

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, σ) 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 σ , 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.

There are some specific features characterising the grain boundary (a) the grain boundary is buried in the sample and (b) the changes of the chemical composition joined with the segregation phenomena are confined in a very thin layer of one or few atomic layers along the interface. Therefore, that technique must be suitable for the study of interfacial chemistry that enables the direct approach to the interface and the localisation of the analysis with atomic resolution in one dimension at least.

The necessary requirements to experimental techniques to study grain boundary segregation following from the above characteristics of grain boundary segregation were identified by Hondros [109] more than 30 years ago as

- (a) High spatial resolution
- (b) Elemental identification without a priori knowledge of segregating element(s)
- (c) Quantitative measurement
- (d) Non-exposure of a grain boundary by fracture in order to study weakly embrittling as well as non-embrittling species
- (e) Determination of chemical bonding

Unfortunately, not all techniques used to study grain boundary segregation fulfil all these requirements. Principally, we can distinguish two groups of methods used for direct study of grain boundary segregation (a) surface analysis techniques and (b) microscopic techniques [13].

3.2.1 Surface Analysis Techniques

As the name of this class of techniques suggests, the methods under consideration have been mainly developed to study chemistry of free surfaces. Similarly to grain boundaries, many features of surface chemistry are confined in a monatomic surface layer. In contrast to buried grain boundaries, however, free surfaces are better accessible to analytical tools. The surface analysis techniques can only be applied to the grain boundaries revealed by brittle intergranular fracture. Indeed, the above requirement (d) of Hondros [109] is not fulfilled and such methods can be applied exclusively on segregation-embrittled systems. Since the fresh fracture surface may be very often – and mainly in case of metals – quickly covered by a layer of environmental oxygen and/or carbon (for example in fractions of seconds under normal pressure in case of iron-based materials), the measurements of untouched grain boundary chemistry have to be performed in high vacuum.

There are two main techniques, Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS), that have frequently been used to study grain boundary segregation and each of which provides little bit different information. Both these techniques operate in ultra-high vacuum (UHV) of the order of 10^{-8} Pa or better. To study grain boundary chemistry, these facilities have to have a possibility to expose the interfaces by fracture in the UHV of the instrument using a suitable fracture stage. If the segregated element embrittles the grain boundary, this fracture may be achieved fairly readily either at room temperature or by cooling the

sample to liquid nitrogen temperatures. In the absence of intrinsic embrittlement, the grain boundary in some materials may be open by impact after cathodic charging the solid with hydrogen to promote hydrogen embrittlement [110]. Unlike the studies of free surfaces, new sample must be prepared for each measurement of the grain boundary state characterised by the heat-treatment time and the temperature. The relative ease of studying free surfaces explains the extent of effort devoted to free surfaces compared with that to grain boundaries [13].

The fact that the grain boundary has to be open by intergranular brittle fracture thus limits the experimental studies to the systems of embrittled grain boundaries. From experimental point of view, it evokes an additional requirement to the experimental techniques of surface analysis – an ultimate lateral resolution of imaging the area to be analysed. The fracture process can introduce various subtle defects to the structure that also appear at the fracture surface to be measured. Such defects affect substantially the measurements of grain boundary chemistry, and thus, suitable area should be chosen for the analysis that is free of any defect [111, 112]. To be absolutely fair and get well-interpretable results, extended experiments should be performed on bicrystals ensuring the identical grain boundary is measured under different conditions. Using polycrystalline samples, different grain boundaries are measured in different samples without taking into account the anisotropy of grain boundary segregation [113].

3.2.1.1 Auger Electron Spectroscopy

The analysis of the intergranular fracture surface in UHV is usually undertaken with the most powerful and popular technique, AES [114]. A focused electron beam of energy of 1–30 keV is used in this technique to excite the atoms of an appropriate area of the target, creating holes in their inner core energy levels. The atoms subsequently decay by emission of either characteristic X-ray (which is the basis of bulk chemical analysis) or by emission of characteristic Auger electron from a thin surface layer: If the initial core hole is created in the orbital w (Fig. 3.1), that is then filled by a higher energy electron from the orbital x , the energy balance is taken by the electron of the orbital y . This electron is ejected from the atom with the energy E_{wxy} and is known as Auger electron. E_{wxy} is characteristic of the particular atom and in this case is given by [115, 116]

$$E_{wxy} = E_w(Z) - E_x(Z') - E_y(Z') + \Phi_S, \quad (3.1)$$

where E_w is the binding energy of ionised level w , E_x and E_y are the energies of the interacting outer levels x and y , $Z' \approx Z \pm 1/2$ corrects for the doubly ionised state and Φ_S is the analyser work function. As it is apparent from (3.1), the Auger transition covers three different electrons; therefore, the elements having less electrons (hydrogen and helium) do not exhibit this transition and, thus, cannot principally be analysed by this technique [117].

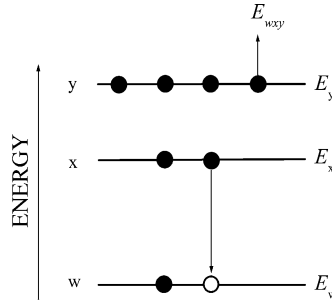


Fig. 3.1 Schematic transition level diagram for electrons in AES

Although many transitions may occur in the volume irradiated by electrons, only few of them are strong enough for each element and these enable the surface atoms to be clearly identified from the emitted electron energy spectrum. Auger electrons ejected by atoms from the depths greater than few atomic layers (1 nm and more) are swallowed up in material and, thus, do not contribute to the emitted line spectrum. In this way, AES is characteristic for the outermost atomic layers of a solid, and by focusing the electron beam, for example via field emission gun (FEG), we may now localise the composition of the grain boundary fracture surfaces with a resolution that currently approaches less than 10 nm and the energy resolution 0.05% [118, 119]. Elements except for H and He as explained above, are generally detected with sensitivities ranging between 0.1 and 1 at.% depending on the nature of the element and the matrix [116, 120]. These concentrations are well reached in case of the grain boundary segregation.

Since its first metallurgical application to explain the origin of the fatal disaster of the Hinkley Point Power Station in the 1970s by Kalderon [121], a large progress has been achieved in both the instrumentation and the quantification of AES in upcoming decades [122]. Based on the inspiration evoked by the above example, AES was mainly used to study grain boundary segregation of impurity elements in iron and ferritic steels in connection to their temper embrittlement [123, 124]. Besides steels, AES studies also provided important results on equilibrium segregation of impurities at grain boundaries in nickel-based superalloys (e.g. [125, 126]), intermetallics (e.g. [127, 128]) and other materials (e.g. copper [105, 129] and molybdenum [130]). Besides the polycrystalline materials providing us with typical “faceted” fracture surfaces (Fig. 3.2), fine measurements on bicrystalline samples have been performed (Fig. 3.3) directed to study the anisotropic segregation phenomena (e.g. [94, 135]). During the time, AES became the most frequently applied technique for studies of grain boundary segregation. Precise quantification of obtained data is made using the standards as well as by means of standardless methods [109–111]. An interesting attempt to determine the grain boundary chemistry without breaking the samples was done using scanning Auger electron spectroscopy (SAES) in case of nickel interfaces decorated by chlorine, sulphur and oxygen [136]. More details on application of AES in grain boundary segregation are given in specialised works [114, 117, 122].

