Effect of titanium additions to low carbon, low manganese steels on sulphide precipitation

Sima Aminorroaya-Yamini
University of Wollongong


This paper is posted at Research Online.
http://ro.uow.edu.au/theses/403
NOTE

This online version of the thesis may have different page formatting and pagination from the paper copy held in the University of Wollongong Library.

UNIVERSITY OF WOLLONGONG

COPYRIGHT WARNING

You may print or download ONE copy of this document for the purpose of your own research or study. The University does not authorise you to copy, communicate or otherwise make available electronically to any other person any copyright material contained on this site. You are reminded of the following:

Copyright owners are entitled to take legal action against persons who infringe their copyright. A reproduction of material that is protected by copyright may be a copyright infringement. A court may impose penalties and award damages in relation to offences and infringements relating to copyright material. Higher penalties may apply, and higher damages may be awarded, for offences and infringements involving the conversion of material into digital or electronic form.
3-1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy was conducted on a Leica Cambridge Stereoscan S440 instrument equipped with energy dispersive spectroscopy (EDS) operating at 25 KV and/or on a JEOL JEM-3000 with an LaB6 gun.

3-1-1 Sample preparation for optical and scanning electron microscopy

Steel samples from slabs and concentrically solidified specimens were cut on a Struers Accutom and mirror polished mechanically down to 1 µm. When an etched surface was required, a 2-pct Nital solution used to etch the surface.

3-1-2 High Resolution Scanning Electron Microscopy (HR-SEM)

A Zeiss, Supra 55 VP High-Resolution Scanning Electron Microscope (HR-SEM) was used for imaging mechanically polished samples. Both the in-lens secondary electron detector
and back-scattered detector were used to image samples. An Oxford INCA microanalysis system was used for energy dispersive spectroscopy (EDS) analysis. An accelerating voltage of 20 kV was used for the majority of the analyses.

3-2 Electron Probe Micro Analysing (EPMA)

Electron probe microanalyses (EPMA) were conducted on a Camebax-SX50 instrument (Cameca, Paris, France).

3-3 Focused Ion Beam- Dual Beam (FIB)

The Focused Ion Beam, Dual Beam facility combines a Gallium ion column with a high resolution field emission gun SEM. The FIB and SEM columns are positioned at different angles to the sample, so that the electron beam can be used for imaging, while the ion beam is used for sectioning. The FIB is roughly similar in architecture to a scanning electron microscope (SEM) but uses a fine (<5nm) focused ion beam with an energy between 5 and 50 KeV instead of an electron beam. A beam of gallium ions (Ga⁺) is focused on the surface of a sample and scanned along a series of parallel paths over a defined area. The interaction of the beam with the sample results in sputtering from the sample surface. A beam limiting aperture is used to control the beam current. While high beam currents >1000pA are used for milling, low beam currents <11pA are used for imaging [79].

3-3-1 Dual Beam

In conventional single beam FIB systems both milling and imaging are accomplished using the ion beam. The Dual Beam system combines the milling abilities with High Resolution SEM. The ability of imaging with electrons rather than ions decreases considerably the undesirable damage or erosion.
The column layout of the Dual Beam system is shown in Figure (3-1). The electron column is mounted in a vertical position on the vacuum chamber while the ion column is positioned at an angle 52° to the horizontal. Both the electron and ion beam can be coincident on the same region of the specimen, provided the plane of the area of interest lies in the eucentric plane. The optical resolution in this arrangement is around 10 nm [79]. The Focused Ion Beam facility used in this investigation is a XT Nova NanoLab 200, Dual Beam FIB, v.2.0.5.

![Figure (3-1): Column layout of the Dual Beam, FIB](image)

3-3-2 Three Dimensional Imaging and Reconstruction

An automated procedure which is called “slice and view” is available in the Dual Beam FIB. In this procedure, a series of progressive trenches is milled which reveal cross-sectional views of the specimen. This method is suitable for the examination of localised inhomogeneities in a specimen such as defects and precipitates. The electron image is recorded after each slice and 3D reconstruction software is employed to produce a fly-through animation of the feature. A set of images taken by this procedure in the Dual Beam FIB were reconstructed by using the Amira 3.1 Image Analysis Software Package [75].
3-4 High Resolution Transmission Electron Microscopy (HR-TEM)

Transmission electron microscopy was conducted using a JEOL JEM 2011 instrument which operated at 200 kV with a LaB₆ filament and a resolution of 0.16 nm. It is equipped with an EDS detector (ultra-thin window, Mg Kα resolution 133 KeV), X-ray mapping with automatic specimen drift correction and side and bottom mounted cameras with SIS image analyser software.

