Critical Evaluation and Thermodynamic Modeling of Phase Equilibria in the Fe-Ca-Mg-Mn-Al-Si-O System

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APRIL 2013

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of MASTER OF SCIENCE (M.Sc.)

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ACKNOWLEDGEMENTS

I would like to acknowledge and express my heartfelt gratitude to Dr. In-Ho Jung, whose continuous guidance and support made the completion of this work possible. He not only supervised me, but also challenged and encouraged me to work harder. I would also like to thank him for his helpful advices and constructive criticism.

I also want to thank all my group members for being like a second family to me. I would like to express my appreciation to all my friends and colleagues in lieu of the help and support I received from them. They have been very supportive whenever I faced a problem during my stay in Canada. I will always remain indebted to them.

I am grateful to have a very supportive family back in India and I would like to dedicate the thesis to them. They have never ceased to offer me the moral support to complete my study.

The present study is a part of a bigger project which is funded by National Sciences and Engineering Research Council of Canada in collaboration with Tata Steel, Hyundai Steel, Posco, Nucor Steel, Rio Tinto, Sumitomo Metals, JFE Steel Corporation, Nippon Steel, RHI and Voest Alpine. I would like to express my thankfulness to all of them for the financial support.
ABSTRACT

The knowledge of phase equilibria and thermodynamic properties of liquid and solid oxides can help us better understand metallurgical, ceramic or geological processes. The main aim of the present study is the critical evaluation and thermodynamic optimization of solid and liquid (MnO-Al₂O₃ based) oxides which are of interest to the steelmaking and ferro-Mn industries. These newly developed databases coupled with the previous databases can be used along with any software for Gibbs energy minimization to predict the phase relationships and the thermodynamic properties of any relevant system. Usually, thermodynamic databases can save both cost and time, which, otherwise would have been spent to optimize the existing process and develop any new process.

The production of steels with higher amounts of manganese and aluminum has gained considerable importance in the recent past. Steels with high concentration of manganese and aluminum like TWIP steel and TRIP steel have exceptional properties which classify them as special steels; needless to say the various range of applications they can cater to. Ferromanganese, which contains a large amount of manganese, is also a very useful product required in the production of high manganese steels. The production of these alloys results in the generation of slags which are rich in MnO and Al₂O₃. Hence, knowledge of the phase relations between these two components is of utmost importance in order to maximize the efficiency of the production process. Only a very good knowledge of Gibbs energy of all the phases present in the binary system MnO-Al₂O₃ can allow us to predict the correct equilibrium conditions during the production process.

The critical evaluation and thermodynamic optimization of all the available phase diagram data and thermodynamic properties of the system Mn-Al-O have been carried out in the first part of the present work. Thermodynamic modeling for different phases such as slag, spinel (cubic and tetragonal) and bixbyite has been performed using Modified Quasichemical Model, Compound Energy Formalism and random mixing model, respectively. The sublattice structure of solid solution phases were properly taken into account in the thermodynamic modeling and their thermodynamic properties and structural data were reproduced using the physically meaningful
All the reliable experimental data of the Mn-Al-O system were reproduced within error limits from room temperature to above the liquidus temperatures at all compositions and oxygen partial pressure ranging from metal saturation to air. The present MnAl₂O₄-Mn₃O₄ spinel solutions can be integrated with all the other spinel solutions developed earlier to obtain an extensive spinel solution database. This database along with the software for Gibbs energy minimization can be utilized to perform various calculations and predict the phase relations at any given condition.

In the next part of the present work, the binary MnO-Al₂O₃ system was extended to the higher order systems like MnO-Al₂O₃-SiO₂, CaO-MnO-Al₂O₃, FeO-MnO-Al₂O₃, MgO-MnO-Al₂O₃ and CaO-MnO-Al₂O₃-SiO₂. Other calculations related to inclusion engineering in steelmaking were also carried out. This was done to check the accuracy of the database developed for the binary MnO-Al₂O₃ system.

The database of model parameters can be used with thermodynamic software like Factsage for thermodynamic modeling of various industrial and natural processes. Calculations pertaining to prediction of thermodynamic properties of phases, cation distribution in spinel solutions, phase equilibria at any temperature, composition and oxygen partial pressure where no experimental data are available can also be performed.
RÉSUMÉ

La connaissance des équilibres de phase et des propriétés thermodynamiques des oxydes solides et liquides peut aider à mieux comprendre les processus métallurgiques, céramiques et géologiques. Le but principal de la présente étude est l’évaluation critique et l’optimisation thermodynamique des oxydes solides et liquides impliquant MnO-Al₂O₃ qui sont d’intérêt pour les industries de l’acier et du ferromanganèse. Les nouvelles bases de données développées, couplées avec d’anciennes bases de données, peuvent être utilisées avec n’importe quel logiciel de minimisation de l’énergie de Gibbs pour prédire les équilibres de phase et les propriétés thermodynamiques de tout système pertinent. Habituellement, les bases de données permettent de sauver temps et argent qui, autrement, auraient pu être utilisés pour optimiser des processus existant et en développer de nouveaux.

La production d’aciers à teneur élevé en manganèse et aluminium a récemment acquis une importance considérable. Les aciers à teneur élevé en manganèse et aluminium, comme l’acier TWIP et l’acier TRIP, ont des propriétés exceptionnelles qui les classifient comme aciers spéciaux; inutile de mentionner le large éventail d’applications auxquels ils peuvent répondre. Le ferromanganèse, qui contient de grandes quantités de manganèse, est aussi un produit très utile dans la production d’aciers à haute teneur de manganèse. La production de tels aciers génère des scories riches en MnO et Al₂O₃. Par conséquent, la connaissance des relations de phases entre ces deux composés est d’une importance capitale pour maximiser l’efficacité du processus de production. Seule une bonne connaissance de l’énergie de Gibbs de toutes les phases présentes dans le système MnO-Al₂O₃ peut nous permettre de prédire les conditions correctes d’équilibre lors du processus de production.

L’évaluation critique et l’optimisation thermodynamique de toutes les données disponibles de diagrammes de phase et de propriétés thermodynamiques du système Mn-Al-O ont été réalisées dans la première partie de ce travail. La modélisation thermodynamique des différentes phases telles que le laitier, le spinelle (cubique et tétragonal) et la bixbyite a été respectivement effectuée à l’aide du Modèle Quasichimique Modifié, du Formalisme de l’Énergie des Composés et du modèle de mélange aléatoire. La structure du sous-réseau des solutions solides fut correctement prise en compte dans la modélisation thermodynamique et les propriétés
thermodynamiques et données structurales furent reproduites en utilisant des paramètres ayant une signification physique. Toutes les données expérimentales fiables du système Mn-Al-O ont été reproduites à l’intérieur des limites d’erreur de la température ambiante à au-dessus du liquidus pour toutes les compositions et à des pressions partielles d’oxygène allant de la saturation en métal jusqu’à l’air. Les solutions de spinelle MnAl$_2$O$_4$-Mn$_3$O$_4$ peuvent être intégrées à toutes les autres solutions de spinelle développées antérieurement afin d’obtenir une base de données étendue pour le spinelle. Cette base de données, combinée à un logiciel de minimisation de l’énergie de Gibbs, peut être utilisée pour effectuer divers calculs et prédir les relations de phase dans n’importe quelles conditions données.

Dans la seconde partie de ce travail, le système binaire MnO-Al$_2$O$_3$ a été ajouté aux systèmes d'ordre supérieur tels que MnO-Al$_2$O$_3$-SiO$_2$, CaO-MnO-Al$_2$O$_3$, FeO-MnO-Al$_2$O$_3$, MgO-MnO-Al$_2$O$_3$ et CaO-MnO-Al$_2$O$_3$-SiO$_2$. Des calculs liés à l’ingénierie des inclusions impliquées dans la fabrication de l’acier ont également été effectuées. Ceci a été fait pour vérifier l'exactitude de la base de données développée pour le système binaire MnO-Al$_2$O$_3$.

La base de données des paramètres du modèle peut être utilisée avec un logiciel de thermodynamique comme FactSage pour la modélisation thermodynamique de divers procédés industriels et naturels. Les calculs relatifs à la prédiction des propriétés thermodynamiques des phases, la distribution des cations dans les solutions spinelle et les équilibres entre phases à n'importe quelle température, composition et pression partielle d'oxygène où aucune donné expérimentale n’est disponible, peuvent également être effectuées.
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<td>Molar Heat Capacity (J/mol-K)</td>
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<td>Standard Gibbs energy of $i$</td>
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<td>$G^m$</td>
<td>Gibbs energy of solution</td>
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<td>$G^E$</td>
<td>Excess Gibbs energy in solution</td>
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<tr>
<td>$g^E$</td>
<td>Molar excess Gibbs energy in Solution</td>
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<tr>
<td>$g^o_i$</td>
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<td>Molar enthalpy of mixing</td>
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<td>Enthalpy of formation of the compound from the elements</td>
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<td>Number of moles of $i$-$j$ bonds in one mole of the solution</td>
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<td>$q^{ij}_{AB}$</td>
<td>Excess interaction parameter between A and B</td>
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<td>$S^o_i$</td>
<td>Standard entropy of component $i$</td>
</tr>
<tr>
<td>$\Delta S_T$</td>
<td>Entropy of formation of the compound from the elements</td>
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Chapter 1

Introduction

Computational thermodynamics have taken a huge leap ahead in the last few decades with the development of computer power. Since then, there have been numerous applications of computational thermodynamics to industrial processes. The availability of an extensive and accurate thermodynamic database is a prerequisite for proper thermodynamic calculations in complex systems. The present study aims at extending the present FactSage [1] oxide databases which can be later used for numerous applications. Prediction of thermodynamic properties and phase equilibria in multicomponent systems is necessary to understand the reaction mechanisms of various industrial processes. This can help us in bringing about considerable improvements and developing new technologies in industries. Numerical simulation is gaining widespread acceptance in almost all industrial applications as this is a powerful tool which helps save both money and time, which would have, otherwise, been spent on performing real experiments. In order to keep pace with the industrial processes, proper thermodynamic models and databases must be developed which would be able to predict the thermodynamic properties and phase equilibria in complex systems.

The aim of the present study is to create an extensive thermodynamic database for multicomponent oxide systems of industrial interest. All the available experimental data in the literature are critically evaluated and this is followed by thermodynamic optimization of the given chemical system which is done by obtaining one set of model equations for the Gibbs energies of all the phases as functions of temperature and composition. The success of this method depends on the choice of the model. The model should predict the Gibbs energy of the phase in a reliable and convenient manner.