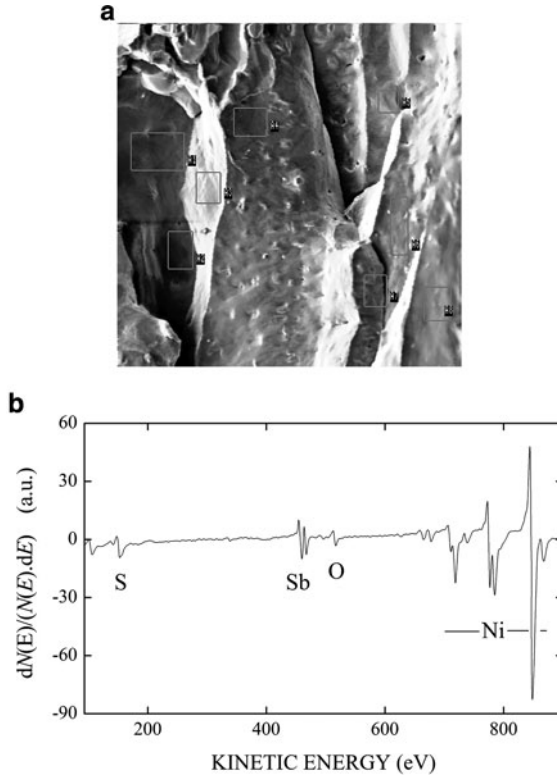


Fig. 3.2 Example of the AES analysis. (a) intergranular fracture surface, (0.4×0.4 mm) (b) AES spectrum of one of the facet. Polycrystalline Ni-0.5at.%Sb alloy showing an extended grain boundary segregation of sulphur and antimony [131]

The thickness of the segregated layer can be determined by AES monitoring of the fracture surface during its slow peeling by in situ ion sputtering. In this way, a composition depth profile may be obtained for all elements present [137]. The results of such ion sputtering made by Seah showed that the segregated atoms are concentrated in the outermost plane of the fracture surface and hence, in the grain boundary plane [138]. The present state of the method also enables to detect fine variations in the content of segregated elements at different parts of both matching fracture surfaces of a bicrystal, that are connected with an asymmetry of the fracture process on the atomic scale [139].

3.2.1.2 Secondary Ion Mass Spectroscopy

SIMS is a well-known technique for highly sensitive elemental analysis. It consists of the layer-by-layer peeling of the surface during its bombardment with primary

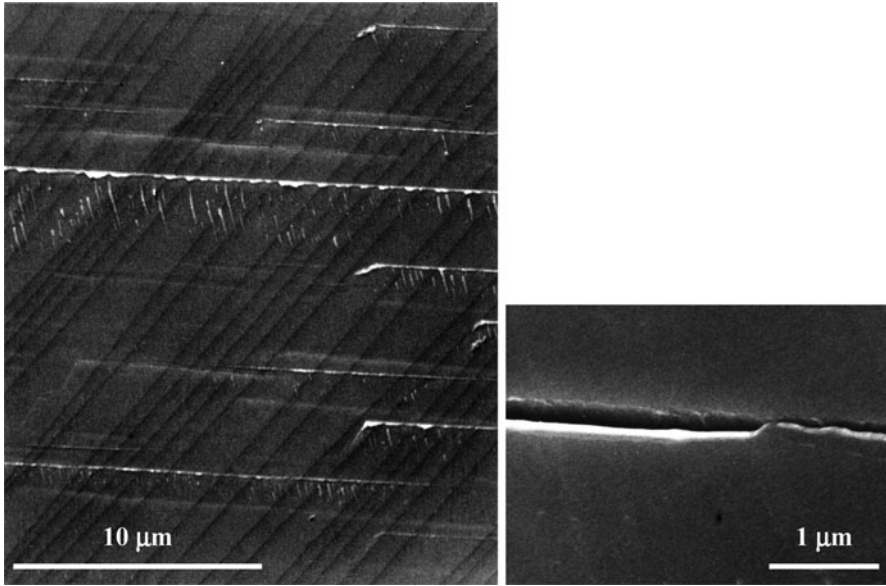


Fig. 3.3 Grain boundary fracture surface of a bicrystal of an Fe–3.5at.%Si alloy. Individual defects introduced by the fracture process are apparent (cleavage tongues (see side detail), mechanical twins, deformation bands) [132–134]

ion beam, usually argon, with energy in the range 1–3 keV and current of units of nA/cm². During interaction of primary ions with the atoms of the target, a fraction of the ion energy is transferred to the lattice atoms. Atomic collisions thereby result in emission of secondary ions from the lattice. The secondary ions characterising the composition of the studied surface are then analysed in a mass spectroscope [140–143], usually of the time-of-flight type. Complex atom groupings of 20 or more atoms represent bonding arrangements at a surface [144] and so, in principle, the interactions of co-segregated elements can be studied. Low primary beam current yields very low sputtering rates that enable to analyse monatomic layers by this technique that can be so considered as *static* [142]. As a technique of surface analysis, it needs an intergranular fracturing of the sample before analysis. SIMS has some advantages over AES in (a) detecting hydrogen [145], (b) being more elemental sensitive than AES (up to ppb range) and (c) providing information about the chemical structure of the surface [143]. Due to many atoms grouping in complex ions, SIMS spectra may be complicated and quantification needs standards. On the other hand, information about the molecules present in the samples can be obtained that is important mainly in case of organic materials. In addition, ion focussing is not so sharp as that of electrons in AES and the measured area is also much larger (about 100 nm [47, 146] although recent development of the instruments approaches to a resolution of about 20–50 nm [147]) so that the finding of an area for analysis that was not damaged during the fracture process may be complicated.

Therefore, SIMS has not yet become popular as a technique to study grain boundary segregation. Despite it, SIMS was used to detect grain boundary segregation of hydrogen in niobium [148] or of boron in 316L austenitic stainless steel [149], 718 cast superalloy [150] and nickel [151]. For another example, yttrium segregation in monatomic layer at alumina grain boundaries was found with relatively uniform lateral homogeneity [152] and silicon, aluminium, sodium, calcium, iron and potassium segregation was detected in yttria-stabilised zirconia [153]. SIMS high-resolution mapping enabled to detect segregation of magnesium at grain boundaries of Al_2O_3 [154].

3.2.1.3 Other Spectroscopic Techniques

Besides AES and SIMS, the group of AEM covers other techniques such as X-ray photoelectron spectroscopy (XPS, also electron spectroscopy for chemical analysis, ESCA [114]), ion scattering spectroscopy (ISS or low-energy ion scattering, LEIS) [155], Rutherford backscattering spectroscopy (RBS) [156], Mössbauer spectroscopy [157], secondary neutron mass spectroscopy (SNMS) [158], fast atom bombardment – mass spectroscopy (FAB–MS), glow discharge mass spectroscopy (GDMS), glow discharge optical emission spectroscopy (GDOES) [159], proton-induced X-ray emission (PIXE), nuclear reaction analysis (NRA) and extended X-ray absorption fine structure (EXAFS) [160]. These techniques were only rarely used to study grain boundary segregation till now and therefore, no large details of them are given here. Although the techniques like ISS or RBS are able to analyse interfaces buried under the surface, many of the listed methods possess the common drawback of AEM techniques – the necessity to open the interface by intergranular brittle fracture. In comparison with AES and SIMS, in addition, they exhibit larger analysed area or lower depth sensitivity: These facts discriminate them for the present application to study grain boundary segregation. However, some of them may be improved in future to such an extent that they will be able to compete to the standard techniques of AES or SIMS [161].