3-4-1 Sample preparation for TEM analysis

Various methods were employed to prepare TEM samples in an attempt to assure that reliable information is obtained.

3-4-1-1 Carbon replica

- Samples were mirror-polished down to 1 µm
- Cleaned in acetone ultrasonically
- Carbon coated by Dynavac Evaporation unit
  - Filter paper placed adjacent to the sample as a guide to the coating thickness
  - Two carbon rods, one with a flat end and the other sharpened to a point were used as the carbon source
  - Evaporation conducted under a vacuum of at least 7.5 x 10⁻⁴ torr (0.1 Pa)
- Cut approximately 2 square mm into carbon using a scalpel
- Placed in 8 pct Nital to separate the carbon coating from the steel substrate
- Replicas were picked up on 200 mesh copper grids and rinsed in:
  - Ethanol
  - 75 % Ethanol + 25 % distilled water
  - 50% Ethanol + 50% distilled water
  - 25% Ethanol + 75% distilled water
Distilled water
- Placed on filter paper to dry
- Labelled and saved in a TEM sample holder

3-4-1-2 Selective Potentiostatic Etching by Electrolytic Dissolution (SPEED)

This procedure outlined by Kurosawa and his colleagues [80, 81], was followed:
- Samples were mirror-polished down to 1 µm
- Cleaned in acetone ultrasonically
- Carbon coated by using the Dynavac Evaporation unit as discussed in section (3-4-1-1)
- Cut approximately 2 square mm into carbon using scalpel
- An electrolytic cell was designed as shown in Figure (3-2):
  - The electrolyte used is (AA type): 1% Tetramethylammonium Chloride and 10% Acetylene acetone in Methyl alcohol
  - Aqueous Silver Chloride/Chlorine (3M) was used as a reference electrode instead of Saturated Calomel Electrode (SCE)
  - From Figures (3-3) and (3-4) can be concluded that potentiostatic electrolysis between -300 and 800 mV vs. SCE is suitable for carbon steel in order to dissolve the matrix but not the precipitates. Potential of -100 mV was selected versus electrode in this study since it was recommended for sulphide observation [80]
- Replicas were picked up on 200 mesh copper grids and rinsed in methanol
Chapter 3 - Experimental instruments and methodology

Figure (3-2): Schematic of electrolytic cell [81]

Please see print copy for Figure 3-2

Figure (3-3): Differences of potential vs. current density curves between steels and carbides in 10% AA type electrolyte [80]

Please see print copy for Figure 3-3

Figure (3-4): Differences of potential vs. current density curves between steels and nitrides in 10% AA type electrolyte [80]

Please see print copy for Figure 3-4
3-4-1-3 Focused Ion Beam

FIB-TEM sample preparation typically involves the generation of electron transparent regions of a sample by milling trenches on either side of a membrane with an ion beam, typically Ga⁺. This method offers two main advantages over traditional specimen preparation techniques. Firstly, the region to be thinned can be chosen with sub-micron precision. This allows preparation of TEM foils of highly site-specific phenomenon for observation. Secondly, coarsely heterogeneous microstructures consisting of chemically and structurally distinct regions can be uniformly thinned using the FIB [82].

Focused Ion Beam (FIB) milling permitted the extraction of thin foils from pre-selected areas of the sample and extracted thin foils were mounted on 200 mesh carbon-coated copper grids. The sequence of steps taken to extract a sample is outlined below and illustrated in Figure (3-5). A precipitate was selected and cross-marks placed as reference points on the surface using the FIB high current ion beam. This procedure was used to ensure the sample is prepared from the exact area of interest. Following deposition of a layer of Pt on the surface of the sample to protect the object from ion bombardment, sections of ~5 µm depth on both sides of the Pt band were removed by controlled bombardment of Ga-ions. Finally, a thin foil was prepared by thinning the foil to less than 100 nm, cutting it loose, extraction and mounting on a carbon-coated copper grid [83].
3-4-2 TEM analysis interpretation by Java Electron Microscopy Software

The software detail available from:
“http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/jems.html”

JEMS was employed to assist the indexing of Selected Area Diffraction Patterns (SADPs) which were taken from different compounds in the TEM. In order to introduce a crystalline material to the software, the crystallographic data of various compounds were extracted from papers or handbooks [84] and introduced to the software and the crystallographic structure was built by JEMS.