The main purpose of the present study is to model the MnAl$_2$O$_4$ spinel solid solution properly considering the excess solubility of Al$_2$O$_3$. Then, the oxide systems containing MnAl$_2$O$_4$ spinel solution are reoptimized. This includes:
i.) MnO-Mn$_2$O$_3$-Al$_2$O$_3$

ii.) MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$

iii.) MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-CaO

iv.) MnO-Mn$_2$O$_3$-Al$_2$O$_3$-MgO

v.) MnO-Mn$_2$O$_3$-Al$_2$O$_3$-FeO
References

Chapter 2

Thermodynamic modeling

2.1 History of CALPHAD

CALPHAD, an abbreviation for CALculation of PHAse Diagrams, means Computer Coupling of Phase Diagrams and Thermochemistry. Phase diagram is an important tool which helps us understand the thermodynamic phase equilibria that exists between multiple phases. Real industrial processes, almost always, involve multicomponent systems whose phase diagrams are not very well known. The construction of phase diagrams for multicomponent systems based only on experiments is very difficult and time consuming. Hence, an attempt was made to construct multicomponent thermodynamic databases in the late 1960’s by using the advancing computational powers. The creation of multicomponent databases would help in understanding the phase equilibria and thermodynamic properties of multicomponent systems in a better manner.

CALPHAD method has been used by several large research groups across the worlds that perform thermodynamic modeling of large systems. The Thermo-Calc group [1] in Sweden, the THERMODATA group [2] in France, Thermotech Inc. [3] in UK, the thermochemical group at NIST [4] in USA, the FACT group (Bale et al. [5], Factsage [6]) in Canada, the MTDATA group [7] in UK and the IRSID group in France are some of the well-known groups in this field. The Scientific Group ThermoData Europe [8] was organised as a consortium of research groups to accelerate the development of alloy databases. These groups have developed several useful softwares and databases which have had useful applications in academic and industrial scales.

2.2 The CALPHAD technique

The CALPHAD technique for the thermodynamic database development includes the following steps:

a. Definition of the system which is to be thermodynamically optimized.
b. Collection of all available experimental data in literature: Experimental data includes thermodynamic data, phase diagram data, crystal structure data and if necessary, data related to physical properties.

i. Thermodynamic data: vapour pressure, chemical potential, activity, heat capacity, enthalpy, etc.

ii. Phase diagram data: isothermal phase diagram, liquidus projection, isopleths, etc.

iii. Crystal structure data: cation distribution between different sublattices, lattice parameters, etc.

iv. Physical properties: magnet data, conductivity, etc.

Moreover, useful data from higher order systems can be interpolated for sub-systems that have very few or no experimental data at all.

c. Selection of proper models:

The choice of a proper thermodynamic model based on the structure of the phase is of utmost importance. This is because only a proper model can yield good predictions for the multicomponent solution properties from the model parameters optimized for model parameters.

d. Critical evaluation of experimental data:

The experimental data on the same system might differ from article to article. Also, two different articles might report different types of experimental data which are actually, connected in terms of Gibbs energy. Hence, all the reported literature data must be evaluated critically based on the sample preparation techniques, experimental conditions involved, experimental and analytical techniques used, etc. The accuracy of the data can be often judged during the optimization of the entire system and in some cases the accuracy of the data in lower-order systems can be evaluated from the data in higher-order systems by interpolation.
e. Optimization of the model parameters:
   The next step after the evaluation of experimental data is optimization of the minimum number of reasonable model parameters for each phase. Once back-calculation reproduces the reliable experimental data within the experimental error limits, the optimization process can be considered to be complete.

f. Back-calculation of all thermodynamic and phase diagram data:
   Any type of thermodynamic calculations can be made by utilizing the optimized model parameters for each phase. The FactSage™ (FactSage 6.3)™ thermochemical software was used in the present study to perform all the calculations.
References


Chapter 3

Thermodynamic models

The thermodynamic model for a particular solution should be chosen based on its actual structure. Each thermodynamic model for solution has different function to calculate entropy of solution, which is one of the key factors affecting the Gibbs energy of solution. Therefore, different models can be used for different solutions depending on the crystal structure of the solution. A good model is one which can describe all the thermodynamic properties with the help of a small number of model parameters. The model also has a high predictive ability when it is based on the real structure of the solution.

General relations between thermodynamic properties

Pure substances:

The standard Gibbs energy of a pure component ‘i’ is written as:

\[ G_i^0 = H_i^0 - TS_i^0 \]  

(3.1)

where \( G_i^0 \), \( H_i^0 \) and \( S_i^0 \) are the standard Gibbs energy, enthalpy and entropy of component ‘i’ respectively and \( T \) is the absolute temperature.

Bragg-Williams Random Mixing Solution:

Let us consider a solution of two components A and B. When the components are mixed randomly, the entropy of the solution can be expressed by the Bragg-Williams random entropy function. The Gibbs energy of the solution is also affected by the interactions between A and B. We assume that there is no interaction between the constituent components for an ideal solution.

The Gibbs energy of an ideal solution can be written as:

\[ g^m = (g_A^0 X_A + g_B^0 X_B) - T \Delta S_{\text{config}} \]  

(3.2)

\[ \Delta S_{\text{config}} = -R (X_A \ln X_A + X_B \ln X_B) \]  

(3.3)
where $g^m$ is the molar Gibbs energy of solution, $g_i^0$ is the molar Gibbs energy of the component ‘$i$’, $\Delta S^{config}$ is the molar configurational entropy of solution and $X$ denotes the mole fraction of any component.

When the interactions between the components are not zero, so the Gibbs energy of solution can be written as:

$$g^m = (g_A^0 X_A + g_B^0 X_B) - T\Delta S^{config} + g^E$$

(3.4)

where $g^E$ is the excess molar Gibbs energy which can be expanded as a polynomial in the mole fractions as:

$$g^E = \sum_{ij} q_{ij} X_i X_j$$

(3.5)

where $q_{ij}$ terms represent the excess interaction parameters which can be expanded in terms of temperature as $a + bT + cT^2 + \ldots$

If only $q_{AB}^{11}$ is used to describe the thermodynamic properties of a solution, it is known as a “regular” solution. If $q_{AB}^{ij}$ terms are dependent on temperature then the non-configurational entropy term is non-zero.

In the present study, solution phases such as liquid slag, spinel, bixbyite and monoxide are described using specific thermodynamic models which are based on the real liquid or crystal structures of the solutions.

### 3.1 Spinel

#### 3.1.1 Crystal structure
Spinel belongs to the space group $Fd\bar{3}m$. The structure of spinel is shown schematically in Fig. 3.1. In the $AB_2O_4$ unit cell, A atoms are located in the 8 tetrahedral positions (represented by green circles in the Fig. 3.1), B atoms in the 16 octahedral positions (represented by red circles) and oxygen atoms in the 32 positions (represented by blue circles). Since the unit cell contains 32 oxygen atoms, so, there are eight $AB_2O_4$ formula units. The lattice parameters in oxide spinels generally ranges between 0.8 – 0.9 nm. A simple spinel usually contains two different cations $A^{2+}$ and $B^{3+}$ in the ratio 1:2. All spinels may be classified theoretically into three classes, normal, inverse and mixed based on the distribution of cations in the sites. A normal spinel is one in which the more abundant ($B^{3+}$) cations reside in the octahedral sites, whereas a fully inverse spinel is one in which the B cations are evenly split between tetrahedral and octahedral sites. However, all real spinels generally fall in the category of ‘mixed spinels’, i.e. both the cations in a simple spinel are present in both tetrahedral and octahedral sites.

All the well-known spinels, e.g., $MgAl_2O_4$ (spinel), $MnAl_2O_4$ (galaxite), $Fe_3O_4$ (magnetite), $FeAl_2O_4$ (hercynite), $FeCr_2O_4$ (iron chromite), $MgFe_2O_4$ (magnesium ferrite), $MgCr_2O_4$ (magnesium chromite), $CoAl_2O_4$, $NiAl_2O_4$, $ZnAl_2O_4$, $NiFe_2O_4$ are stable at 1 bar total pressure. However, some spinels are stable at high-pressures because, the olivine structure ($A_2SiO_4$) transforms to spinel structure at high-pressures. The oxide spinels can dissolve oxides of the type $\gamma-A_2O_3$, e.g., $\gamma-Al_2O_3$, $\gamma-Fe_2O_3$, $\gamma-Cr_2O_3$, etc. This leads to the introduction of vacancies in the octahedral sites which eventually results into wide ranges of solid solution.

The distributions of the cations in a spinel structure vary with the temperature. Now, we will define two terms (unquenchable temperature and frozen temperature) in order to elucidate the variation of cation distribution with temperature. The unquenchable temperature, abbreviated as $T_{unquench}$, is the minimum temperature above which cation distribution between the tetrahedral and octahedral sites is unquenchable. The reason for this is that the ordering-disordering process is fast at this temperature and quenching is not a good choice to get a proper value for cation distribution. The frozen temperature, abbreviated as $T_{froz}$, is the maximum temperature below which an equilibrium distribution of cations is not reached because the ordering-disordering process becomes slow at this temperature. Jung [1] concluded that $T_{froz}$ in the case of $MgAl_2O_4$
spinel was found to be around 973K (i.e. as those samples were cooled from a temperature lower than 973K, the cation distribution for the spinel was found to be frozen). Similarly, he concluded that the $T_{unquench}$ was around 1200K as the high-temperature cation distribution could not be retained by quenching. The probable solution to this problem is *in situ* measurements.

In case of spinels like Fe$_3$O$_4$ (magnetite), FeAl$_2$O$_4$ (hercynite), FeCr$_2$O$_4$ (iron chromite), etc. which have ferro- or antiferro-magnetic properties or other anomalies, special considerations must be made during the thermodynamic modeling of the spinel solutions.

