Chapter 3
Approaches to Study Grain Boundary Segregation

3.1 Basic Definitions and Terminology

As was shown in Chap. 2, grain boundaries are characterised by increased Gibbs energy (grain boundary energy, $\sigma$) comparing to the bulk crystal. The system containing grain boundaries will tend to reduce this energy in many ways. One group of them is interaction of the grain boundaries with other crystal defects. If the interaction of the grain boundaries with the point defects – foreign atoms – results in reduction of $\sigma$, an accumulation of foreign atoms at the grain boundary can occur. This thermodynamically preferred process then leads to segregation of alloying or impurity elements at the grain boundary. Under the term grain boundary segregation, we will understand here all changes of concentration of any element at a grain boundary in the form of a solid solution [13]. Let us mention that the limit of solute solubility in the basic material may be different for grain boundaries and for the bulk [105]: It can allow formation of few solute atom layers at a grain boundary that is still considered as a single phase. If secondary phase particles (precipitates) are situated at grain boundaries, we will speak about grain boundary precipitation. In fact, grain boundary precipitation is a continuation of the process of interfacial enrichment started by the grain boundary segregation when new particles appear at the interface due to supersaturation of the above-mentioned grain boundary solid solution [106].

According to the nature of the forces causing grain boundary segregation, we can distinguish two basic types of this phenomenon (a) equilibrium and (b) non-equilibrium grain boundary segregation. The term equilibrium grain boundary segregation will be used here to denote the very local redistribution of solutes at grain boundaries caused by minimisation of the total Gibbs energy of the system that is quite analogous to the adsorption phenomena well-known in surface science. It is supposed that the chemical potentials of all species involved in solid solution are constant throughout the system. At equilibrium, there is a partitioning that results in enrichment of grain boundaries by the surface-active species. The levels of the enrichment are defined only by the system parameters at equilibrium and not by the history of the material. The chemical enrichment at any interface can be reproduced simply by re-establishing the identical physicochemical conditions.
The nature of the non-equilibrium grain boundary segregation consists in interaction of solute atoms with the excess of vacancies in the system. A solute concentration is thus built up around the boundary because of dragging the vacancy–solute pairs when the vacancies flow to the grain boundaries in order to preserve their thermal equilibrium value. This phenomenon may occur in consequence of certain metallurgical operations such as quenching and irradiation. In contrast to the equilibrium segregation, non-equilibrium segregation may extend up to the distances of several μm across grain boundaries. This effect is sensitive to the rate of cooling from a high temperature [13, 18] and is briefly presented in Chap. 6.

Grain boundary segregation and precipitation represent only particular examples of different chemical composition of interfaces. At heterophase boundaries such as oxide/metal interfaces, the chemical differences are driven by chemical reactions at the contact plane between metal and oxide components (i.e. between oxygen or metal atomic layers) and can also alter according to their crystallography [20, 107]. Similar differences occur at the interfaces between metals on the one hand, and superconductors or semiconductors on the other hand, or at the grain boundaries of various chemical compounds, for example polymers [20, 108]. Such changes of chemical composition will not be treated here.

There are two basic approaches to study chemical composition of grain boundaries: experimental measurement and theoretical simulation. In the following, we will briefly address the main methods of both these approaches.

### 3.2 Experimental Methods for Study of Grain Boundary Segregation

Grain boundary segregation has been detected in the last century by various methods starting from indirect and mostly qualitative approaches. At first, the effort has been made to detect the suspected contaminants at the grain boundaries, which gave rise to various metallurgical effects. These techniques covered such measurements as electrode potential on grain boundary fracture surfaces, variations in X-ray lattice parameter with varied grain size, internal friction, micro-hardness, spectrographic analysis of material extracted from the grain boundary region, autoradiography and deductions made from anomalous grain growth behaviour and from subtle metallographic features observed at the grain boundaries [13, 21]. Although these measurements provided us with numerous interesting results, the main drawback of them is principal impossibility to determine the nature and concentration of the segregated element. However, this knowledge is fundamental for understanding the role of grain boundary chemistry in changes of a property. It is also hardly applicable to ternary and more complex systems, where the effects of individual elements may overlap. The importance of indirect methods has been superseded in the last decades with the development of a range of sophisticated direct techniques of surface analysis based upon various electron and ion emission processes. In these methods, the segregated elements are qualitatively and quantitatively detected from an appropriate spectrum.