The software allows the user to select elements and specify Wichnoff notation, x, y, z coordinates for each element. Then the unit cell parameters and the space-group are defined and saved as a retrievable file by JEMS. Finally, the software enables users to have a three dimensional view of the crystal as well as selected area diffraction patterns of various orientations. It is even possible to measure the d-space and the angle between planes in the crystal.
3-5 High Temperature Laser Scanning Confocal Microscopy (HT-LSCM)

In confocal microscopy, laser light is focused by an objective lens on to the object and the reflected beam is focused via a beam splitter, as shown in Figure (3-6). An image is built up by scanning the focussed spot relative to the object, which is then stored in an imaging system for subsequent display. Through the use of a confocal pinhole, only light incident from the focal plane is permitted to pass through to the photo detector, represented schematically in Figure (3-7). Light not returning from the specific optical plane is blocked by the pinhole. Hence, an extremely thin optical section is created, providing a high resolution image. Because thermal radiation is blocked by the confocal pinhole, only the polarised reflection of the high intensity laser beam reaches the imaging sensor and a sharp image is produced. The use of pinhole optics increases the resolution such that with a 0.5 µm diameter beam, the effective resolution is 0.25µm [85].

Please see print copy for Figure 3-6

Figure (3-6): Schematic representation of the confocal microscope [85]
A LSCM supplied by Lasetec was used in this investigation. It uses a He-Ne laser with a wavelength of 632.8 nm. The 0.5 µm diameter reflected laser beam is scanned by an acoustic optical deflector in the horizontal direction at a rate of 15.7 kHz and a galvanomirror in the vertical direction at 60 Hz. Specimens are placed at the focal point of a gold plated ellipsoidal cavity in an infrared furnace beneath a quartz view port, as shown in Figure (3-8).

A 1.5 kW- halogen lamp located at the other focal point of the ellipsoidal cavity heats the specimen by radiation. The specimen and lamp chambers are separated by quartz glass so that the atmosphere of the specimen chamber can be controlled and the lamp can be air-
cooled. The temperature measured by thermocouples incorporated in the crucible holder is displayed on a monitor and simultaneously recorded with the digital image on a computer at the rate of 30 frames per second. Specimen holders consist of 5 or 10 mm diameter round holders constructed from a polymeric end-piece, alumina tube with an outer silica support tube and a platinum holder welded to a B type thermocouple wire.

### 3-5-1 Concentric Solidification technique (CST)

The concentric solidification experimental technique is defined as the formation of a centralized pool of liquid metal contained by a rim of solid of the same material under a radial thermal gradient. A schematic diagram of the liquid pool contained by a solid rim is shown in Figure (3-9) [26].

![Schematic diagram of concentric solidification](image)

**Figure (3-9): Schematic diagram of concentric solidification [26]**

In this system, a specimen of 10mm diameter is placed in in a gold plated ellipsoid infrared heating furnace, under an ultra-high purity inert atmosphere (usually Ar). A 1.5 kW-halogen lamp located at one focal point of the cavity heats, by radiation, the specimen located at the other focal point. The temperature, measured by thermocouples incorporated in the crucible holder, is displayed on a monitor and simultaneously recorded with the image on the computer at a rate of 30 frames per second. Magnifications up to 1350-times at a resolution of 0.25 µm can be obtained, using a He–Ne laser with a wavelength of 632.8 nm. In the system used, a laser beam 0.5 µm in diameter is reflected and scanned by an acoustic optical deflector in the horizontal direction at a rate of 15.7 kHz and a galvano-mirror in the vertical direction at 60 Hz [86].
3-5-2 Sample preparation for Laser Scanning Confocal Microscopy