### 3.1.2 Compound Energy Formalism (CEF) for spinel solid solution

The two-sublattice spinel model given by Degterov *et al.* [2] in the framework of the Compound Energy Formalism (CEF) (Hillert *et al.* [3]) has been used to model the spinel phase in the present study. The Gibbs energy of spinel solution in the CEF per formula unit can be expressed as:

$$G = \sum_i \sum_j y_i^T y_j^O G_{ij} - TS_{\text{config}} + G^{\text{excess}}$$

(3.6)

where, $y_i^T$ and $y_j^O$ represents the site fractions of cations in the tetrahedral and octahedral sites respectively; $G_{ij}$ is the Gibbs energy of any end-member $(i)^T(j)^O O_4$ in which cation ‘i’ occupies the tetrahedral site and cation ‘j’ occupies the octahedral site; $S_{\text{config}}$ is the configurational entropy which takes into account the random mixing of the cations on each sublattice and it can be expressed as:

$$S_{\text{config}} = -R\left(\sum_i y_i^T \ln y_i^T + 2\sum_j y_j^O \ln y_j^O\right)$$

(3.7)

$G^{\text{excess}}$ ($G^E$) is expressed as:

$$G^E = \sum_i \sum_j \sum_k y_i^T y_j^O y_k^O L_{gjk} + \sum_i \sum_j \sum_k y_i^T y_j^O y_k^O L_{kij}$$

(3.8)
where, $L_{i,j,k}$ parameters denote the interaction between cations ‘$i$’ and ‘$j$’ on the first sublattice when the second sublattice is occupied only by ‘$k$’ cations and similarly the parameters $L_{k:i,j}$ denote the interaction between cations ‘$i$’ and ‘$j$’ on the second sublattice when the first sublattice is occupied only by ‘$k$’ cations. One important assumption according to the model is that the interaction between the same two cations present on one sublattice will not change on changing the cation on the other sublattice, i.e.,

$$L_{k:i,j} = L_{q:i,j} = .......$$  \hspace{1cm} (3.9)  \\

$$L_{q:j,k} = L_{q:j,i} = .......$$  \hspace{1cm} (3.10)  \\

Redlich-Kister power series expansions given by Redlich and Kister \cite{4} and Pelton and Bale \cite{5} can be used to express the dependence of interaction energies on composition as follows:

$$L_{q:j,k} = \sum_{m}^{m} L_{q:j,k} (y_{j}^{T} - y_{i}^{T})^{m}$$  \hspace{1cm} (3.11)  \\

$$L_{k:i,j} = \sum_{m}^{m} L_{k:i,j} (y_{j}^{O} - y_{i}^{O})^{m}$$  \hspace{1cm} (3.12)  \\

The end-member Gibbs energies $G_{ij}$ are used to describe the concerned system. However, it is difficult to experimentally determine all the end-member Gibbs energies. Certain linear combinations of the end-member Gibbs energies pertaining to certain site exchange reactions occurring between the cations present in the system were chosen as the model parameters. High predictive ability of the model could be obtained in this case. Moreover, it’s more reasonable and logical to choose combinations of $G_{ij}$, which have certain physical significance, as the model parameters rather than fixing the $G_{ij}$ to some arbitrary value. $G_{AB} = G_{O}^{O}(AB_{2}O_{4})$, the measurable Gibbs energy of pure normal $AB_{2}O_{4}$ is used as a model parameter for a fully normal spinel.
The combinations of Gibbs energies are actually the Gibbs energies of site exchange reactions of the cations present in the tetrahedral and octahedral sites and they are usually denoted as $\Delta$ and $I$ parameters.

The Gibbs energies similar to the following reaction:

$$\text{AB} + \text{BA} = \text{AA} + \text{BB} \quad (3.13)$$

given by $\Delta_{AB} (= G_{AA} + G_{BB} - G_{AB} - G_{BA})$ are used as model parameters. O’Neill and Navrotsky [6] found out that the parameters should have values of about 40kJ/mol.

Inversion ($I$) parameters, described as:

$$I_{AB} = G_{BB} + G_{BA} - 2G_{AB} \quad (3.14)$$

usually determine the cation distribution of the spinels.

The present study is concerned mainly with the modeling and optimization of spinel containing Mn in variable valency states such as 2+, 3+, and 4+. Therefore, the structure of the spinel solution and the Gibbs energy functions are more complex. These things will be elaborated in chapter 4.

3.2 Slag (molten oxide)

3.2.1 Structure

Fig. 3.2 shows the structure of sodium silicate glass by Warren and Biscoe [7]). The silicon atoms are surrounded by 4 oxygen atoms which are arranged in the form of a tetrahedron. The Si and O atoms form SiO$_4$ tetrahedra which forms chains or rings joined by bridging oxygens (BO). Cations such as Na$^+$, Fe$^{2+}$, Mn$^{2+}$, Ca$^{2+}$, etc. tend to break these BO and form non-bridging oxygens (NBO), O$^-$, or free oxygen ions, O$^{2-}$. The silicate melt contains various 3 dimensional interconnected anion units such as SiO$_4^{4-}$, Si$_2$O$_5^{2-}$, etc. which are observed in the melt. If $T$ is the
number of tetrahedrally coordinated atoms such as Si, then the ratio ‘NBO/T’ signifies the degree of depolymerisation of a silicate melt. This ratio affects the physical properties of the melts such as viscosity, thermal conductivity, etc.

### 3.2.2 The Modified Quasichemical Model (MQM)

The Modified Quasichemical Model (MQM), which takes into account the short-range-ordering of second-nearest-neighbor cations, has been used to describe the molten oxide. The model has been described in details by Pelton and Blander [8] and Pelton and Blander [9] and more recently by Pelton et al. [10] and Pelton and Chartrand [11].

The reaction depicting the formation of two 1-2 pair bonds from a 1-1 and a 2-2 pair in a binary system is shown below:

\[(1-1) + (2-2) = 2 (1-2)\]  \hspace{1cm} (3.15)

If the Gibbs energy change for the reaction is considered to be \(\Delta g_{12}\) and the coordination numbers of atoms (or molecules) 1 and 2 be \(Z_1\) and \(Z_2\) respectively, then the total number of bonds emanating from an ‘i’ atom, ion or molecule will be \(Z_iX_i\). The mass balance equations can be written as:

\[Z_1X_1 = 2n_{11} + n_{12} \hspace{1cm} \text{and} \hspace{1cm} Z_2X_2 = 2n_{22} + n_{12}\]  \hspace{1cm} (3.16)

where \(n_{ij}\) is the total number of bonds in one mole of the solution.

Three important quantities, namely pair fractions \(X_{ij}\), overall mole (or site) fractions \(X_i\) (or \(y_i\)) and coordination-equivalent fractions \(Y_i\) have been defined in the equations 3.17, 3.18 and 3.19 respectively.
\[ X_{ij} = \frac{n_{ij}}{n_{11} + n_{22} + n_{12}} \]  
(3.17)

\[ X_1 = 1 - X_2 = \frac{n_1}{n_1 + n_2} \]  
(3.18)

\[ Y_1 = 1 - Y_2 = \frac{Z_1 X_1}{(Z_1 X_1 + Z_2 X_2)} \]  
(3.19)

where the total number of pairs in one mole of solution is \((Z_1 X_1 + Z_2 X_2)/2\). Equation 3.16 can now be rewritten in terms of pair fractions as follows:

\[ Y_1 = X_{11} + X_{12}/2 \quad \text{and} \quad Y_2 = X_{22} + X_{12}/2 \]  
(3.20)

Hence, we may express the Gibbs energy of the solution as:

\[ G = (n_1 g_1^o + n_2 g_2^o) - T \Delta S^{\text{config}} + (n_{12}/2) \Delta g_{12} \]  
(3.21)

where \(g_1^o\) and \(g_2^o\) are the molar Gibbs energies of the pure components, and \(\Delta S^{\text{config}}\) is the configurational entropy of mixing considering random mixing of the (1-1), (2-2) and (1-2) pairs.

\[ \Delta S^{\text{config}} = -R(n_1 \ln X_1 + n_2 \ln X_2) - R[n_1 \ln (X_{11}/Y_1^2)] \]

\[ + n_{22} \ln (X_{22}/Y_2^2) + n_{12} \ln (X_{12}/2Y_1 Y_2)] \]  
(3.22)

The equilibrium distribution can be calculated by minimizing \(G\) with respect to \(n_{12}\) at constant composition. This gives us a quasichemical equilibrium constant for the reaction (3.15) which may be written as:

\[ \frac{X_{12}^2}{X_{11} X_{22}} = 4 \exp(-\frac{\Delta g_{12}}{RT}) \]  
(3.23)
When $\Delta g_{12} = 0$, the solution of the equations (3.19) and (3.20) gives a random distribution with $X_{11} = Y_1^2$, $X_{22} = Y_2^2$ and $X_{12} = 2Y_1Y_2$, and equation (3.22) reduces to ideal Raoultian entropy of mixing.

When $\Delta g_{12}$ becomes very negative, 1-2 pairs predominate resulting in the plot of enthalpy versus composition to become V-shaped and plot of $\Delta S^{\text{config}}$ versus composition to become m-shaped with minima at $Y_1 = Y_2 = \frac{1}{2}$.

When $\Delta g_{12}$ becomes positive, (1-1) and (2-2) pairs dominate. Hence, the quasichemical model can also treat such clustering which involves positive deviation from ideality. In the modified quasichemical model, $\Delta g_{12}$ is the model parameter which has to be optimized. The $\Delta g_{12}$ parameter is usually expanded as a polynomial in terms of equivalent fractions.

**3.2.3 Interpolation techniques**

The binary model parameters of the liquid phase can be interpolated in order to estimate the properties of ternary and higher order liquid solution. This can be performed using various geometric models (Pelton and Chartrand [11]). The selection of the geometric model for the interpolation of the binary model parameters to ternary system can be made depending on the nature of each binary system bounding the ternary system.

Several geometric models may be proposed for ternary system. Fig. 3.3 illustrates some of the models that may be used.

Fig. 3.3 (a) and (b) show the Kohler and the Muggianu models respectively, which are symmetric models. Fig. 3.3(c) and (d) show the Kohler/Toop and Muggianu/Toop models respectively, which are asymmetric (component 1 is asymmetric). Gibbs energy of ternary or multicomponent solution can be expressed as:

$$G = \sum_i n_i g_i - T \Delta S^{\text{config}} + \sum_{i \neq j} \frac{n_i n_j}{2} \Delta g_{ij}$$

(3.24)
where $\Delta g_{ij} = \Delta g_{ij}^0 + \sum_j q_{ij}^{mn} Y_i^m Y_j^n$

$\Delta g_{ij}^0$ and $q_{ij}^{mn}$ are empirical binary coefficients, which may be functions of temperature and pressure and $Y_i^m, Y_j^n$ are equivalent fractions. Depending on the interpolation technique, the interaction energy $\Delta g_{ij}$ can be expressed differently:

(a). Symmetric Model:

$\Delta g_{12}$ in the binary subsystem can be expressed as a polynomial in terms of the equivalent fractions as:

$$\Delta g_{12} = (\Delta g_{12}^0 + \sum_{i+j \neq 1} q_{ij}^{12} \left( \frac{Y_1}{Y_1 + Y_2} \right)^i \left( \frac{Y_2}{Y_1 + Y_2} \right)^j) + \sum_{\kappa \neq 1 \atop j \geq 0} q_{i12(3)}^{jk} \left( \frac{Y_1}{Y_1 + Y_2} \right)^i \left( \frac{Y_2}{Y_1 + Y_2} \right)^j \left( \frac{Y_3}{Y_2 + Y_3} \right)^k$$

The first term of the above equation is constant along line 3-a in Fig. 3.3 (a) and is equal to $\Delta g_{12}$ in the 1-2 binary at point a. The second summation term consists of ‘ternary terms’ that are all zero in the 1-2 binary system and it depicts the effect of presence of component 3 on the $\Delta g_{12}$ term. The empirical coefficients $q_{i12(3)}^{jk}$ are found by the optimization of ternary experimental data.