ESCA is based on the photoelectric effect: A beam of X-rays with energy E_X striking the sample surface under high vacuum induces emission of photoelectrons (core electrons) of kinetic energy E_k and their escape from thin (2–10 monolayers) surface layer. The energy of these electrons can be used for analysis, and the characteristic binding energy

$$E_b = E_X - E_k - \Phi_s \quad (3.2)$$

is obtained. Similarly to AES, hydrogen and helium cannot be detected in this method. Present lateral resolution of ESCA is better than $3\ \mu\text{m}$ and energy resolution is about 0.28 eV (with a monochromator). Currently, available computers can significantly improve the technological limits of the available instruments [119]. In connection with synchrotron radiation, the ultimate lateral resolution of 150 nm can be reached. The method enables to perform multi-element qualitative and

quantitative analysis of surfaces and the depth distribution of segregated elements. The substantial advantage of this method is its ability to provide chemical bonding of the surface atoms and identification of their oxidation states [160]. ESCA was used to study grain boundary segregation of bismuth in copper [162, 163], of manganese, sulphur, antimony [164, 165] and phosphorus [166] in ferritic steels or of sulphur in nickel [167]. It was proved by this technique that phosphorus and tin segregate at grain boundaries of ferritic steels in their elemental states [168]. Recently, ESCA was applied to study grain boundary segregation of lead at grain boundaries of ancient silver coins, which causes a large embrittlement of these archaeological artefacts of the Roman age [169, 170].

A group of techniques is based on the ion scattering. In these techniques, a beam of ions of well-defined mass and energy is directed to a target (sample). The energy distribution of the particles scattered from the surface (or subsurface) layers in a specific direction with respect to that of the primary beam is measured to deduce information about the composition and atomic arrangement of solid surfaces [171]. The most used methods in this group are ISS and RBS.

In ISS, a well collimated mono-energetic (0.1–5 keV) primary ion beam of noble gases (He^+ , Ne^+), alkali metals (Li^+ , Na^+ , K^+) or other light elements (B^+ , N^+ , O^+ , F^+) of energy E_0 impinges on the surface. The ISS signal originates – similarly to AES – from the topmost layers only. The ions are scattered in collision from the target nuclei and their energy, E , defined by the mass of the surface target atom,

$$\frac{E}{E_0} = \frac{m^2}{(m + M)^2} \left[\cos \zeta + \left(\frac{M^2}{m^2} - \sin^2 \zeta \right)^{1/2} \right]^{1/2}, \quad (3.3)$$

is detected in an analysing spectrometer at a scattering angle ζ . The surface atoms of all elements can be identified from the energy spectra with high surface sensitivity (less than 1 nm) with detection limit ranging from 10^{-1} for light elements to 10^{-4} for heavy ones [171]. Although this method exhibits excellent surface sensitivity, provides simple quantification and is virtually non-destructive, it has only limited application in studies of interfacial composition [156]. The use of this technique can be demonstrated, for example on detection of strong segregation of copper at surfaces of Cu–Ni alloys [172].

In contrast to ISS, in RBS, high-energy light ions (e.g. H^+ , D^+ , He^+ or C^+ ions) accelerated usually by van de Graaff accelerator to energies 0.5–3 MeV, strike the target and penetrate into the sample interior. Some of the ions are back-scattered by the lattice atoms close to the sample surface and the scattering angle is related to the mass of the scattering atom via the ion energy. The detection limits are similar to those of ISS [171]. Unfortunately, the depth resolution of the method is of the order of 25 nm and the signal sensitivity mainly for the elements lighter than the primary ions is rather low although also here, all elements can be detected. The advantage of the low sensitivity to the light elements and the low-depth resolution is that the samples can be fractured on air without the danger of shadowing the information about the surface composition by oxygen or carbon adsorption on the fracture surface

[173]. Due to the low sensitivity and the basic requirements for experimental conditions, however, this method has only rarely been used to study grain boundary segregation. An example is the study of antimony segregation in manganese steel [174, 175].

EXAFS was used in studies of chemistry of Ni–Ti and Co–Ti interfaces [176] and for determination of atomic structural environment of yttrium and zirconium atoms segregated at the grain boundaries of Al_2O_3 [177]. EXAFS data indicate that yttrium and zirconium ions segregated at the grain boundary of an Al_2O_3 alloy, preferentially occupied the sites in the grain boundary core region, which are characterised by a well-defined dopant (Y,Zr)-O nearest neighbour co-ordinations, but the dopant (Y,Zr)-cation next nearest neighbour co-ordination is changing from site to site either within the same boundary or within different boundaries. The dopant (Y,Zr)-oxygen nearest neighbour bond length in the grain boundary, is on average fully relaxed to that in the parent oxides [178].

Combination of emission and transmission modes of Mössbauer Spectroscopy (MS) was used to study the surrounding of the ^{57}Fe isotope that penetrated intergranularly into polycrystalline Fe–23.7at.%Si alloy during annealing at 700°C [157] and to deduce the grain boundary segregation [179]. Although this method is only indirect and rather time consuming, it brought the results that were very well comparable to the AES measurements (Fig. 3.4).

Recently, a very promising technique was proposed to identify individual atoms on sample surfaces on the basis of atomic force microscopy [180].

It was shown that surprisingly, the electron probe microanalysis (EPMA) method, which is basically focussed on characterisation of much thicker surface layers, is – in combination with the wavelength-dispersive X-ray spectroscopy (WDS) technique – also able to provide information about the monolayer segregation at the

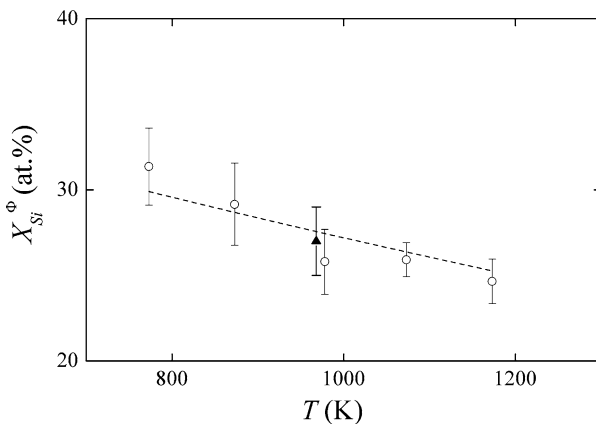


Fig. 3.4 Temperature dependence of silicon grain boundary concentration in polycrystalline Fe–23.7at.%Si alloy. Experimental data were measured by AES (*circles*) and by MS (*solid triangle*). Theoretical curve was calculated according to the model of segregation in ordered alloys [157]

surfaces and interfaces [181, 182]. This technique consists of combination of a SEM microprobe with a number of WDS spectrometers, each of them containing several mobile crystals dispersing the X-rays according to their wavelength following the Bragg's law. The intensity of a particular line is obtained by measurement of diffracted X-ray intensity (measured using the gaseous proportional counters) at the spectral position of the top of the peak and subtracting the background intensity. Since the characteristic peak-to-background ratio of the WDS technique is about tens of ppm, the sensitivity of the method can be very good. The quantification of the data is usually done by means of the StratagemTM [183] software. This technique was applied to study sulphur segregation at grain boundaries of an Fe-42%Ni alloy and documents high preciseness of the technique and its insensitivity to surface contamination [182].

