB and bulk diffusion is about 0.5) and the relation between the GB structure (energy) and diffusivity, the authors present interesting new results on the possible mechanisms and on the role of internal stresses. It was obtained from atomistic computer simulations that vacancies and interstitials are equally important even for GB self-diffusion and that large internal stresses and stress-gradients exist in GB, resulting in unusual behaviour of point defects and in a multiplicity of diffusion mechanisms. These statements are challenges for future experiments.

It is well known from classical treatments of grain- or interface diffusion that there are three different grain-boundary diffusion regimes: type A, B and C. In type C regime the diffusion takes place only along the grain- boundaries, in B regime there is also diffusion into the bulk and in type A regime the bulk diffusion fields are overlapping.

In type A regime a significant enhancement of intermixing or solid state reactions is observed, with a high effective interdiffusion coefficient (e.g. in surface alloying). In the contribution by Belova and Murch it is shown that for the estimation of this effective diffusivity the generally accepted Hart equation should be replaced by the Maxwell equation (known from the random resistor network problem) on nanoscale (in order to avoid an overestimation by about 50%). It was also found from Monte Carlo simulations that the usual condition for type A regime (the diffusion length, λ, should be much larger than d) is too stringent and the transition occurs at λ=0.2d.

In many cases the diffusion process will take part dominantly along grain- or phase boundaries (close to type C regime) leading to phenomena such as degradation of multilayers by grain-boundary grooving, pinhole formation and coarsening (see also the contribution by Bobeth et al.), or solid state phase transformations in thin films. Although it is easy to show that the B regime would not be realized in a nanocrystalline material (because with decreasing d below about 10 nm, the “pure B regime” can not be reached: one will be either in C or A regime, depending on the annealing time, t) if only one single value of the GB diffusivity, D_{gb}, would exist in the system. However, it is well-known already from GB diffusion measurements in microcrystalline materials, that the presence of different type of GB’s is manifested in the presence of a wide distribution of D_{gb}. In nanomaterials it can happen that dominantly two different types of grain or interphase boundaries exist with characteristically different D_{gb} values. Already in this simple (bimodal structural) limit a variety of the possible cases can be treated ((C-C, B-B, AB-B, A-B sub-regimes as compared to the classical division for A, B and C regimes) and investigated experimentally (see the contributions by Divinski et al. and by Bokstein et al.).

In hetero-GB diffusion experiments by radiotracers (i.e. when the tracer is different from the matrix atoms) segregation coefficients describing the matching conditions between the diffusion source and the grain-boundary (as well as between the grain-boundary and the free surface, if there is a terminal free surface present in the experiment) should be also taken into account. Thus segregation effects are important in the evaluation of the diffusion kinetics or profiles. In two contributions (Bernardin et al., Divinski et al.) these aspects are treated and experimental results, obtained in the last five-six years summarized.
Another interesting question has been raised during the interpretation of the already existing data on grain-boundary diffusion in nanocrystalline materials: Whether the grain-boundary diffusion coefficients measured in these alloys are identical to those obtained in microcrystalline state or not? We will see that there is an increasing number of experimental evidences that the above diffusion coefficients agree very well with each other, i.e. in most of the cases the structure of relaxed grain-boundaries in nanocrystalline and polycrystalline samples is very similar. Nevertheless in some cases the diffusion coefficients and thus the nature of GB seems to depend on the technique applied for the synthesis of the material more than on the grain size. This can be caused either by non-relaxed structures of the boundaries and/or by contamination effects (Bernardini et al. and Bokstein et al.).

Diffusion in nanostructures presents challenging features even if the role of structural defects (dislocations, phase- or grain-boundaries) can be neglected. This can be the case for diffusion in amorphous materials or in epitaxial, highly ideal thin films or multilayers where diffusion along short circuits can be ignored and “only” principal difficulties, related to nanoscale effects, raise (see chapters by Beke et al., Thomas et al. and Bobeth et al.). For example, for diffusion in such crystalline materials, one of the most important differences – as compared to diffusion along long distances (orders of magnitude longer than the atomic spacing, \(a\)) – is that the continuum approach can not be automatically applied. Another important feature is the gradient energy correction to the driving force for diffusion. This correction becomes important if large changes in the concentration take place along distances comparable with \(a\), and results in an additional term in the atomic flux, proportional to higher derivatives of the concentration. The role of the composition dependence of the diffusion coefficient is crucial: for strong dependence the above non-linear effects are stronger leading to surprising effects such as linear shift of a sharp interface or sharpening of an originally diffuse interface even in ideal systems (Beke et al.) on nanoscale.

Further difficulty can be related to the role of (either diffusion-induced or built-in) stresses. In many treatments of diffusion (at least in metallic systems) it is supposed that the relaxation of diffusion-induced stresses, proportional to stress free strains created by the differences in atomic volumes and intrinsic diffusion coefficients, is fast and complete (see e.g. Darken’s treatment of interdiffusion). However, for short diffusion distances, the time of relaxation of stresses can be longer than the time of diffusion. Thus feedback effects of stresses can become important, and cannot be ignored anymore (Beke et al., Bernardini et al., Bokstein et al. and Thomas et al.). Furthermore, owing to the very short length of the internal interfaces large stress gradients can exist along the them, and this can explain the large differences in \(D_{gb}\) values obtained in different thin film systems under different stress states (Bokstein et al.).

Thermal stability and the quality of interfaces in bi- and multilayered materials is very crucial: in most of their applications (e.g., X-ray mirrors, GMR systems etc.) the stability and the sharpness of the interfaces is a basic requirements (see chapters by Thomas et al. and by Bobeth et al.). Stress effects and dynamic segregation (leading to formation of two different – abrupt and diffuse - type interfaces even in a binary A/B type multiplayer) are typical examples related to such a nanometre fabrication of functional materials (Thomas et al.). Understanding of different destratification mechanisms of coherent multilayers is similarly important (Bobeth et al.) especially in improvements of nano-products for magnetoelectronics.

I am convinced that this book offers a good contemporary overview of nanodiffusion and successfully covers the present status of this rapidly growing field. New, basic aspects of the diffusion processes on nanoscale are treated, and many useful considerations and results on diffusion kinetics in different types of technologically important nanomaterials are presented.

Debrecen, January 2004

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