(b). Asymmetric Model:

$\Delta g_{12}$ in the ternary solution can be expressed as:

$$\Delta g_{12} = (\Delta g_{12}^0 + \sum_{i+j \leq 1} q_{ij}^{12} Y_i^j (1-Y_1)^i + \sum_{\kappa \neq 1 \atop j \geq 0} q_{i12(3)}^{jk} Y_1^i (1-Y_1)^i \left( \frac{Y_3}{Y_2 + Y_3} \right)^k$$

The binary terms are constant along the line a-c and equal to their values at point a in Fig. 3.3 (c).
3.3 Monoxide solution

3.3.1 Crystal structure

The monoxide solid solution belongs to the space group $Fd\bar{3}m$. The monoxide solution is also known as the “halite (rock salt)” solution since its structure is same to that of NaCl (halite). A schematic structure of NaCl is shown in Fig. 3.4. The monoxide is generally of the type MO oxides where M is a divalent cation such as Mn$^{2+}$, Mg$^{2+}$, Fe$^{2+}$, Ca$^{2+}$, etc. Almost complete solid solubility can be observed across the entire range of compositions in most of the cases. Moreover, additional solubilities of N$_2$O$_3$ type of oxides can be observed (N is a trivalent cation such as Fe$^{3+}$, Cr$^{3+}$, Al$^{3+}$, etc.). The mixing occurs only on the cation sites for divalent metals when two MO oxides mix in the monoxide solution. However, it is not quite well understood how the dissolution of the N$_2$O$_3$ type of oxides take place.

3.3.2 Random mixing model

The Gibbs energy of the monoxide solution can be expressed as follows:

$$ G = \sum_i y_i G_i^O - T \Delta S_{\text{config}} + G^E $$

$$ G^E = y_i^m y_j^n \sum_i \sum_j I_{ij}^{mn} $$

where $y_i$, $y_j$ denote the site fraction of cations ‘$i$’ and ‘$j$’ respectively in the first sublattice; $G_i^O$ is the Gibbs energy of pure member; $L_{ij}$ is the binary interaction parameter; m, n are the power terms of the interaction parameter.

3.4 Bixbyite solution

3.4.1 Crystal structure

Bixbyite is Mn$_2$O$_3$-rich solid solution. It has a cubic structure above room temperature and can dissolve certain amount of trivalent N$_2$O$_3$ type oxides (N is a trivalent cation such as Fe$^{3+}$, Cr$^{3+}$, Al$^{3+}$, etc.). Fig. 3.5 shows the schematic crystal structure of bixbyite. The bixbyite solid solution
has $I\alpha\bar{3}$ symmetry. Mn and O ions are octahedrally and tetrahedrally coordinated, respectively. Mn and O ions fill 3/4 of the tetrahedral interstitials. The $\alpha$-Mn$_2$O$_3$ transforms from cubic to orthorhombic structure with $Pbca$ symmetry below 300K (Cockayne et al. [12]).

### 3.4.2 Random mixing model

The Gibbs energy of the bixbyite solid solution can be expressed in a way similar to that as shown in equation (3.27). The sublattice structure is

$$[Mn^{3+}, N^{3+}]_2O_3$$

where $N^{3+}$ is a trivalent cation $Al^{3+}, Cr^{3+}, Fe^{3+}$, etc.

### 3.5 Corundum solution

#### 3.5.1 Crystal structure

Corundum phase implies $Al_2O_3$-rich solid solutions which have trigonal structure where the O atoms are hexagonally coordinated as shown in Fig. 3.6 (a). Pauling and Hendricks [13] stated that each aluminium atom is surrounded by six oxygen atoms, which are not at the corners of a regular octahedron. Three of the O atoms were nearer to the metal atom than the other three indicating that location of electrons in the outer shells of an ion causes them to have different effective radii in different directions.

They also stated that each O atom was surrounded by four Al atoms, two of which are closer than the other two. Fig. 3.6 (b) shows the findings of Pauling and Hendricks [13]. Corundum crystallizes in the space group $R3\bar{c}$. It can also dissolve $N_2O_3$ type of oxides (N is a trivalent cation such as $Fe^{3+}, Cr^{3+}, Mn^{3+}$, etc.). The corundum solid solution can form complete solid solution between $Al_2O_3$, $Cr_2O_3$ and $Fe_2O_3$.

#### 3.5.2 Random mixing model

The Gibbs energy of the corundum solution can be expressed in a way similar to that as shown in equation (3.27). The sublattice structure can be expressed as:
\[ [Al^{3+}, M^{3+}]_2O_3 \]  \hspace{1cm} (3.30)

where \( M^{3+} \) is a trivalent cation like \( Mn^{3+}, Cr^{3+}, Fe^{3+} \), etc.

**3.6 Liquid Fe solution**

A thermodynamic model for the deoxidation equilibria was proposed by Jung *et al.* [14] and it was found to work very well in most of the systems. The parameters related to the Gibbs energy of formation of each associate during deoxidation reactions in steelmaking are stored in the FTmisc-FeLQ database [15]. All the calculations related to liquid iron solution in the present study were performed by using the FTmisc-FeLQ database [15].
References


Figure 3.1: Structure of a unit cell of spinel $\text{AB}_2\text{O}_4$ (From Mathew [17]).

Figure 3.2: Structure of sodium silicate glass by Warren and Biscoe [7].
Figure 3.3: Geometric models used to estimate ternary thermodynamic data from optimized binary data (Chartrand and Pelton [16]).

Figure 3.4: Crystal structure of a NaCl which is isostructural with monoxides.
Figure 3.5: Crystal structure of bixbyite (Cockayne et al. [12]).

Figure 3.6: Crystal structures of corundum (α-Al₂O₃): (a) From Askeland and Phulé [18] and (b) From Pauling and Hendricks [13].
Chapter 4

Thermodynamic modeling of the MnO-Mn₂O₃-Al₂O₃ system

4.1 Introduction

The binary system have been studied by a number of researchers earlier (Hay et al. [1], Oelsen and Heynert [2], Ranganathan et al. [3], Novokhatskii et al.[4], Fischer and Bardenheuer [5], Dekker and Rieck [6], Jacob [7] and Golikov et al. [8]). Many researchers also tried to optimize the system previously (Eriksson et al. [9], Jung et al. [10], Farina and Neto [11] and Navarro et al. [12]). Profound experimental data on the Gibbs energy of formation of MnAl₂O₄ (the spinel present in the MnO-Al₂O₃ system) is available in the literature. However, the activity data of MnO is limited in the system. Hence, it is of utmost importance that we pay proper attention to the thermodynamic data of MnAl₂O₄ in order to achieve good results in optimization. Eriksson et al. [9] were able to reproduce the activities of MnO in the ‘MnAl₂O₄ and liquid’ two phase region, but, they were unsuccessful in reproducing the activities of MnO in the ‘Al₂O₃ and MnAl₂O₄’ region. The optimized parameters by Eriksson et al. [9] when later used to calculate the phase diagrams and thermodynamic properties of the multicomponent systems containing the MnO-Al₂O₃ system gave erroneous results. Jung et al. [10] carried out the optimization of the MnO-Al₂O₃ system by considering the spinel solid solution MnAl₂O₄ as a line compound. Moreover, they considered only Mn²⁺ species in the slag. The optimized Gibbs energy of MnAl₂O₄ by Farina and Neto [11] was not in agreement with any of the experimentally determined values. They were also unable to reproduce the activities of MnO in the ‘Al₂O₃ and MnAl₂O₄’ region although they could calculate the congruent melting behaviour of MnAl₂O₄.

Recently, Navarro et al. [12] modeled the slag phase in the MnO-Al₂O₃ system using the Kapoor-Frohberg-Gaye quasi-chemical model and they considered spinel solid solution MnAl₂O₄ as a stoichiometric compound.

In the present study, a complete thermodynamic description of the Mn-Al-O (MnO-Mn₂O₃-Al₂O₃) system has been carried out. The MnAl₂O₄ phase has been modeled as a spinel solution which has actual cation distribution using the two sublattice spinel model by Degterov et al. [13] in the framework of Compound Energy Formalism (Hillert et al. [14]). The slag phase has been
modeled considering both the Mn\textsuperscript{2+} and Mn\textsuperscript{3+} species using the Modified Quasichemical Model (Pelton and Blander [15], Pelton and Blander [16], Pelton et al. [17], Pelton and Chartrand [18]). The main aim of the present study is to carry out a critical evaluation and thermodynamic optimization of all the properties and phase diagrams related to the MnO-Al\textsubscript{2}O\textsubscript{3} system at pressures ranging from metal saturation to air in order to obtain Gibbs energies of all phases as functions of temperature and composition.

**4.2 Phases and thermodynamic models**

The calculated phase diagram of the (Mn-Al-O) MnO-Mn\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} system at 1000°C and 1 bar total pressure is shown in Fig. 4.1. The following solution phases are found in the Mn-Al-O system:

Cubic spinel (encompassing cubic-Mn\textsubscript{3}O\textsubscript{4}, MnAl\textsubscript{2}O\textsubscript{4} with limited solubility of Al\textsubscript{2}O\textsubscript{3}):

\((\text{Mn}^{2+}, \text{Al}^{3+})^T [\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Mn}^{4+}, \text{Al}^{3+}, \text{Va}]_2^0 \text{O}_4\)

Tetragonal spinel (limited solution extended from tetragonal-Mn\textsubscript{3}O\textsubscript{4}):

\((\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Al}^{3+})^T [\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Al}^{3+}, \text{Va}]_2^0 \text{O}_4\)

Slag (molten oxide phase): MnO-MnO\textsubscript{1.5}-AlO\textsubscript{1.5}

Monoxide: MnO-rich solution containing small amount of AlO\textsubscript{1.5} and MnO\textsubscript{1.5}

Bixbyite: Mn\textsubscript{2}O\textsubscript{3}-rich solution containing small amount of Al\textsubscript{2}O\textsubscript{3}

Corundum: Al\textsubscript{2}O\textsubscript{3}-rich solution containing small amount of Mn\textsubscript{2}O\textsubscript{3}

Alloy phases: liquid, bcc, fcc, sigma and so on

Cations shown within a set of brackets for spinels occupy the same sublattice. T and O represent the tetrahedral and octahedral cationic sites in spinel respectively. The magnetic properties of spinel and bixbyite were not seriously modeled in the present study because the critical temperatures are less than 100 K and its contributions to heat capacities were considered to the entropy of 298 K.
4.2.1. Spinel: Cubic and Tetragonal

There are two different cation sites in spinels: tetrahedral and octahedral sites. Thus, distribution of cations between these two sublattices is the most important physical and thermodynamic property of spinel. There are two types of spinel phases in the Mn-Al-O system: cubic and tetragonal spinels. Mn₃O₄ has tetragonal spinel structure and it transforms to cubic spinel over 1180°C in air. Although tetragonal Mn₃O₄ spinel can dissolve small amount of Al, cubic Mn₃O₄ spinel can extend up to Al₃O₄. Dorris and Mason [19] found that these two Mn₃O₄ spinels have different ionic configuration from their electrochemical seed-back experimental technique. In the case of cubic spinel, Mn²⁺ are on tetrahedral sites and Mn²⁺, Mn³⁺ and Mn⁴⁺ are on octahedral sites: \((\text{Mn}^{2+})\text{T}[\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Mn}^{4+}]\text{O}_4\). However, in the case of tetragonal spinel, both Mn²⁺ and Mn³⁺ cations can enter both tetrahedral and octahedral sites: \((\text{Mn}^{2+}, \text{Mn}^{3+})\text{T}[\text{Mn}^{2+}, \text{Mn}^{3+}]\text{O}_4\). When Mn₃O₄ spinel is mixed with MnAl₂O₄ spinel to form spinel solid solution, Al³⁺ can enter in both tetragonal and octahedral sites of the spinel. Vacancy could exist on octahedral sites for both cubic and tetragonal spinels. This structural information was properly implemented in the development of the present thermodynamic models for the cubic and tetragonal spinel phases in the Mn-Al-O system.