More information on experimental details of individual techniques and their application to measurements of grain boundary chemistry can be found in specialised literature devoted to individual techniques.

3.2.2 Microscopic Techniques

Two microscopic techniques have mainly been used in the study of grain boundary segregation (a) analytical electron microscopy (AEM) and (b) atom-probe field ion microscopy (AP FIM). The crucial advantage of these techniques over the techniques discussed above is that they can provide measurements for grain boundaries without fracture. They, thus, enable another family of systems to be studied.

3.2.2.1 Analytical Electron Microscopy

AEM represents a unique combination of high-resolution imaging of the high-resolution electron microscopy (HRTEM) (or scanning transmission electron microscopy (STEM)) dedicated to providing images with high spatial resolution, with highly localised analytical tools such as energy dispersive X-ray analysis (EDX) [184] or electron-energy loss spectroscopy (EELS) [185, 186]. Here a thin foil of a material (usually thinner than 100 nm) is prepared with the grain boundary perpendicular to the surface. The sample is then imaged in the electron microscope and analysed. In this technique, all requirements on the experimental methods to study grain boundary segregation [109] are fulfilled. The advantage of this technique does not only consist in its ability to analyse layers of segregation but also small precipitates and inclusions on the grain boundary by X-rays and electron diffraction and – in combination with modelling the atomic and electronic structures of grain boundaries – to localise the segregation sites of impurities and their bonding states [187]. On the other hand, however, it has some important disadvantages because it is not able to analyse light elements ($Z < 10$) and the preparation of the samples may be rather difficult and time consuming. In the last decade, the X-ray method was improved to identify quantitatively the crystallographic sites, distribution and types of impurities in many materials. This method using the incident electron beam

orientation dependence of localised atomic characteristic X-ray emission is known as Atom Location CHannelling Enhanced MICROanalysis (ALCHEMI) [188].

The present high-resolution microanalytical STEMs operate at acceleration voltages ranging between 100 and 400 keV. The electron beam can be focussed to the diameter less than 1 nm using FEG [189]. The spatial resolution and the minimum quantity of an analysed element are interrelated: The higher spatial resolution provides a smaller analysed volume, thus, reducing the signal intensity. In addition, the beam coming through the foil is broadened to some extent and the localised information is somehow dissolved, however, this broadening can later be removed by deconvolution methods [47, 190–192]. The segregation at the level of 0.01 monolayer can be identified with an electron beam of the diameter less than 2 nm by EDX [193], for example about 4% of molybdenum and 0.1% of phosphorus were detected at grain boundaries of a low alloy steel [194]. Let us mention that the recent progress in microshaping the samples by focussed ion beam (FIB) opened the possibility to prepare successfully the foils for AEM that enable to determine the chemistry of selected grain boundaries as well as of their triple junctions (Fig. 3.5) [195].

AEM offers an exclusive possibility to study the grain boundary segregation of solutes despite the fact whether they embrittle the matrix or not. It was applied to study the grain boundary segregation of manganese, tin, phosphorus and silicon in ferritic steels [196, 197], of boron in Ni_3Al [198], bismuth in copper [199], titanium in Fe–Ni alloy [200], phosphorus, chromium, nickel and molybdenum in ferritic–martensitic steel (FV448) [201], sulphur in nickel [202], of silicon [200] and iron [203] in aluminium and the depletion of chromium in austenitic stainless steels [204, 205]. As for the non-metallic systems, grain boundary segregation was detected for arsenic in silicon and calcium in MgO [206], and titanium [191] and yttrium [178, 207–209] in Al_2O_3 in this way. In addition, varied copper concentration and depletion of oxygen along the grain boundaries were detected by AEM in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ high-temperature superconductor [210].

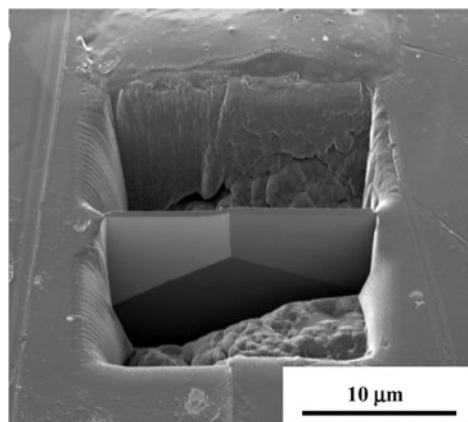


Fig. 3.5 Ion-induced image of the progressing lift-out procedure for preparation of a TEM foil containing a triple junction. Let us notice that the triple junction is located within 5 μm under the sample surface [195]

If the dimensions of the segregated and matrix atoms differ substantially as, for example in case of segregation of bismuth in copper, the positions of large atoms can be identified at the grain boundary by HRTEM in combination with the theoretical study of a segregated boundary without any other analytical method. Using this combination, Luzzi et al. [211–213] described with a great accuracy the structure of the segregated grain boundaries containing multiple atomic sites. The cross-sectional analytical TEM was successfully applied to study the intergranular corrosion and cracking in 316 austenitic steel and nickel-based 600 alloy [214].

3.2.2.2 Atom-Probe Field Ion Microscopy

Another microscopic technique applied to study the grain boundary segregation is AP FIM [215–217]. This method represents a combination of the field ion microscope (FIM) possessing atomic spatial resolution with a mass spectrometer. In FIM, the atoms of an inert gas (helium or neon) at pressure of about $10^{-3} - 10^{-2}$ Pa are ionised in a localised electric field ($4.5-5.0 \times 10^{10} \text{ Vm}^{-1}$) via tunnelling mechanism. Each ion created in this way is then ejected from positively charged surface of the sharp (but round) tip of the needle-like sample in the perpendicular trajectory to its local surface. In this way, the arrangement of individual atoms on the end of the sharp tip is imaged on a screen. The mass spectrometer provides chemical analysis of selected atoms removed from the tip by electric field evaporation, with the single atom sensitivity [216, 218]. In principle, individual atoms in vicinity of a grain boundary or a precipitate/matrix interface may, thus, be analysed and counted. In an alternative variant of the instrument, the atoms of the selected masses may be field-evaporated by ultra-short (10–25 ns) high-voltage ($3-6 \times 10^{10} \text{ Vm}^{-1}$ under high vacuum) pulses of electric field and analysed. In this way, the images of the trace of the grain boundary may be constructed with nearly atomic resolution [216, 218]: The lateral spatial resolution in FIM is of the order of 10^{-1} nm, but the AP FIM analysis is limited to the diameter of the probe hole, typically 1–10 nm with the depth resolution comparable with the interplanar spacing [219].

AP FIM technique meets many advantages – the possibility of observation of the interfaces with atomic resolution, crystallographic information about the interface and quick quantitative and standardless analysis of all elements. On the other hand, there are serious disadvantages that prevent the massive spreading of this method for application to segregation experiments: The procedure of the preparation of the sample in form of a thin needle with the chosen interface located just in the tip is rather complicated, and there is still a danger of mechanical failure of the samples by high-electric field required for pulse-field evaporation [218]. As regards the problems of the sample preparation, the FIB microshaping of the samples promises a large progress in preparing the needles for AP FIM [220].