Small pieces of steel that were sectioned from the columnar zone of an industrially continuously-cast slab were machined into a discs (10 mm diameter, 0.4 mm thick), mirror polished on both sides, placed in an alumina crucible (10 mm diameter and 2 mm height) and heated at a rate of 100°C/min under ultra high purity argon gas. The accurate position and size of samples will be explained in related chapters. Because samples are positioned in the furnace chamber at one focal point of the ellipsoidal cavity and the heating element is situated at the other focal point, radiative heating is concentrated in the centre of the disk-shaped specimen and a radial temperature gradient develops in the specimen [26]. The centre of the sample is melted, heated to approximately 1600°C and kept at this temperature for 6 minutes. This procedure ensures that a stable melt-pool is formed with a solid rim surrounding the liquid pool. The specimen can then be cooled to the required temperature (usually 700°C) at various rates, typically 20°C/min, followed by cooling to room temperature at a rate of 100°C/min. The image of the specimen surface is continuously recorded and once a stable liquid pool has been established, solidification initiates at the liquid/delta-ferrite interface upon cooling and delta-ferrite grows radially inwards while the liquid with its continuously changing composition and enrichment in alloying elements, remains at the centre of the disc until fully solidified.

3-6 Three dimensional local electrode Atom Probe

A three dimensional local electrode atom probe at the University of Sydney was employed to study the nano-precipitates in as-cast steels. This technique has the ability to visualise the microstructure of alloys at nanometer scale. The technique has been successful in characterisation and analysis of precipitates and segregation in various steels [87-90]. The technique development, instrumentation, specimen preparation and a wide range of applications have been described in detail elsewhere [91].
3-6-1 Sample preparation for Atom Probe investigations

The aim of sample preparation is to produce a very sharp and smooth needle with an end radius of less than 100 nm. The principle and method of preparation have been described in detail elsewhere [91] and only a brief outline of the process will be presented here:

- The bulk material was cut into \( \approx 0.25 \times 0.25 \times 10 \) mm rods using an Accutum disc-cutting facility. The rods were then electro-polished in two stages to produce tips suitable for imaging.

- Rods were cleaned with acetone

- The first stage of electro-polishing was performed in 20% perchloric acid (70%) in glacial acetic acid with the DC voltage of 20 V and then finer polishing was done at 15 V. A schematic illustration of this stage is shown in Figure (3-10).

- After ensuring that the tip was of the correct shape under the optical microscope, it was moved to the second stage of polishing so called micro-electro-polishing.

- The second electrolyte used was 2% perchloric acid in 2-butoxyethanol and polishing was done with a DC voltage of about 5-15 V. The micro-electro-polishing process is shown schematically in Figure (3-11).

Please see print copy for Figure 3-10

Figure (3-10): Schematic diagram of stage 1 electro-polishing [91]
Chapter 3- Experimental instruments and methodology

3-6-2 Principles of three-Dimensional Atom Probe

The schematic diagram of a three-dimensional atom probe (3DAP) is illustrated in Figure (3-12). Prior to probing, the specimen is loaded into the specimen chamber and cooled to around 30 K. Then, small amount of Hydrogen is introduced into the chamber and the oxide layer on the surface of the tip is removed gradually by increasing the tip voltage. After removing the oxide layer, atomic planes of the matrix become visible. Under extremely high electric field on the tip surface, hydrogen atoms are ionised at the tip surface and accelerated towards the phosphorous screen where the tip surface image is formed. When a clear image is obtained, hydrogen is evacuated and the surface atoms are field evaporated by applying an additional voltage to the specimen in a series of high voltage pulses. By measuring the time of flight of ions, the charge and the x and y coordinates of ions, a two dimensional elemental distribution in one layer can be mapped.
Field evaporation of subsequent layers enables the reconstruction of a 3D elemental map of layers. The detection efficiency of the atom probe detector is not more than 60% of the evaporated ions [92].

![Please see print copy for Figure 3-12](image)

Figure (3-12): Schematic diagram of Three-Dimensional Atom Probe [91]

### 3-6-3 Data analysis

In order to visualise and analyse data, it is necessary to analyse the mass spectrum. The mass to charge ratio is calculated from the known travelling distance of ions from the specimen to the detector. Thus the isotopes of each type of atom can be identified and further analysed by using PoSAP 1.75 software [93]. The principles involved in atom probe data analysis are well documented [91].