Both spinel models were developed within the framework of the Compound Energy Formalism (CEF) (Hillert et al. [14]). The Gibbs energy expression in the CEF per formula unit is:

\[
G = \sum_i \sum_j Y_i^T Y_j^O G_{ij} - TS_C + G^E
\]

(4.1)

where \(Y_i^T\) and \(Y_j^O\) represent the site fractions of constituents \(i\) and \(j\) on the tetrahedral and octahedral sublattices, \(G_{ij}\) is the Gibbs energy of an “end-member” \((i)\text{T}[j]\text{O}_4\) of the solution, in which the first sublattice is occupied only by cation \(i\) and the second only by cation \(j\), \(G^E\) is the excess Gibbs energy, and \(S_C\) is the configurational entropy assuming random mixing on each sublattice:

\[
S_C = -R\left(\sum_i Y_i^T \ln Y_i^T + 2\sum_j Y_j^O \ln Y_j^O\right)
\]

(4.2)
The excess Gibbs energy is expanded as:

\[ G^E = \sum_i \sum_j \sum_k Y_i^T Y_j^T Y_k^O L_{ij:k} + \sum_i \sum_j \sum_k Y_i^T Y_j^O Y_k^O L_{k:ij} \]  \hspace{1cm} (4.3)

where the parameters \( L_{ij:k} \) are related to interactions between cations \( i \) and \( j \) on tetrahedral sites when all octahedral sites are occupied by \( k \) cations, and similarly the parameters \( L_{k:ij} \) are related to interactions between \( i \) and \( j \) cations on octahedral sites when the tetrahedral sites are all occupied by \( k \) cations. One important assumption according to the model is that the interaction between the same two cations present on one sublattice will not change on changing the cation on the other sublattice, i.e.,

\[ L_{k:ij} = L_{k:ji} = \ldots \]  \hspace{1cm} (4.4)

\[ L_{ij:k} = L_{ji:k} = \ldots \]  \hspace{1cm} (4.5)

Redlich-Kister power series expansions given by Redlich and Kister [20] and Pelton and Bale [21] can be used to express the dependence of interaction energies on composition as follows:

\[ L_{ij:k} = \sum_m^m L_{ij:k} (y_j^T - y_i^T)^m \]  \hspace{1cm} (4.6)

\[ L_{k:ij} = \sum_m^m L_{k:ij} (y_j^O - y_i^O)^m \]  \hspace{1cm} (4.7)

The main model parameters are the end-member Gibbs energies, \( G_{ij} \). Certain linear combinations of the \( G_{ij} \) parameters which have physical significance are used as the optimized model parameters. Degterov et al. [13] had already discussed the physical significance of these linear combinations (\( I \) and \( \Delta \)). These linear combinations are related to the energies of classical site exchange reactions of cations. In this way, the model parameters could have certain physical meaning and it was found (Degterov et al. [13], Jung et al. [22], Jung et al. [23], Jung et al. [24], and Jung [25]) to be much easier to complete the thermodynamic modeling than individual
setting of $G_{ij}$ parameters without any reason. Moreover, high predictive ability of the model could be obtained. Details of the linear combinations of $G_{ij}$ parameters for both cubic and tetragonal spinels are given in Table 1. Please note that notations F, J, K, L and V were used for $\text{Al}^{3+}$, $\text{Mn}^{2+}$, $\text{Mn}^{3+}$, $\text{Mn}^{4+}$ and vacancy, respectively.

4.2.1.1. Cubic spinel

Cubic spinel has $(\text{Mn}^{2+}, \text{Al}^{3+})_2[\text{Mn}^{2+}, \text{Mn}^{3+}, \text{Mn}^{4+}, \text{Al}^{3+}, \text{Va}]_2\text{O}_4$ structure including vacancy (Va) on octahedral sites. The Gibbs energy diagram for the spinel is depicted in Fig. 4.2. Ten end-member Gibbs energies are required for the model. Among them, four Gibbs energies were already determined from the Mn-O system ($\text{Mn}_3\text{O}_4$) (Kang et al. [26]) and another two Gibbs energies ($G_{FF}$ and $G_{FV}$) were determined from the previous study of the Mg-Al-O system (Jung et al. [27]). Four other Gibbs energies have been determined in the present study. It should be also noted that many end-members have charges other than neutral. The real spinel solution should have neutral charge. In the diagram of Fig. 4.2, the neutral charge lines are depicted as dotted lines.

In order to determine the Gibbs energy of end-members, physically meaningful combinations of $G_{ij}$ have been considered. These are the model parameters optimized in the present study.

$G_{JF}$: Gibbs energy of completely normal $\text{MnAl}_2\text{O}_4$ spinel end-member

$$2JF = FF + FJ: \Delta G_{\text{rnx}} = I_{JF} = G_{FF} + G_{FJ} - 2G_{JF} \quad (4.9)$$

$$FF + JK = FK + JF: \Delta G_{\text{rnx}} = \Delta_{FJ,KF} = G_{FK} + G_{JF} - (G_{FF} + G_{JK}) \quad (4.10)$$

$$FF + JL = FL + JF: \Delta G_{\text{rnx}} = \Delta_{FJ,LF} = G_{FL} + G_{JF} - (G_{FF} + G_{JL}) \quad (4.11)$$

For example, the reaction (4.9) is basically a site exchange reaction between the normal and the inverse spinel. Hence, the Gibbs energy of this reaction ($I_{JF}$) should be the one which affects the degree of inversion of the spinel the most. So, proper variation in this ‘I’ parameter has been performed in order to reproduce the experimental cation distribution data and Gibbs energy of formation of the spinel, after determination of $G_{JF}$. Similarly, $\Delta$ parameters of two other site
exchange reactions ($\Delta_{FJ,KF}$ and $\Delta_{FJ,LF}$) have been optimized in such a way that they are able to correctly reproduce all other experimental phase diagram data. Excess Gibbs energy parameters have also been mainly optimized in order to reproduce the solubility of corundum in the spinel phase at high temperature along with the cation distribution data. All the optimized model parameters are listed in Table 4.1.

4.2.1.2. Tetragonal spinel
Tetragonal spinel has $(Mn^{2+}, Mn^{3+}, Al^{3+})^\uparrow [Mn^{2+}, Mn^{3+}, Al^{3+}, Va]_2^\uparrow O_4$ structure including vacancy (Va) on octahedral sites. Like cubic spinel, among twelve end-members Gibbs energies eight Gibbs energies had already been determined from the Mn-O (Kang et al. [26]) and Al-O (Jung et al. [27]) systems. Four other Gibbs energies have been determined in the present study. The model parameters are presented in Table 4.1. Due to the limited homogeneity region (small solubility of Al), the most important model parameter is Gibbs energy of tetragonal MnAl$_2$O$_4$ spinel ($([Mn^{2+}]^\uparrow [Al^{3+}]_2^\uparrow O_4$) that is unstable in normal condition. This Gibbs energy has been determined to reproduce the solubility limit of Al in tetragonal spinel.

The $G_{JF}$ (Gibbs energy of normal spinel, $([Mn^{2+}]^\uparrow [Al^{3+}]_2^\uparrow O_4$) and one $\Delta$ ($\Delta_{HF}$) parameter have been optimized and all the remaining parameters are set to zero. The optimization of the parameters for the tetragonal spinel has been performed in a manner similar to the one done for the cubic spinel.

4.2.2. Molten Oxide (slag)
The Modified Quasichemical Model (Pelton and Blander [15], Pelton and Blander [16], Pelton et al. [17], Pelton and Chartrand [18]) which takes into account the short-range ordering of second-nearest-neighbor cations in the ionic melt, is used for modeling the slag.

The components of the slag are taken as MnO-MnO$_{1.5}$-AlO$_{1.5}$. Although Mn can have higher oxidation states, only the divalent and trivalent oxidation states which predominate at oxygen partial pressures less than 1.0 bar are considered in the present study. Mn$_2$O$_3$ and Al$_2$O$_3$ are taken
as MnO$_{1.5}$ and AlO$_{1.5}$ to indicate that all Mn$^{3+}$ and Al$^{3+}$ cations are distributed independently between oxygen.

In the binary MnO-AlO$_{1.5}$ solution, for example short range ordering is taken into account by considering the second-nearest-neighbor pair exchange reaction:

$$(\text{Mn-Mn}) + (\text{Al-Al}) = 2 (\text{Mn-Al}): \Delta g_{\text{MnAl}}$$

(4.12)

where (m-n) represents a second-nearest-neighbor pair. The Gibbs energy of the solution is given by

$$G = (n_{\text{MnO}} g_{\text{MnO}}^0 + n_{\text{AlO}_{1.5}} g_{\text{AlO}_{1.5}}^0) - T \Delta S_{\text{config}} - n_{\text{MnAl}} (\Delta g_{\text{MnAl}} / 2)$$

(4.13)

where $n_i$ and $g_i^0$ are the number of moles and molar Gibbs energies of the components, $n_{\text{MnAl}}$ is the number of moles of (Mn-Al) bonds at equilibrium. $\Delta S_{\text{config}}$ is the configurational entropy of mixing expression for the random mixing of the bonds over ‘bond sites’ in the Ising approximation and is a function of $n_{\text{MnAl}}$. $\Delta g_{\text{MnAl}}$ is the molar Gibbs energy change of reaction (4.12). It can be expanded as an empirical polynomial function in the mole fractions of the components. The coefficients of this polynomial are obtained by optimization of the available experimental data. The value of $n_{\text{MnAl}}$ at equilibrium is obtained by setting $\partial G / \partial n_{\text{MnAl}} = 0$ at constant composition. This results effectively in a ‘quasichemical equilibrium constant’ for the reaction (4.12). The equilibrium shifts to the right or left as $\Delta g_{\text{MnAl}}$ is negative or positive, respectively. For small $\Delta g_{\text{MnAl}}$, the model reduces in the limit to a random mixture of Mn$^{2+}$ and Al$^{3+}$ ions on cation sites, with the excess Gibbs energy expressed as a polynomial expansion in the component mole fractions.

