Introduction

Grain boundary (GB) diffusion is a particularly important and interesting topic from the viewpoints of technology and basic understanding of diffusion processes in solids. It plays a crucial role in different processes such as sintering, creep, grain growth, or solid state reactions, all of them affecting the properties of a polycrystalline material. GB diffusion is crucial, for example, for corrosion in metals and transport properties of oxides. That is why this phenomenon attracts great attention, leading to a huge number of experimental and (still increasing number of) theoretical works on this subject. Recently, very interesting experimental techniques, like secondary ion mass spectroscopy (SIMS) [Sou04] and Auger electron spectroscopy [WanJ04], were improved in order to understand the diffusion phenomenon on the nanoscale. Simultaneously, the capabilities of theoretical computational methods as well as the performance of modern computers have increased drastically [Nak98]. Both theoretical and experimental approaches help each other in understanding GB diffusion. While the theoretical methods like *ab initio* methods [Liu02] help us to understand the interactions between the diffusing atoms and GBs, it is the phenomenological approach which serves as a bridge between the atomistic methods and the experiment, on the one hand, and

explains physical processes on the basis of macroparameters, on the other hand. The phenomenological (continuum) equations (typically differential equations) are used in the experimental evaluations to provide a desired physical quantity. For GB diffusion, this is, of course, the GB diffusivity (D_{gb}). A very actual question is what happens with diffusion, if the sample reduces in size. Owing to the importance of the problem, the number of phenomenological studies on nanocrystalline materials is steadily increasing. Despite this fact, D_{gb} for nanocrystalline materials is mostly obtained by using the methods suggested several decades ago. The aim of the present phenomenological studies is to analyze „size effects“ caused by the increasing volume fraction of GBs in nanocrystalline materials, to estimate possible errors arising with the application of conventional models to find D_{gb}, and to suggest new methods, if possible.

The first chapter of the present dissertation is devoted to the phenomenological theory for describing GB diffusion. The main ideas and equations comprising the actual phenomenological theory of GB diffusion [Kau95] are considered. The kinetics of GB diffusion is explained on the basis of three main diffusion regimes: type-A, -B and -C as proposed by Harrison [Harr61]. Also a new classification proposed by Mishin [Mis95] is mentioned as far as the small grain sizes are concerned. The main equations which are used to deduce D_{gb} from the measured diffusion profiles in one of the diffusion regimes are discussed as well. The derivation of Fisher's system is given and the important assumptions stemming from this derivation are emphasized. Moreover, Le Claire's equation [Cla63] serving as the main tool for deducing D_{gb} for the measured concentration gradient in the B-regime is discussed in detail. Hart's equation [Hart57], being the more popular equation that allows one to find D_{gb} from the diffusion profile measured under conditions of the type-A kinetics, is also taken account of. The segregation modifications of this equation [Mor60] as well as of Maxwell-Garnett's equation [Kal02] are addressed too.

Chapter two deals with the application of finite element method (FEM) for numerical integration of the diffusion equations for cases where analytical solutions cannot be obtained. In the present study two such cases are met, namely by simulating realistic polycrystalline microstructures and blocking space charge effects. Particularly, the derivation of the equations used in the finite element program is explicitly explained for the problem of GB diffusion. Since the finite element program FLUX-EXPERT [Flu00] is used in the present study, its main structure is discussed in the second chapter.

In the third chapter, the main effects which lead to significant errors of deducing D_{gb} from the diffusion profile measured at extremely short diffusion lengths are discussed in