A large progress of AP FIM was reached recently by its modification as the 3-D tomography (or tomographic atom probe, TAP [221, 222], or 3-D atom probe, 3DAP [223]). In this modification, the finest details of the grain boundary segregation are studied by consecutive field evaporation of individual layers from the tip of

the material. All atoms removed from the needle tip are analysed in the positioned detectors. Using the computer treatment of the obtained data, a 3-D reconstruction of the distribution of segregated atoms in a small volume can be obtained with the resolution better than 0.5 nm [224, 225].

AP FIM was applied to detect the grain boundary segregation of boron in Ni₃Al [216, 226], NiAl [227], 316L austenitic stainless steel [150, 228] and 2.25Cr–1Mo ferritic steel [229], carbon in NiAl [230], silicon in iron [231] and niobium and molybdenum in bcc iron [232]. Enrichment of molybdenum, nitrogen, silicon, boron and iron were measured at the grain boundaries of NiAl base material [233]. Grain boundary segregation of boron and carbon in IN 600 nickel-based superalloy was also shown [186] similarly to titanium, phosphorus and boron in 308 stainless steel [234]. In addition, palladium was detected in modified 4130 steel [235], oxygen in molybdenum [236] and osmium and nickel in tungsten [237]. This method was further applied to detect the Suzuki segregation of niobium and iron at stacking faults of cobalt [238–240] and to measure structural dependence of silicon segregation in bcc iron [241]. Phosphorus segregation in pressure vessel steels was found to be in good agreement with predictions based on McLean model of grain boundary segregation showing that the atom probe technique is a reliable method for characterising the solute segregation to interfaces [242].

Application of 3-D tomography to study the grain boundary segregation is still not yet extended. It was used to describe and quantify niobium and molybdenum segregation at high-angle grain boundaries in bcc iron [243]. These measurements enabled to determine the Gibbs energy of segregation of particular solutes at 800°C on basis of the Langmuir–McLean segregation isotherm (see Chap. 4 for more details). This method also unambiguously proved that the segregation effects are confined in approximately two monolayers along the grain boundary in equilibrium [244]. 3-D tomography was also used to study boron segregation to extended defects (e.g. dislocations) in FeAl base intermetallics [245, 246]. Atom probe tomography has also revealed segregation of zirconium, boron and carbon and depletion of oxygen at the grain boundaries of a Mo–0.15mass%Zr alloy in the base metal and in the heat-affected zone [247]. Recently, bismuth segregation was proved at the grain boundaries of nanocrystalline copper [248] and solute segregation was detected at various defects in irradiated Fe–Ni–P model alloy [249]. Laser-assisted 3-D tomography enabled to detect the segregation of the silicon enriched clusters at the grain boundaries of austenitic matrix of irradiated CW 316 stainless steel and their further enrichment by nickel [250].

3.3 Theoretical Approaches to Study Grain Boundary Segregation

Theoretical approaches to study the grain boundary segregation are principally identical to the simulations of the grain boundary structure and energetics in pure material. The only difference is that one or more foreign atoms are considered in

the studied ensemble. These studies are fundamentally based on the research of the chemical and physical aspects of interatomic forces acting in vicinity of the interface [12]. The reliable methods of calculation of interfacial segregation should be based on two approaches [251]. The first approach – the *quantum mechanical calculations* from *first principles* (ab initio) – is aimed to solution of the Schrödinger equation. However, such calculations are complicated and time consuming. Therefore, suitable approximations and processes such as Hartree–Fock theory or density functional theory are applied. The second approach – the *molecular mechanics* – consists of two subsequent steps. At beginning, suitable interatomic potentials must be developed or applied describing reasonably the atomic bonds in an ensemble of atoms describing expected structure of a bicrystal with chosen grain boundary. The following step consists in calculations of the equilibrium structure. In this way, the energetics of the interface with regard to the location of the atoms of individual components is obtained. The reasonable potentials describing the structure and properties of the material can be developed on basis of ab initio quantum mechanical calculations or by using empirical or semi-empirical potentials describing the properties of the material. In the latter step, computer simulation methods like *molecular* (or *lattice*) *statics* (MS), *molecular dynamics* (MD) or *Monte Carlo* (MC) techniques are usually used. Let us state that the results on grain boundary structure and energetics obtained from atomistic simulations are never totally reliable, because there is generally too large number of degrees of freedom, so that all of them cannot be explored simultaneously [46]. Nevertheless, very good approximations of both the above features can be obtained in this way. Both above-mentioned approaches to the theoretical calculations of grain boundary segregation can also overlap, for example in ab initio molecular dynamics or quantum Monte Carlo method [251].

3.3.1 Quantum Mechanical Methods

Interfacial segregation can be calculated on basis of ab initio or first principles methods of quantum mechanics by accurate approximate solution of the many-electron Schrödinger equation. This is definitely the most precise way to calculate the segregation phenomena, however, time consuming in comparison to the methods based on the use of the potentials described below.

Quantum mechanical methods are based on the solution of time independent electronic Schrödinger equation

$$\hat{H}\Psi = E\Psi \quad (3.4)$$

where Ψ is the wave function and \hat{H} is the non-relativistic Hamiltonian in atomic units,

$$\hat{H} = \frac{1}{2} \sum_i \nabla_i^2 - \sum_i \sum_{\alpha} \frac{Z_{\alpha}}{|r_i - d_{\alpha}|} + \sum_i \sum_{j>1} \frac{1}{|r_i - r_j|} + \sum_{\alpha} \sum_{\beta>\alpha} \frac{Z_{\alpha}Z_{\beta}}{|d_{\beta} - d_{\alpha}|}. \quad (3.5)$$

In (3.5), r_i are the electron positions, d_α are the nuclear positions and Z_α are the nuclear charges. The four terms in (3.5) represent the kinetic energy of the electrons, the electron–nuclear attractions, the electron–electron repulsions and the nuclear–nuclear repulsion, respectively. Due to complexity of the systems, the Schrödinger equation can only be solved approximately by using simple functions instead of the true wave functions.

A very suitable approximation is the *orbital approximation*. According to the *Hartree–Fock theory*, the many-electron wave function is expressed as the antisymmetrised product of one-electron wave function (Slater determinant)

$$\Psi(x_1, x_2, \dots) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(x_1) & \psi_1(x_2) & \dots & \psi_1(x_N) \\ \psi_2(x_1) & \psi_2(x_2) & \dots & \psi_2(x_N) \\ \dots & \dots & \dots & \dots \\ \psi_N(x_1) & \psi_N(x_2) & \dots & \psi_N(x_N) \end{vmatrix}. \quad (3.6)$$

Eventually, the Schrödinger equation (3.4) transforms to the self-consistent Hartree–Fock equation

$$\hat{f} \psi_i = \varepsilon_i \psi_i, \quad (3.7)$$

where ε_i are the orbital energies and \hat{f} is the Fock operator

$$\hat{f} = -\frac{1}{2} \nabla^2 + V_{\text{nuc}} + J - K \quad (3.8)$$

containing the kinetic energy operator, the electron–nuclear potential energy, V_{nuc} , the Coulomb term J and the exchange term K . Hartree–Fock theory is relatively simple although the evaluation of a large number of 6-D integrals is required. This problem can be simplified by application of semi-empirical methods such as the Hückel theory or tight-binding technique, where many of these integrals are either simplified or even neglected or adjusted to reproduce some known thermodynamic properties of the system [251].