All second-nearest-neighbor “coordination numbers” used in the present model for the slag are the same as in previous studies (Kang et al. [26]). The binary sub-system MnO-MnO$_{1.5}$ (Kang et al. [26]) has been already critically evaluated and optimized, and these optimized model
parameters are used in the present study without any modification. Optimized binary parameters for the MnO-AlO\(_{1.5}\) and MnO\(_{1.5}\)-AlO\(_{1.5}\) slag solutions have been obtained in the present study as described in the following sections. These are listed in Table 4.1. The Gibbs energy of the ternary liquid solution has been estimated using the symmetric “Kohler-like” (Pelton [28]) interpolation technique. No ternary model parameter has been used in the present study.

4.2.3. MnO (monoxide)

Monoxide solution has rock-salt structure. It is modeled as a simple random mixture of Mn\(^{2+}\), Mn\(^{3+}\) and Al\(^{3+}\) ions on cation sites. It is assumed that cation vacancies remain associated with Mn\(^{3+}\) or Al\(^{3+}\) ions and so do not contribute to the configurational entropy. Binary excess Gibbs energies were modeled by simple polynomial expansions in the mole fraction (Pelton [28]). The properties of the ternary monoxide solution were calculated from the binary parameters of the MnO-AlO\(_{1.5}\) (Eriksson et al. [9]) and MnO-MnO\(_{1.5}\) (Kang et al. [26]) solutions with the symmetric “Kohler-like” approximation (Pelton [28]). The Gibbs energy per mole of the solution is expressed as follows:

\[
G_m = \sum_i X_i G_i^o + RT \sum_i X_i \ln X_i + \sum_i \sum_j X_i X_j \left( \frac{X_i}{X_i + X_j} \right)^m \left( \frac{X_j}{X_i + X_j} \right)^n q_{ij}^{mn} + g_{ternary}^{ex} \tag{4.14}
\]

where \( G_i^o \) is the Gibbs energy of component like MnO, MnO\(_{1.5}\) and AlO\(_{1.5}\), and \( X_i \) is mole fractions of component. The binary model parameters \( q_{ij}^{mn} \) of MnO-AlO\(_{1.5}\) (Eriksson et al. [9]) and MnO-MnO\(_{1.5}\) (Kang et al. [26]) were optimized previously. There is no binary parameter for the MnO\(_{1.5}\)-AlO\(_{1.5}\) system and no ternary excess parameter \( g_{ternary}^{ex} \) has used in the present study.

4.2.4. Mn\(_2\)O\(_3\) (bixbyite) and Al\(_2\)O\(_3\) (corundum)

Bixbyite phase is Mn\(_2\)O\(_3\)-rich solid solution which has a cubic structure above room temperature and dissolves certain amount of Al oxide (Al\(_2\)O\(_3\)). On the other hand, corundum phase is Al\(_2\)O\(_3\) rich solid solution which has trigonal structure based on the hcp oxygen-packing scheme. Small
amount of Mn oxide (Mn\(_2\)O\(_3\)) can be dissolved into corundum phase. The Gibbs energy per mole of the each binary solution is expressed as:

\[ G_m = (X_A G_A^o + X_B G_B^o) + 2RT(X_A \ln X_A + X_B \ln X_B) + \sum q_{AB}^{mn} (X_A)^m (X_B)^n \]  

(4.15)

where \( G_i^o \) is the Gibbs energy of components like Mn\(_2\)O\(_3\) and Al\(_2\)O\(_3\), and \( X_i \) is mole fraction of the component. The binary model parameters \( q_{ij}^{mn} \) for the bixbyite phase have been optimized in the present study. The binary model parameters \( q_{ij}^{mn} \) for the corundum phase were optimized previously (Eriksson et al. [9]). The optimized model parameters for the corundum phase have been used in the present study without any modification. All the optimized model parameters are listed in Table 4.1.

4.2.5. Metallic phases

In this study, FSStel database [29] is used for Al-Mn metallic system. There are many intermetallic phases. The thermodynamic properties of all phases were optimized previously (Jansson [30]) based on phase diagrams, activities, heat of mixing, etc. This is used for the calculations of phase equilibria at metallic saturation.

4.3 Critical evaluation and optimization

4.3.1 Thermodynamic properties of MnAl\(_2\)O\(_4\) spinel solution

4.3.1.1 Heat capacity of MnAl\(_2\)O\(_4\)

Fig. 4.3 shows the calculated heat capacity of MnAl\(_2\)O\(_4\) from the present spinel model in comparison with experimental data by Navarro et al. [12]. It should be noted that the calculated curve is not obtained from theoretical end-member spinel model but the real MnAl\(_2\)O\(_4\) spinel solution which has cation distribution. Navarro et al. [12] recently measured the heat capacity (\( C_p \)) of stoichiometric MnAl\(_2\)O\(_4\) spinel using thermal relaxation calorimetry at the temperatures from 2 to 300K. The experimental data are the average value of 3 independent \( C_p \) measurements at each temperature. They calculated the molar entropy of MnAl\(_2\)O\(_4\) spinel at 298.15K (\( S_{298.15}^0 \))
to be 116 ± 5 J/mol-K by integrating the low temperature Cp data. High temperature (323 < T < 873K) Cp measurements were done with the help of a differential scanning calorimeter. First of all, the MnAl2O4 samples were heated from 373K to 873K at constant rate of 20 K/min. Then they were cooled from 873K to 323K at constant rate of 20 K/min with isothermal stages at systematically separated temperatures. Each isothermal temperature was maintained for two minutes, enough to reach a constant heat flux. A polynomial function of temperature was used to fit the measured isothermal flux. The heat capacity of MnAl2O4 was then calculated based on the knowledge of few properties of standard (Al2O3) and the crucible (Al).

Experimental Cp in fig 4.3 is in fact the Cp of (Mn2+, Al3+)T[Mn2+, Al3+]2O4 spinel at stoichiometric MnAl2O4 composition. This means that the cation distribution may change with change in temperature. However, the cation distribution data of MnAl2O4 spinel show highly normal distribution (inversion is less than 0.05 at 500K), the heat capacity should be close to the experimental heat capacity of (Mn2+)T[Al3+]2O4 end-member. In the present study, the heat capacity of (Mn2+)T[Al3+]2O4 was determined from this experimental data. However, the calculated line in Fig. 4.3 is obtained after considering cation distribution of real stoichiometric spinel, which will be discussed below. The calculated heat capacity curve is in very good agreement with the experimental Cp data. Our calculations give a value of 115.32 J/mol-K for the S"298.15 which is nearly equal to the experimental value of 116 ± 5 J/mol-K.

4.3.1.2 Gibbs energy of MnAl2O4

Many researchers carried out independent measurements of the Gibbs energy of formation of MnAl2O4 from MnO and Al2O3 as shown in Fig. 4.4. Lenev and Novokhatkii [31] were the first to carry out the investigation on the Gibbs energy of formation of the MnAl2O4 spinel by employing the reduction reaction of MnAl2O4 with hydrogen gas. From MnAl2O4 + Mn + O2 + Al2O3 equilibration with known partial pressure of O2, they could evaluate the Gibbs energy of formation of MnAl2O4 from MnO and Al2O3 at the temperature range from 1550 to 1700°C. Kim and McLean [32] equilibrated liquid Fe and Al2O3 with additions of FeAl2O4-MnAl2O4 spinel solid solutions at 1550, 1600 and 1650°C. From the known activities of Mn and O in liquid Fe, the Gibbs energy of MnAl2O4 was calculated. Jacob [7] and Zhao et al. [33] also performed
similar experiment where MnAl₂O₄ and Al₂O₃ were equilibrated with Pt-Mn and Ag-Mn alloys under fixed partial pressure of oxygen, respectively. From the known activity of Mn in the alloys and the analyzed Mn concentration, the Gibbs energy of MnAl₂O₄ was calculated. Timucin and Muan [34] equilibrated NiO-MnO/Al₂O₃-MnAl₂O₄/Ni under fixed partial pressure of oxygen at 1300 and 1400°C. After the equilibration experiment, they were able to calculate the Gibbs energy of formation of the spinel MnAl₂O₄ from MnO and Al₂O₃ using a ternary Gibbs-Duhem integration technique. Dimitrov et al. [35] equilibrated liquid Fe with Al₂O₃ and MnAl₂O₄ and used a solid electrolyte to measure the partial pressure of oxygen. They calculated the Gibbs energy of MnAl₂O₄ from measurements of partial pressure of oxygen from emf and calculated activities of Mn in liquid Fe.

As can be seen in Fig. 4.4, the optimized Gibbs energy of MnAl₂O₄ spinel solid solution is in good agreement with experimental data within the experimental error ranges. It should be noted that the previous thermodynamic modeling result regarding Gibbs energy of MnAl₂O₄ by Navarro et al. [12] is far away from the experimental data. In addition, the compiled data from Barin [36] are much more negative than the experimental data. It should be noted that the Gibbs energy of MgAl₂O₄ from MgO and Al₂O₃ is also about – 40 kJ/mol at 1600°C (Jung et al. [27]) which is similar to the Gibbs energy of MnAl₂O₄ in Fig. 4.4.

4.3.1.3 Cation distribution of MnAl₂O₄ spinel solution

MnAl₂O₄ is considered as a normal spinel (Greenwald et al. [37], Roth [38], Murthy et al. [39], Essene and Peacor [40], Lucchesi [41], Tristan et al. [42], Halenius [43], Halenius [44]) at low temperature (that is, Mn²⁺ and Al³⁺ cations occupy the tetrahedral and octahedral sites respectively). However, there is a certain degree of disorderliness of cations between the sites, and this degree of inversion also increases with increasing temperatures. Fig. 4.5 shows the variation of cation distribution in MnAl₂O₄ as a function of temperature.

Greenwald et al. [37] prepared the spinel sample and annealed at 1400°C for 1 or 2 hours followed by quenching to room temperature. The cation distribution of the quenched samples was determined using XRD technique to be 0.29±0.04. Roth [38] prepared MnAl₂O₄ samples
under controlled partial pressure of oxygen, annealed them and the structural analysis was performed using neutron diffraction technique. They obtained a value of 0.084±0.044 for the degree of inversion of the samples. Tristan et al. [42] carried out similar experiment using XRD with Rietveld analysis and obtained a value of 0.06 for the degree of inversion. Tristan et al. [42] obtained a value which is lower than that obtained by Roth [38] probably because of lower sample preparation temperature as compared to that of Roth [38]. Roth [38] stated that cation diffusion below 600°C is negligible. Tristan et al. [42] believed that only at temperatures greater than 500°C mixing of cations from different sites can occur. Jung et al. [27] considered the $T_{\text{froz}}$ of MgAl$_2$O$_4$ spinel to be 700°C. Since no specific temperature was mentioned in the studies of Roth [38] and Tristan et al. [42], the $T_{\text{froz}}$ (i.e. the temperature below which there is no inversion due to slow kinetics) was chosen as 700°C in the case of MnAl$_2$O$_4$ based on logical reasoning and critical evaluation of literature data. Recently, Halenius [44] determined the cation distribution of MnAl$_2$O$_4$ sample quenched from 900°C using single crystal structural refinement technique. They obtained a value of 0.16 for the degree of inversion of the spinel at 900°C.