The composition of precipitates was determined by selecting a small “box” perpendicular to the precipitate surface in which a particle and the matrix on both sides of the precipitate were contained. The number of selected element atoms was plotted against the total number of atoms in selected volume.
3-7 Computational thermodynamics and kinetics

The increasing importance of mathematical modelling in support of product developments and process control has highlighted the need for computational thermodynamic and kinetic calculations [28]. In response to this need, Thermo-Calc Classic (TCC) and DICTRA (DIffusion Controlled TRAnsformation) have been developed in the Department of Materials Science and Engineering at The Royal Institute of Technology (KTH), Stockholm, Sweden, and these software packages have been used in the present investigation.

3-7-1 Thermo-Calc

The software package Thermo-Calc, version R [28] was used for thermodynamic calculations. It is based on minimization of the Gibbs free energy of the individual phases in the equilibrium state. It uses the CALPHAD (CALculation of PHAse Diagrams) method to extrapolate thermodynamic descriptions for use in an n-component system based on the assessment of binary and available ternary and quaternary experimental data which are stored in a thermodynamic database. The thermodynamics of the liquid phase is described by a regular solution model and the solid phases by sub-lattice models. The phase equilibria are calculated by a free-energy minimization determined by a Newton-Raphson technique. The databases are used to calculate phase fractions, phase compositions as well as transformation temperatures under thermodynamic equilibrium conditions [94, 95]. Thermo-Calc therefore provides an efficient calculation technique to predict the equilibrium amount and composition of the stable phases of complex system under a given set of conditions [96].

Phase diagram sections can be determined with up to five independent variables in a very complex multi-component and heterogeneous system (up to 40 elements and 1000 species) [28].
Thermo-Calc Windows (TCW) released in 2000, simplifies thermodynamic calculations since calculations are done in a straightforward way under a user-friendly Windows environment.

Thermo-Calc Classic (TCC), version R, Thermo-Calc Windows (TCW4) [28] and the thermodynamic database, TCFE4 [29] which are designed for Steels/Fe alloys were used in the current study.

3-7-2 DICTRA

DICTRA (DIffusion Controlled TRAnsformation) is based on a numerical solution of the multi-component diffusion equations and local thermodynamic equilibrium at phase interfaces [97]. Diffusion controlled transformations are treated by DICTRA on the basis of the following fundamental concepts [98]:

- The movement of a phase interface is controlled by the mass balance obtained from the fluxes of the elements diffusing across the interface.

- Local equilibrium is assumed at the moving interface. In a binary system at a given temperature, the variance of a two-phase equilibrium is zero. Therefore, in this instance, local equilibrium is identical to global equilibrium and the compositions of the phases at the interface are given by the tie-line of the two-phase equilibrium. The velocity of the interface is then controlled by the mass balance. In multi-component systems, there remain degrees of freedom and the operating tie-line is determined by the condition that the mass balance of every diffusing element gives the same interface velocity. This boundary condition varies with time, i.e., during the course of the reaction.

- Diffusion is treated in terms of mobilities and true thermodynamic driving forces, i.e., chemical potential gradients. The thermodynamic functions like chemical potentials are
calculated with Thermo-Calc [28] which runs as a subroutine to DICTRA [27]. The mobility database MOB2 [99] was used in the DICTRA calculations.

- Diffusion-controlled phase transformations are treated in geometries with one space variable, i.e., in planar, cylindrical, or ellipsoidal cells with one or more different phases.

DICTRA is particularly suitable for treating problems involving a moving boundary. The boundary conditions may be given in a rather flexible way which enables the user to treat problems of practical interest [27].

3-7-2-1 DICTRA and diffusivities

DICTRA uses both thermodynamic and kinetic descriptions to perform simulations. Thermodynamic data taken from Thermo-Calc and kinetic descriptions are available through mobility database MOB2 which contains kinetic data for several binary, some ternary and a few higher order systems [27]. In order to reduce the number of stored values in databases, atomic mobilities are saved rather than diffusion coefficients. The diffusion coefficients are then calculated by thermodynamic and kinetic factors [27].