Presently, the most popular method to calculate the electronic properties of solids is the *density functional theory*. It is based on the theorem stating that the properties of the ground state of a many-electron system can be obtained by minimising the energy functional $E[\rho]$ of the electron density $\rho(r)$ [252]. Here, the electron density of the interacting system can be expressed in terms of one-electron wave function of the non-interacting system,

$$\rho(r) = \sum_{i=1}^N |\psi_i(r)|^2. \quad (3.9)$$

The energy functional is then

$$E[\rho] = T_S[\rho] + V_{\text{nuc}}[\rho] + J[\rho] - E_{\text{xc}}[\rho], \quad (3.10)$$

where $T_S[\rho]$ is the kinetic energy of the non-interacting system, $V_{\text{nuc}}[\rho]$ is the electron–nuclear attraction, $J[\rho]$ is the Coulomb term and E_{xc} is the exchange–correlation energy. The latter term is usually determined on basis of the *local density approximation*.

The first principles based methods were widely applied to compute the interfacial segregation and its consequences for various grain boundary affected phenomena. In this way, the effect of grain boundary segregation of boron and sulphur on grain boundary cohesion was explained on basis of the density functional theory [253] and the co-segregation of boron, titanium and oxygen at the grain boundaries of α -iron was determined on basis of the density-of-states analysis [254]. Segregated gallium was found to draw charge from the surrounding aluminium atoms, thus, to reduce the cohesion of aluminium [255]. The first principles calculations of boron segregation at the $\{013\}$ tilt grain boundary in B2 FeAl intermetallics showed strong Fe–B interactions [256]. On the basis of the local density functional equations, several phenomena were also determined: the structure and the electronic properties of boron and sulphur at the coherent twin boundary in ferritic iron [257], the embrittlement of the same boundary induced by phosphorus segregation [258], hydrogen segregation [259] or the effect of boron on the cohesion of iron [260]. The first-principles quantum mechanical calculations showed that large bismuth atoms weaken the interatomic bonding by pushing apart the copper atoms at the interface [261].

The density-functional theory was further applied to study the geometric and magnetic structures of fully relaxed symmetrical tilt $\{013\}$ grain boundary in iron and $\{012\}$ grain boundary in nickel. In both cases, enhancements of the local magnetic moments of the atoms in the grain boundary plane were found. Calculated values of the segregation enthalpy of silicon and tin at these grain boundaries are in good agreement with experiment [262].

3.3.2 Interatomic Potentials

As the first step of the simulations of the grain boundary structure and chemistry, reliable models are required, which are able to evaluate sufficiently the energetics of various physically reasonable atomic configurations. The realisation of this approach is based on application of various interatomic potentials. The interatomic potentials can be obtained in various ways, for example by ab initio calculations representing the most accurate way to do this [263] or using empirical or semi-empirical approaches such as the *embedded atom method* (EAM) [264], *Finnis–Sinclair potentials* [265] and *glue model* [266]. Here, we will discuss the most applied type of the potentials based on the EAM technique. Usually, it is accepted in energy calculations that the electronic co-ordinates are mutually dependent variables (Born–Oppenheimer (adiabatic) variations). Then the total potential energy of the solid is the unique function of the atomic co-ordinates. The forces on individual

atoms can be then calculated on basis of pure electrostatics (Hellmann–Feynman theorem), however, until now, it was performed only for systems consisting of few atoms or for pure metals. For more complicated systems, the use of empirical or semi-empirical methods seems to be more efficient [70].

3.3.2.1 Pairwise Potentials

The simplest approach to describe the atomic structure of metals and some other materials and to search for the total internal energy of the system is application of *pairwise potentials* [70]. The internal energy has simple analytical form

$$U = \frac{1}{2} \sum_{ij, j \neq i} \phi_{ij}(R_{ij}), \quad (3.11)$$

where $\phi_{ij}(R_{ij})$ is the pairwise interatomic potential, which can be considered as the central-force repulsive energy between atoms i and j with $R_{ij} = |R_i - R_j|$ and which can be fitted to experimental data [70]. The potential ϕ_{ij} involves the parameters that should be fitted to suitable materials properties. This potential can rigorously be derived for metals with simple s–p bonding such as alkali metals, magnesium and aluminium from the electrostatics of the interacting spherical screening clouds of electrons. Here, it is accepted that the ion cores in these metals exhibit negligible effects on conduction electrons that screen them in a linear additive way. The electron density is then a superposition of the spherical charge densities and corresponding pairwise potentials can be obtained directly from ab initio calculations [70, 267–269]. Presence of non-spherical orbitals (d-electrons) deviates the screening from the linear way, and therefore, the ab initio potentials cannot be derived [70]. The tight-binding approach used by Masuda-Jindo to the calculation of segregation of various s–p metals to the 36.87° [100], {013} symmetrical tilt grain boundary in α -iron [270] resulted in quite reasonable results that are comparable with the experimental data especially in the case of phosphorus and silicon [271].

Typical example of pairwise potential

$$\phi_{ij}(R_{ij}) = -\frac{A}{r^n} + \frac{B}{r^m} \quad (3.12)$$

was proposed by Lennard-Jones ($n = 6$, $m = 12$) [272]. Similar potential, although, in exponential form, was proposed by Morse [273]. Pairwise potential of the Morse type was used, for example for simulations of segregation of various solutes to a 38.21° [110], {122} symmetrical tilt grain boundary in copper showing that the solute atoms with larger atomic diameter than the matrix atoms decrease the grain boundary energy [274].

3.3.2.2 Embedded Atom Method

EAM is a semi-empirical technique, which allows to calculate the total energy of an arbitrary arrangement of atoms [70,264]. In this approach, the internal energy U of a metal is composed of two terms,

$$U = \sum_i F_i \left(\sum_{j \neq i} \rho_j(R_{ij}) \right) + \frac{1}{2} \sum_{ij, j \neq i} \phi_{ij}(R_{ij}). \quad (3.13)$$

F_i – the embedding (or glue) function – is the energy that is necessary to place the atom i (embed) to the homogeneous environment (free electron gas) with the local electron density ρ_j at the given atomic site. The function $\rho_j(R_{ij})$ is the radial density function of atom j at distance R_{ij} and it is considered as the electronic charge density of a free atom or as a measure of the squared interatomic matrix elements of a tight-binding Hamiltonian. It can be most simply interpreted as an empirical quantity, which defines the local density of atoms [70]. The three functions – F , ρ and ϕ – are fitted to the experimental values or to the first-principles results, for example from simplified tight-binding description of the electronic densities of states.

EAM potentials were successfully applied to represent the metallic bonding, for example to determine the bismuth segregation in copper [253], to study the interfacial chemistry in L1₂-ordered intermetallics [252, 275] or to study the site competition effect of phosphorus, sulphur, silicon, oxygen, nitrogen and boron in α -iron and tungsten and its consequences for the intergranular cohesion [276].