As can be seen in Fig 4.5, the variation of cation distribution of MnAl$_2$O$_4$ with temperature can be well reproduced by the present spinel model.

### 4.3.1.4 Activity of MnO in the MnO-Al$_2$O$_3$ system

Sharma and Richardson [45] and Jacob [7] equilibrated the MnO-Al$_2$O$_3$ mixtures with Pt-Mn foils under fixed partial pressures of oxygen at 1600 and 1650°C. Then, the activity of MnO in MnO-Al$_2$O$_3$ mixture was calculated from the known activity of Mn and controlled oxygen partial pressure. The experimental data are plotted in Fig. 4.6.

The optimization of the activity of MnO in the MnO-Al$_2$O$_3$ system is compared with experimental data in Fig. 4.6. The present results are very similar to those of previous optimization by Jung et al. [10]. It should be noted that the activity of MnO in two phase region of ‘Al$_2$O$_3$+MnAl$_2$O$_4$’ is directly related to the Gibbs energy of MnAl$_2$O$_4$ shown in Fig. 4.4. The experimental activities of MnO on the MnO-rich side are well reproduced in the present study.
4.3.2 Phase diagram of the MnO-Mn$_2$O$_3$-Al$_2$O$_3$ system

4.3.2.1 Under reducing atmosphere: MnO-Al$_2$O$_3$

Fig. 4.7 shows the calculated phase diagram of the Mn-Al-O system at reduced oxygen partial pressures along with the experimental data.

Hay et al. [1] employed heating and cooling curve measurement to determine the phase diagram at MnO-rich (wt.% Al$_2$O$_3$ ≤ 50%) region. They reported the liquidus of spinel (they claimed it was MnAl$_2$O$_4$) and MnO and also the eutectic reaction at MnO-rich region. They also proposed peritectic melting of spinel at 1560°C. Unfortunately, the gas atmosphere at the experiment was not tightly controlled and it seems that the oxygen partial pressure was not sufficiently low. Later, Oelsen and Heynert [2] reported the phase diagram of MnO-Al$_2$O$_3$ system at reduced condition from the extrapolation of the liquidus of the FeO-MnO-Al$_2$O$_3$ system saturated with liquid Fe. The samples contained in Al$_2$O$_3$ crucible were quenched after equilibration to determine the phase. They reported eutectic and peritectic temperatures of 1520°C at MnO-rich region and 1720°C at Al$_2$O$_3$-rich region, respectively, measured by a calorimetric technique. However, no experimental details are given. Fischer and Bardenheuer [5] also employed similar technique and reported the eutectic reaction at MnO-rich region to occur at about 70 wt. % MnO and 1580 ± 5°C. Novokhatskii et al. [4] investigated the melting points of MnAl$_2$O$_4$ spinel phase using visual observation under controlled oxygen partial pressure using a gas mixture of Ar and H$_2$. They reported the congruent melting of MnAl$_2$O$_4$ spinel at 1850°C and eutectic reactions of MnO-rich side at 1520 ± 10°C and of Al$_2$O$_3$-rich side at 1770± 15°C. Novokhatskii et al. [4] claimed, from XRD results, that Al$_2$O$_3$ and MnAl$_2$O$_4$ exhibit virtually no mutual solid solubility.

Jacob [7] measured the liquidus temperatures shown in Fig. 4.7 at 1600°C and 1650°C by equilibration under controlled oxygen pressures of 10$^{-5}$ to 10$^{-6}$ bar, followed by quenching and electron microprobe analysis. These same experiments showed approximately 1 % solubility of Al$_2$O$_3$ in solid MnO and no solubility of MnO in MnAl$_2$O$_4$. In similar experiments, Jacob heated Mn and MnO in sealed Al$_2$O$_3$ crucibles at 1600°C and 1650°C, followed by quenching and electron microprobe analysis (EPMA). A solubility of MnO in Al$_2$O$_3$ of approximately 1 % and a solubility of Al$_2$O$_3$ in MnAl$_2$O$_4$ of approximately 3 % were observed. The invariant
temperatures and the melting points of pure MnO, Al₂O₃ and MnAl₂O₄ were measured by Jacob [7] by examination, either visual or under an optical microscope, of pellets quenched from high temperature under purified Ar. He reported that MnAl₂O₄ melts congruently at 1850°C and hence that the invariant shown at 1769°C in Fig. 4.7 is actually a eutectic.

The calculated phase diagram of MnO-Al₂O₃ system at oxygen pressures of 10⁻⁵ to 10⁻⁶ atm are presented in Fig. 4.7. Fig 4.7 shows a predicted phase diagram at 10⁻⁸ atm. At the reducing conditions, the amount of Mn³⁺ in liquid phase is negligible. The maximum amount of Mn₂O₃ in the slag at 1600°C is around 2.7 wt%. Therefore, Gibbs energy of liquid phase is mainly determined by the interaction between MnO and Al₂O₃. That is, in the present modeling, the MQM parameters for liquid MnO-Al₂O₃ solution was determined to reproduce the phase diagram in Fig. 4.7, after the Gibbs energy of MnAl₂O₄ spinel phase was determined as shown in Fig. 4.4. The experimental liquidus reported by Jacob [7], which is considered to be the most reliable one out of all the experimental results, is well reproduced except the congruent melting of MnAl₂O₄ spinel. The same difficulty was found in the previous optimization by Jung et al. [10]. As it was mentioned in the previous work by Jung et al. [10], in order to reproduce the phase diagram accurately with congruent melting, the Gibbs energy of MnAl₂O₄ spinel in Fig. 4.4 should be much more negative. As pointed out by Jung et al. [10], more negative Gibbs energy of MnAl₂O₄ induces more negative interaction of MnO and Al₂O₃ in liquid phase, which causes the poor description of activity of MnO in MnO-Al₂O₃-CaO-SiO₂ system. The optimized MQM parameters for liquid MnO-Al₂O₃ are listed in Table 1.

The newly optimized phase diagram in MnO-rich region is almost the same as the one optimized previously Jung et al. [10]. It should be noted that MnAl₂O₄ was considered as stoichiometric phase in the previous study by Jung et al. [10]. In the present modeling, the spinel solution between Mn₃O₄ and MnAl₂O₄ with excess solubility of Al₂O₃ was considered. As can be seen in Fig. 4.7, the wide spinel solution at sub-solidus temperature is predicted nearly from Mn₃O₄ (MnO side) at the oxygen partial pressures of 10⁻⁵ to 10⁻⁶ bar. The amount of excess Al₂O₃ solubility in MnAl₂O₄ at Al₂O₃-rich side is a bit larger than the experimental data by Jacob. In
the modeling, however, it is found that this solubility is highly related to the excess solubility of \( \text{Al}_2\text{O}_3 \) in oxidizing condition shown in Fig. 4.8.

### 4.3.2.2. Under oxidizing atmosphere: \( \text{Mn}_2\text{O}_3\text{-Al}_2\text{O}_3 \) system

Fig. 4.8 shows the calculated phase diagram of the Mn-Al-O system in air from the present optimization along with the experimental data.

Ranganathan et al. [3] were the first to determine the phase relations in the \( \text{Mn}_2\text{O}_3\text{-Al}_2\text{O}_3 \) system in air using the classical quenching technique followed by optical microscopy and XRD phase determination. They prepared the samples of entire composition and equilibrated them at the temperature range between 800 and 1700°C. The main feature of the phase diagram in air was determined by Ranganathan et al. [3]. Dekker and Rieck [6] used the similar technique to determine the sub-solidus phase equilibria. Bobov et al. [46] prepared the sample at \( \text{Mn}_3\text{O}_4 \) rich region at temperature range from 800 to 1000°C to determine the phase boundary of tetragonal spinel more accurately. Golikov et al. [8] also concentrated their investigation at the temperature between 900 and 1300°C to determine the phase boundary of tetragonal spinel and cubic spinel using quenching technique and in-situ high temperature radiography technique.

Due to the presence of a Jahn-Teller effect in spinel structure with \( \text{Mn}^{3+} \) ion, the quenched cubic spinel phase is tetragonally distorted and is easily misinterpreted as tetragonal spinel. In the present study, the tetragonally distorted cubic spinel due to Jahn-Teller effect is treated as second order transformation of cubic spinel, which is different from first order transformation to tetragonal spinel. For example, Ranganathan et al. [3] using the quenching technique reported that \( \text{Mn}_3\text{O}_4 \)-rich region (\( \text{Mn}/(\text{Mn}+\text{Al}) > 0.4 \)) at about 1000°C was occupied by tetragonal \( \text{Mn}_3\text{O}_4 \) spinel (Hausmannite). This region was more carefully studied by Dekker and Rieck [6], Bobov et al. [46] and Golikov et al. [8] to clearly distinguish the boundary of tetragonal spinel and cubic spinel as can be seen in Fig. 4.8(b).

The present modeling for the spinel solution can successfully reproduce the experimental phase diagram data as can be seen in Fig. 4.8. As discussed above, the phase boundary of two spinels
regions (tetragonal + cubic spinels) was determined mostly based on the studies of Dekker and Rieck [6], Bobov et al. [46] and Golikov et al. [8], while other areas are determined mostly based on the experimental data of Ranganathan et al. [3]. As mentioned in the previous section, the excess solubility of Al$_2$O$_3$ in MnAl$_2$O$_4$ spinel in reducing condition in Fig. 4.7 is related to the limit of homogeneity range of cubic spinel phase toward Al-rich side at about 1700°C (up to Al/(Mn+Al) = 0.75) in Fig. 4.8. That is, in order to reproduce the extent of the homogeneity range of cubic spinel towards Al$_2$O$_3$ side in air, the noticeable amount of excess solubility of Al$_2$O$_3$ in MnAl$_2$O$_4$ is also expected in reducing condition. The homogeneity range of tetragonal spinel was mainly determined by the end-member Gibbs energy of tetragonal $(Mn^{2+})_2[Al^{3+}]O_4$. The homogeneity range of bixbyite was also reproduced by excess interaction parameter. The MQM parameter for Mn$_2$O$_3$-Al$_2$O$_3$ binary system was determined to reproduce the liquidus and solidus of Mn-Al-O system in air. All the optimized model parameters are summarized in Table 1.

4.3.2.2. Predictions in the Mn-Al-O system

Based on the optimized model parameters, the experimentally unexplored phase diagrams can be predicted. For example, the oxygen partial pressure – composition diagrams for the Mn-Al-O system at various temperatures (1000 - 1600°C) are calculated in Fig. 4.9 with the help of newly optimized database and the FSStel [29] database.