detail. For this case the diffusion profiles were calculated by using Whipple's solution [Whi54] with varying diffusion times (t) in the range $2 \cdot 10^3 - 10^6$ seconds for different ratios of diffusivities (Δ) between the GB (D_{gb}) and the bulk (grain) (D_g). Consequently, the results of the second chapter correspond to diffusion in the B-regime. It is important to note that the parameter $\beta = [(\Delta-1)\delta]/[2\sqrt{D_g t}]$ was allowed to vary over the orders of magnitude from several thousands to tens (here δ is the GB thickness). The errors in finding D_{gb} by using Le Claire's relation were estimated. The relation itself is discussed rigorously under different conditions, and the reasons of arising errors are explained. New equations for deducing the ratio Δ are suggested on the basis of calculated diffusion profiles. Namely, the equation is proposed to calculate properly the derivative $\partial \ln C_{av}/\partial w^{6/5}$ depending on the diffusion time, which was suggested by Le Claire [Cla63] to be treated as a constant (here w is the dimensionless coordinate). Additionally, a criterion was found deciding on whether the new method is to be preferred or Le Claire's method is still sufficient, based on the knowledge of dimensionless parameter $\alpha = \delta/(2\sqrt{D_g t})$. The main suggestion to improve D_{gb} determination proposed in this study is based on plotting the derivative of the diffusion profile, i.e. $\partial \ln C_{av}/\partial y^{6/5}$, as a function of $y^{6/5}$ (y is the coordinate along the diffusion direction) and to analyze it. The derivative is characterized by the maximum which always gives the correct D_{gb}. The analytical dependences are suggested for the positions of this maximum as well as its value. Additionally, the numerical problems of integrating the Whipple solution used in an integral form [Whi54] are discussed.

How realistic microstructures can be simulated by using FEM is discussed in the fourth chapter. The important issue is the accuracy of finite element calculations with emphasis on the diffusion problems. With respect to the accuracy, mesh of integration and influence of boundaries of geometrical models proposed in this chapter are especially considered. Another parameter considered is the time increment used in the transient kinetics problems. This parameter determines the overall result, if extremely short diffusion times are concerned. A special procedure for simulating GB diffusion at short diffusion times using FEM is proposed. Several microstructures are discussed and different angles between a particular GB of the microstructure to the diffusion direction were probed. The results obtained for these microstructures are compared with those obtained for two main models of polycrystalline materials, i.e. the model of parallel boundaries and the model of square grains. It is shown that the model of square grains is a quite reasonable approximation, if the number of parallel and perpendicular paths is comparable. The area fractions of GBs were varied and the impact on the diffusion profile analyzed. Not only short but also long diffusion times were

studied, i.e. the A-regime of GB diffusion was simulated too. Since the problems of using Hart's equation [Hart57] for increasing GB volume fractions have already been discussed by Belova and Murch [Bel03], in the present study emphasis is laid on the diffusion accompanied with impurity segregation. Both Hart's equation and Maxwell-Garnett's equation (in its improved form suggested by Kalnin *et al.* for the segregation problems [Kal02]) are compared by varying the segregation coefficient from unity to several hundreds. Specifically, the Hart equation gives large errors in D_{gb} due to the linear dependence of the effective diffusivity (which is the only quantity measurable in the A-regime) on the segregation coefficient. For the segregation coefficient only Henry's [Cab91] law is considered.

The conventional GB diffusion models, starting out from Fisher's model [Fis51], completely ignore the existence of space charge regions in ionic solids. However, the role of the space charge effects has already been discussed in many contributions [Mai95]. Recently, it was shown experimentally that the depletion space charge layers (SCLs) can significantly alter the diffusion profile [Sou05], [WanR05]. In this case improved models are necessary. In the fifth chapter the significance of space charge effects is discussed with a focus on the depletion layers [Gou02]. A mathematical model was obtained which takes into account analogous approximations for the GBs as Fisher proposed [Fis51]. The main difference is related to the incorporation of a third diffusivity in order to simulate the space charge effects. Consequently, the mathematical description comprises three differential equations which are needed to simulate space charge effects. Again, FEM is used here to numerically integrate the diffusion equations. Errors in obtaining D_{gb} by means of conventional models (both the Le Claire equation and the Hart equation) were estimated. The calculated diffusion profiles and their properties are discussed. It is shown how the apparent GB diffusivity ($D_{gb,app}$) can be estimated by using new expressions, discussed in the third chapter. However, the use of those is possible in the B-regime only. The diffusion profiles were simulated under conditions of type-A kinetics for the models of parallel boundaries and square grains too. The diffusion times needed to exclude the space charge effects strongly depend on the ratio $\Lambda = D_g/D_{scl}$, where D_{scl} is the diffusion coefficient used in the SCL. This ratio was varied here from 0.1 to 10^3. In the fifth chapter some numerical problems which can arise when simulating diffusion with blocking SCLs are considered. This is done to demonstrate the accuracy of obtained results and give important hints for future studies.

Lastly, the main results are summarized in Conclusions. In this part the procedures to improve D_{gb} determination are also explained.