3.3.3 Simulation Techniques

To obtain an equilibrium grain boundary structure including the energetics of solute segregation at individual sites, an ensemble containing a number of atoms (simulation cell or box [70]) has to be defined. The simulation cell usually contains the periodically repeated structural unit of the chosen grain boundary inside several tens of atomic planes parallel to the interface on its both sides. This cell also repeats in three dimensions and the simulation represents the finite pattern of that interface. To define the border conditions, there are either two free surfaces introduced well distant from the interface to suppress their interaction with the grain boundary or two semi-infinite rigid crystals considered on both sides of the interface. In the latter scheme, the surface effects are eliminated. In some cases, Möbius or antiperiodic border conditions can be used [277].

Starting from a chosen structure, there are various ways how to calculate the structures of the segregated grain boundaries. The most advantageous are the techniques of molecular statics, molecular dynamics and Monte Carlo. They may provide us with the values of the enthalpy – and in some cases also the entropy – of the solute segregation to individual grain boundary sites.

3.3.3.1 Molecular Statics

Molecular (or lattice) statics represents the simplest way of atomistic simulation of atomic structure of the grain boundaries possessing the lowest energy. It is based on determination of the atomic configuration providing minimum energy of the system, $\partial U/\partial r_i = 0$. Starting from a chosen initial configuration, the forces among atoms are calculated and atoms are slightly shifted in direction of these forces. A stable (equilibrium) configuration is reached when all forces vanish. During this minimisation entropy is neglected and therefore, obtained results are related to the temperature of 0 K (i.e. all vibrational effects are neglected). The minimisation, however, indicates only local energy minima albeit not the global minimum. Therefore, this technique is sensitive to the choice of the starting configuration. On the other hand, it is a very fast computational procedure and is widely used in atomistic simulations of grain boundary structure [251].

In the field of the grain boundaries and their properties, molecular statics is primarily used to simulate the atomic structure of the interfaces at 0 K. To apply this technique to studies of the grain boundary segregation, the grain boundary structure has also to be determined: first as relaxed without the solute, thus, providing the internal energy (enthalpy) of the system, U_α^Φ . Then one solvent atom at a chosen site in the structural unit is replaced by the solute atom and the simulation procedure is repeated. In this way, the energy U_β^Φ of such “segregated” interface is determined. The same procedure is performed for the bulk crystal with and without one solute atom thus providing the energies U_β^v and U_α^v , respectively. The segregation energy is then determined as

$$\Delta U_I = \left(U_\beta^\Phi - U_\alpha^\Phi \right) - \left(U_\beta^v - U_\alpha^v \right). \quad (3.14)$$

Molecular statics was used to describe hydrogen and helium trapping at the 28.07° [100], {035}, 38.94° [110], {114} and 50.48° [110], {113} tilt grain boundaries in nickel and showed that the grain boundaries are a major sink for interstitials [278]. Another study using this technique was devoted to solute segregation at the $\Sigma = 7$ symmetrical tilt grain boundary of copper [279].

3.3.3.2 Molecular Dynamics

In molecular dynamics, the atom positions are determined as time dependent. For this purpose, numerical integration of the Newton equation of motion of each atom has to be performed. As a discrete time step used in integration, usually few percent of the atomic vibration frequency is applied. As a consequence, this technique is time consuming. The major advantage of this technique is the calculation of the thermodynamic averages of the equilibrium atomic co-ordinates at elevated temperatures [280].

The first step of this procedure is to describe all atoms in a chosen box of the starting configuration in a microcanonical ensemble by their positions r_i and

velocities v_i . For a given temperature, the velocities can be considered as randomly distributed according to a Maxwell distribution. The force f_i on each atom (i.e. the acceleration) is calculated using the interatomic potentials. This force is assumed to remain constant during a chosen time step Δt and corresponding r_i and v_i are found. The time step should be chosen smaller than typical periods of atomic vibrations (10^{-12} – 10^{-13} s) but too small time steps require very long computer times. On the other hand, large time steps may cause large truncation errors and result in instabilities when the atoms go near too closely. Typical time step is 10^{-15} s [251]. The process runs until the system properties converge to equilibrium.

The early attempt of applying the molecular dynamics to theoretical studies of grain boundary chemistry was done by Hashimoto et al. for phosphorus and boron segregation in α -iron. It was shown that both phosphorus and boron segregate preferentially at interstitial sites of $\Sigma = 5$, {013} and $\Sigma = 9$, {114} symmetrical tilt grain boundaries [281]. This pioneering work started the effort in simulations of the segregation behaviour of the grain boundaries despite the obtained values of the segregation energies calculated by Hashimoto et al. are too high comparing to the experimental data. Quenched molecular dynamics providing the Helmholtz energy of segregation at 0 K was applied to simulate the segregation effects at the {113} and {233} symmetrical tilt grain boundaries in Ni–Ag and Ag–Ni alloys [274].

3.3.3.3 Monte Carlo Simulations

Similarly to molecular dynamics, Monte Carlo (MC) simulations allow to obtain the grain boundary structures at elevated temperatures. Here, the dynamics of the system is not taken in account, and the time necessary for successful equilibration is much shorter compared to molecular dynamics. Therefore, this technique is optimal for determination of thermodynamic averages. According to statistical mechanics, the average value of a thermodynamic function, $\langle Q \rangle$, is given as

$$\langle Q \rangle = \int Q(Z) \Pi_i(Z). \quad (3.15)$$

The probability Π_i of finding a particular configuration in a chosen statistical ensemble is given as

$$\Pi_i = \frac{\exp[-U(Z)/kT]}{\int \exp[-U(Z)/kT] dZ} \approx \frac{1}{Z} \exp\left(-\frac{U(Z)}{kT}\right). \quad (3.16)$$

In (3.15) and (3.16), Z is the partition function of the system and U is the internal energy. In practice, series of configurations of the grain boundary structure are generated in these ensembles usually by means of the Metropolis algorithm [282]. Starting from an initial configuration, new configurations with changed atomic

co-ordinates are randomly produced. The ratio of the probabilities for the initial and new configurations is

$$\frac{\Pi_n}{\Pi_i} = \exp\left(-\frac{U_n - U_i}{kT}\right). \quad (3.17)$$

In the calculations, only $\Pi_n > \Pi_i$ is accepted as a new initial configuration. If $\Pi_i > \Pi_n$, this configuration is accepted with the probability Π_n/Π_i . Each repetition of the procedure with new initial configuration is called MC step. In this procedure, the configuration used as initial ones (which were chosen arbitrarily) are not included in the ensemble. Due to some temporal correlation, the produced configurations are not completely independent, and therefore, it is necessary to consider only the configurations uncorrelated with those produced before and after them. In each MC step, atoms are chosen randomly and are displaced by random vectors of the lengths of fractions of the maximum permitted displacement.

Theoretically, the Monte Carlo technique simulates the equilibrium state of the system. Practically, the equilibrium may not be sometimes reached, for example if a highly metastable initial configuration is used. Since the grain boundary also represents high-energy metastable state comparing to the crystal interior, the equilibrium reached in MC simulations indicates generation of a stable grain boundary structure. Different configurations of the statistical ensemble implicitly cover thermal fluctuations in the system. Therefore, MC simulations can also be used to represent the “annealing” of the grain boundary structure – obtained, for example from molecular statics simulations – at chosen temperature and to testing its stability [219].