3-7-2-1-1 Relations between diffusion coefficients and atomic mobilities

1. Phenomenological coefficients

A vacancy-exchange diffusion mechanism is dominant in crystalline phases. It is assumed that the vacancy concentration is governed by thermodynamic equilibrium and therefore the diffusional flux of component k in the z-direction can be expressed as:

\[ J = -c_k y_{\text{va}} \Omega_{\text{va}} \frac{\partial \mu_k}{\partial z} \]

(3-1)
Chapter 3- Experimental instruments and methodology

$c_k$: Amount of k per unit volume

$y_{VA}$: Fraction of vacancies on the sublattice where k is dissolved

$\Omega_{kVA}$: A kinetic parameter which gives the rate of exchange if there is a vacancy adjacent to a k-atom

$\mu_k$: Chemical potential of component k

The mobility of component k is defined as:

\[ M_k = y_{VA} \Omega_{kVA} \]  \hspace{1cm} \text{when } k \text{ is substitutional} \tag{3-2} \\

\[ M_k = \Omega_{kVA} \]  \hspace{1cm} \text{when } k \text{ is interstitial} \tag{3-3} \\

Therefore, phenomenological parameters which relate the flux of k to driving forces are equal to:

\[ L_{kk} = c_k M_k \]  \hspace{1cm} \text{when } k \text{ is substitutional} \tag{3-4} \\

\[ L_{kk} = c_k y_{VA} M_k \]  \hspace{1cm} \text{when } k \text{ is interstitial} \tag{3-5} \\

\[ L_{ki} = 0 \]  \hspace{1cm} \text{when } k \neq i \tag{3-6} \\

Therefore, equation (3-1) can be expressed as:

\[ J = -\sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial z} = -L_{kk} \frac{\partial \mu_k}{\partial z} \tag{3-7} \]

DICTRA assumes that partial molar volumes are independent of concentration and the partial molar volumes of interstitials are neglected hence:

\[ J_k = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_j}{\partial z} \tag{3-8} \]

Where:

\[ L'_{ki} = \sum_{j=1}^{n} (\delta_{jk} - c_k V_j) L_{ji} \tag{3-9} \]

Where $\delta_{jk}$ is the Kronecker delta, which is equal to 1 when j=k and equal to 0 otherwise. $V_j$ is the partial molar volume of element j.
2. Interdiffusion coefficients

It is more convenient to express the fluxes as functions of concentration gradients rather than chemical potential. This is accomplished by rewriting equation (3-8) using the chain rule of derivation, that is:

\[
J_k = -\sum_{i=1}^{n} L_{ki} \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial z} = -\sum_{j=1}^{n} D_{kj} \frac{\partial c_j}{\partial z}
\]  

(3-10)

Where

\[
D_{kj} = \sum_{i=1}^{n} L_{ki} \frac{\partial \mu_i}{\partial c_j}
\]  

(3-11)

It is assumed that all substitutional species have the same partial molar volumes and only the substitutional species contribute to the volume and expressed as:

\[
D_{kj}^0 = D_{kj} - D_{kn}
\]  

where j is substitutional

(3-12)

\[
D_{kj}^a = D_{kj}
\]  

where j is interstitial

(3-13)

\[
J_k = -\sum_{j=1}^{n} D_{kj}^a \frac{\partial c_j}{\partial z}
\]  

(3-14)

\[D_{kj}^a\] is the interdiffusion coefficient and can be evaluated experimentally.

3-7-2-1-2 Modelling of the atomic mobility

From absolute reaction rate theory, the mobility coefficient for an element B can be divided into a frequency factor, \( M_B^0 \), and activation enthalpy, \( Q_a \) [100]:

\[
M_B = M_B^0 \exp\left(-\frac{Q_a}{RT}\right) \frac{1}{\Gamma^{mg}}
\]  

(3-15)

\[\Gamma^{mg}\] : Factor taking into account the effect of ferromagnetic transition
R: Gas constant
There is a linear dependency between composition and the logarithm of mobility [100]:
\[ \phi_B = \sum_i x_i \phi'_B + \sum_{i<j} x_i x_j \left( \sum_{r=0}^m \phi_{ij}^r (x_i - x_j)^r \right) \]  

(3-16)

\[ \phi_B = \ln M_B^0 = Q_B \]

\[ \phi'_B: \text{ Value of } \phi_B \text{ for pure } i \]

\[ \phi_{ij}^r: \text{ Binary interaction parameter} \]

\( x_i \) and \( x_j \): Mole fractions for elements i and j respectively

The interdiffusion coefficients can always be calculated from the mobilities when the thermodynamic factors are known.