Similarly to molecular statics simulation, the ensembles with and without solute atoms are generated and their energetics are compared. The positions of the atoms, their chemical identities and the volume of the system can change in this procedure supposing constant temperature, pressure, total number of atoms and difference in chemical potentials, $\Delta\mu$, of atomic species. Using a transmutational ensemble with chosen bulk solute concentration, the grain boundary segregation can be simulated at chosen temperature with

$$\frac{\Pi_n}{\Pi_i} = \exp\left(-\frac{U_n - U_i + \Delta\mu}{kT}\right). \quad (3.18)$$

Here, $\Delta\mu$ represents the difference of chemical potentials of the solute and the solvent between the actual chemical potential and the chemical potential of an ideal gas with the same composition and volume [12].

Monte Carlo simulations with transmutational ensemble have been presently used to simulate solute segregation to twist grain boundaries [283–287]. Besides this procedure, the overlapping distribution MC (ODMC) method is used to determine the values of ΔF_I [219]. This is applied because the Helmholtz energy, ΔF_I , cannot be expressed as ensemble average and, thus, cannot be directly calculated from MC simulations. According to statistical mechanics,

$$F = -kT \ln(Z), \quad (3.19)$$

where Z is the partition function given as

$$Z = \int \exp\left(-\frac{\hat{H}}{kT}\right) dp dq \quad (3.20)$$

and p and q are the momentum and position vectors for A atoms in the ensemble. \hat{H} is the Hamiltonian, defined as

$$\hat{H} = \sum_{i=1}^N \frac{p_i^2}{2m_i} + U \quad (3.21)$$

with m_i being the mass of the i th atom. If the atoms in the ensemble are identical, the partition function is

$$Z = \int \exp\left(-\frac{p^2}{2mkT}\right) dp^N \int \exp\left(-\frac{U}{kT}\right) dq = (2\pi mkT)^{3N/2} \int \exp\left(-\frac{U}{kT}\right) dq. \quad (3.22)$$

The difference of the Helmholtz energy between the arbitrary ensembles A and B is

$$\Delta F = F_B - F_A = -kT \ln\left(\frac{Z_B}{Z_A}\right). \quad (3.23)$$

Supposing a single solute atom B is present in ensemble A , the ratio Z_B/Z_A is

$$\begin{aligned} \frac{Z_B}{Z_A} &= \left(\frac{m_B}{m_A}\right)^{3/2} \frac{\int \exp[-(U_B - U_A)/kT] \exp[-U_A/kT] dq}{\int \exp[-U_A/kT] dq} \\ &= \left\langle \exp\left(-\frac{U_B - U_A}{kT}\right) \right\rangle_A, \end{aligned} \quad (3.24)$$

that represents the thermodynamic average over the ensemble A . The difference in ΔF can be calculated for each atom in the simulation cell [219]. If there is a large overlap of the distributions, one can obtain reliable values of ΔF .

Because the degree of the overlap is not known a priori, it is necessary to determine the thermodynamic averages for MC runs of various lengths to determine the number of steps per atom required for a given degree of accuracy.

The use of MC technique has widely been applied since 1990s starting by the first attempts of Foiles et al. [288]. Using this method, Foiles showed that copper segregation at $\Sigma = 5$, $\Sigma = 13$ and $\Sigma = 61$ (001) twist grain boundaries in nickel is confined in few atomic layers near the grain boundary and is stronger at high-angle grain boundaries [289]. MC calculations were also used to study solute segregation at 36.87° [100], $\{013\}$ symmetrical tilt grain boundary in the Cu–Ag system [290] and in the NiAl intermetallics [291], or to determinations of solute segregation at low-angle [285] and high-angle [292] twist grain boundaries in the Ni–Pt system. Segregated magnesium at grain boundaries of Ni₃Al intermetallics

preferentially substitutes the aluminium atoms rather than nickel ones. The segregation of magnesium additionally reduces the grain boundary energy thus increases the grain boundary cohesion [293].

The ODMC method was applied to study platinum segregation at two sites of the $\Sigma = 5$, (001) twist grain boundary in gold at 850 and 1,650 K [294]. Ab initio calculated many-body potentials (linear muffin-tin-orbital method) and MC were successfully used to simulate the structure and energy of bismuth segregated twin grain boundary of copper [213].

3.3.3.4 Minimisation of the Helmholtz Energy

Another approach to obtaining the values of the Helmholtz energy is so-called free energy minimisation (FEM) [295]. In this method, an approximation is used to calculate the entropy of the system. The atoms in a solid can be considered as harmonic oscillators. The vibrational contribution to the Helmholtz energy, F_{vib} , at the classical limit for high temperatures is given as

$$F_{\text{vib}} = kT \sum_{i=1}^N \sum_{j=1}^3 \ln \left(\frac{h\omega_{ij}}{2\pi kT} \right), \quad (3.25)$$

where ω_{ij} are the vibrational eigenfrequencies of the atoms and h is the Planck constant. The values of ω_{ij} are calculated on basis of the quasi-harmonic (QH) approximation by so-called local harmonic (LH) model. This model accepts the harmonic approximation keeping only the second-order terms but neglecting the coupling of vibrations between the atoms. Each atom is considered as an independent oscillator and the computation is reduced from the diagonalisation of the full $3N \times 3N$ dynamic matrix to the evaluation of N local dynamic 3×3 matrices for N atoms in the ensemble.

The configurational entropy S_c is calculated as

$$S_c = -k \{X_A(i) \ln [X_A(i)] + X_B(i) \ln [X_B(i)]\}, \quad (3.26)$$

where X_A and X_B represent the concentrations of “effective” atoms, which represent the time average probability that a site is occupied by an atom of type A or B , respectively ($X_B = 1 - X_A$). Equation (3.26) is only valid for an ideal solid solution; real configurational entropy will possess different values.

In case of solute segregation the grand potential, Ω , is given as

$$\Omega = U + F_{\text{vib}} - TS_c + \Delta\mu \sum_{i=1}^N X_A(i). \quad (3.27)$$

In very dilute solid solutions, $\Delta\mu = \text{const}$ and $S_c = 0$ so that [294]

$$\Omega = U + F_{\text{vib}}. \quad (3.28)$$

Computer simulation provides us with the values of the internal energy U of the system as well as of the segregation at various types of the grain boundary sites. However, no information about the entropy of interfacial segregation, which represents an important component of the Helmholtz energy of segregation, can directly be obtained. In fact, the Helmholtz energy of segregation depends on temperature,

$$\Delta F_I(T) = \Delta U_I(T) - T\Delta S_I(T). \quad (3.29)$$

In general, both ΔU_I and ΔS_I depend on temperature although it may be weakly and therefore, they are often considered as constant. As the entropy of segregation cannot be calculated directly, ΔS_I can be determined as

$$\Delta S_I = \frac{1}{T}(\Delta U_I - \Delta F_I(T)). \quad (3.30)$$

The FEM method was applied to determination of copper segregation to (001) twist grain boundaries in nickel within the misorientation range 15° – 45° at temperatures $600 \text{ K} < T < 1,100 \text{ K}$ [296]: The obtained results are comparable to those obtained by MC simulations [289]. In fact, copper was found to segregate to $36.87^\circ[100]$, $\{013\}$ symmetrical tilt grain boundary even in copper-rich alloys [297]. Similar results were also obtained for segregation of gold in palladium while in the system Ag–Au, the majority element segregates at the grain boundary [298].