4.4 Summary

All the thermodynamic and phase diagram data in the Mn-Al-O system from reducing condition to oxidizing condition were collected and critically evaluated for the thermodynamic optimization of the system. Compared with previous optimizations, the present optimization properly takes into account of the cubic and tetragonal spinel solution phases (Mn$_3$O$_4$-MnAl$_2$O$_4$ with excess Al$_2$O$_3$) for the first time. All the cation distribution data and thermodynamic data of the spinel and phase diagram related to the spinel solution were well reproduced. The optimized model parameters can reproduce all the reliable experimental data of the Mn-Al-O system at any oxygen partial pressure from room temperature to above liquidus temperature. The optimized
database has been also used to predict the experimentally unexplored phase diagrams of the Mn-Al-O system.
References


Table 4.1: Optimized model parameters of all the solutions present in the MnO-Mn₂O₃-Al₂O₃ system (J/mol and J/mol K).

<table>
<thead>
<tr>
<th>Cubic Spinel: (Mn²⁺, Al³⁺)₆(Mn²⁺, Mn³⁺, Mn⁴⁺, Al³⁺, Va)₂O₄</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_{298.15}^O ) = –2,073,402</td>
<td></td>
</tr>
<tr>
<td>( \Delta S_{298.15}^O ) = 115.3203912</td>
<td></td>
</tr>
<tr>
<td>( C_p = 156.0116005 + 0.028696657T - 3294506.682T^{-2} - 0.00000426112T^2 ) (T &lt; 2500K)</td>
<td></td>
</tr>
<tr>
<td>( G_{JK} = -1,327,895.531 + 1,454.74T - 225.89T \ln T - 289,129.75T^{-1} - 2552.69 ) T^{–0.5} – 16,033.5ln T(298K &lt; T &lt; 3000K)⁵⁰</td>
<td></td>
</tr>
<tr>
<td>( G_{JJ} = -1,443,047 + 1,460.26T + 1,890,756T^{-1} - 240.5906T \ln T - 0.0162984T^{2} ) (298K &lt; T &lt; 3000K)⁵⁰</td>
<td></td>
</tr>
<tr>
<td>( I_{JF} = G_{FF} + G_{FJ} - 2G_{JF} = 31,380 + 12.552T )</td>
<td></td>
</tr>
<tr>
<td>( \Delta_{FJ:KF} = G_{FK} + G_{JF} - (G_{FF} + G_{JK}) = 41,840 )</td>
<td></td>
</tr>
<tr>
<td>( \Delta_{FJ:LF} = G_{FL} + G_{JF} - (G_{FF} + G_{JL}) = 125,520 )</td>
<td></td>
</tr>
<tr>
<td>( 1L_{FJ:V} = 1L_{FJ:B} = 1L_{FJ:F} = 1L_{FJ:J} = 1L_{FJ:K} = 1L_{FJ:L} = -13,388.8 )</td>
<td></td>
</tr>
<tr>
<td>( G_{JL} = 5/7G_{JK} + 679,021.36 - 264.997T^{50} = 26,210 - 17.46T^{50} )</td>
<td></td>
</tr>
</tbody>
</table>

Notations F, J, K, L and V were used for Al³⁺, Mn²⁺, Mn³⁺, Mn⁴⁺ and vacancy, respectively. The model parameters for Al-O spinel solution could be found elsewhere (Jung et al. [27]).

<table>
<thead>
<tr>
<th>Tetragonal Spinel: (Mn²⁺, Mn³⁺, Al³⁺)₆(Mn²⁺, Mn³⁺, Mn³⁺, Al³⁺, Va)₂O₄</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_{298.15}^O ) = –2,045,579</td>
<td></td>
</tr>
<tr>
<td>( \Delta S_{298.15}^O ) = 115.3203912</td>
<td></td>
</tr>
<tr>
<td>( C_p = 156.0116005 + 0.028696657T - 3294506.682T^{-2} - 0.00000426112T^2 ) (T &lt; 2500K)</td>
<td></td>
</tr>
<tr>
<td>( G_{JK} = -1,345,888.32 + 1,469.23T - 225.89T \ln T - 289,129.75T^{-1} - 2552.69 ) T^{–0.5} – 16,033.5ln T(298K &lt; T &lt; 3000K)⁵⁰</td>
<td></td>
</tr>
<tr>
<td>( G_{JK} = G_{JK}^{50} )</td>
<td></td>
</tr>
</tbody>
</table>
$$G_{KV} = 8G^O(\gamma\text{-Mn}_2\text{O}_3) - 2RT(5\ln 5 - 6\ln 6) - 5G_{JK} - 5I_{JK},$$

where $G^O(\gamma\text{-Mn}_2\text{O}_3) = G^O(\beta\text{-Mn}_2\text{O}_3) + 20,920^a$

$$\Delta_{FJ} = G_{FF} + G_{JJ} - G_{JF} - G_{FJ} = 0$$

$$\Delta_{JK} = G_{FJ} + G_{JK} - G_{JF} - G_{FK} = -125,520$$

$$\Delta_{KF} = G_{KK} + G_{BF} - G_{BK} - G_{KF} = 0$$

$$I_{JK} = G_{KK} + G_{KJ} - 2G_{JK} = 98,324^a$$

$$\Delta_{JKJK} = G_{JJ} + G_{KK} - G_{JF} - G_{KJ} = 40,000^a$$

$$\Delta_{JKJV} = G_{JJ} + G_{KJ} - G_{KJ} - G_{JF} = -941,190.8 + 627.6T^a$$

Notations F, J, K, L and V were used for $\text{Al}^{3+}$, $\text{Mn}^{2+}$, $\text{Mn}^{3+}$, $\text{Mn}^{4+}$ and vacancy, respectively. The model parameters for Al-O spinel solution could be found elsewhere (Jung et al. [27]).

### Liquid Oxide: MnO-MnO$_{1.5}$-AlO$_{1.5}$

$$G(\text{MnO}) = G^O(\text{MnO,liquid})$$

$$G(\text{MnO}_{1.5}) = 1.25G^O(\text{MnO,liquid}) + 25,731.6^a$$

$$G(\text{AlO}_{1.5}) = 1/2G^O(\text{Al}_2\text{O}_3,\text{liquid})$$

$$q_{\text{MnO,AlO}_{1.5}}^{00} = -6,694.4$$

$$q_{\text{MnO,AlO}_{1.5}}^{01} = 5,439.2$$

$$q_{\text{MnO,AlO}_{1.5}}^{02} = -39,329.6$$

$$q_{\text{MnO}_{1.5},\text{AlO}_{1.5}}^{00} = -25,104$$

$$q_{\text{MnO}_{1.5},\text{AlO}_{1.5}}^{01} = 31,380$$

$$q_{\text{MnO}_{1.5},\text{AlO}_{1.5}}^{10} = -25,104$$

The quasichemical parameters are defined in Refs. Pelton et al. [17] and Pelton and Chartrand [18].

### Monoxide: MnO-MnO$_{1.5}$-AlO$_{1.5}$

$$G(\text{monoxide-MnO}) = G^O(\text{MnO})$$

$$G(\text{monoxide-MnO}_{1.5}) = 0.5G^O(\text{Mn}_2\text{O}_3,\beta) + 12,001.8 - 4.87T^a$$
\[ G(\text{monoxide-AlO}_{1.5}) = 0.5G^o(\text{Al}_2\text{O}_3) + 38,702 \]
\[ q_{\text{MnO-MnO}_{3}}^{31} = -20,920" \]

No excess parameter was required for the MnO\textsubscript{1.5}-AlO\textsubscript{1.5} solution.

**Bixbyite: Mn\textsubscript{2}O\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3}**

\[ G(\text{bixbyite-MnO}_3) = a \]
\[ -1,512,892 + 26,796.59T - 5081T \ln T + 15.56T^2 - 0.0081T^3 \quad (298K < T < 320K) \]
\[ -945,439 + 813.45T - 133.5T \ln T - 0.006T^2 + 143,152.38T^{-1} - 10,000 \ln T \quad (320K < T < 3000K) \]

\[ G(\text{bixbyite-Al}_2\text{O}_3) = G^o(\text{Al}_2\text{O}_3) + 37,656 \]
\[ q_{\text{MnO}_{3.5},\text{AlO}_{3}}^{31} = 8,368 - 13.3888T \]

**Corundum: Al\textsubscript{2}O\textsubscript{3}-Mn\textsubscript{2}O\textsubscript{3}**

\[ G(\text{corundum-Al}_2\text{O}_3) = G^o(\text{corundum-Al}_2\text{O}_3) \]
\[ G(\text{corundum-Mn}_2\text{O}_3) = G^o(\text{bixbyite-Mn}_2\text{O}_3) \]

Other Gibbs energies of the gas components are obtained from the FACTPS database (Factsage [47]).

\(^a\)The model parameters for the Mn-O system were optimized previously by Kang *et al.* [26].

\(^b\)The Gibbs energy of the corundum species are obtained from the FToxid database (Factsage [47]).
Figure 4.1: Calculated phase diagram of the MnO-Mn$_2$O$_3$-Al$_2$O$_3$ system at 1000°C and 1 bar total pressure.

Figure 4.2: Gibbs energy diagram for the spinel Mn$_3$O$_4$-MnAl$_2$O$_4$ solution
Figure 4.3: Heat capacity of MnAl$_2$O$_4$ calculated from the present spinel solution model along with experimental data by Navarro et al. [12].

Figure 4.4: Optimized isothermal Gibbs energy of formation of MnAl$_2$O$_4$ from solid MnO and Al$_2$O$_3$ along with experimental data by Lenev and Novokhatskii [31], Kim and McLean [32], Jacob [7], Timucin and Muan [34], Dimitrov et al. [35] and Zhao et al. [33] and evaluated and calculated results obtained from previous studies by Barin [36], Jung et al. [10] and Navarro et al. [12].
Figure 4.5: Calculated variation of cation distribution in MnAl$_2$O$_4$ as a function of temperature in °C along with experimental data of Greenwald et al. [37], Roth [38], Tristan et al. [42] and Halenius [44].

Figure 4.6: The activity of MnO in the MnO-Al$_2$O$_3$ system at 1600°C (blue line) and 1650°C (red line) under reducing atmosphere. Points are from Sharma and Richardson [45] and Jacob [7] and the lines are calculated from the present study.
Figure 4.7 (a): Calculated phase diagram of the Mn-Al-O system under reducing condition ($p_{O_2} = 10^{-5}$ atm) with experimental points by Hay et al. [1], Oelsen and Heynert [2], Kubashchewski and Evans [50], Singleton et al. [48], Fischer and Bardenheuer [5], Trömel et al. [49] and Jacob [7].

Figure 4.7 (b): Calculated phase diagram of the Mn-Al-O system under reducing condition ($p_{O_2} = 10^{-6}$ atm).
Figure 4.7 (c): Predicted phase diagram of the Mn-Al-O system under reducing condition ($p_{O_2} = 10^{-8}$ atm).

Figure 4.8 (a): Calculated phase diagrams of the Mn-Al-O system in air along with the experimental points by Ranganathan et al. [3].
Figure 4.8 (b): Calculated phase diagrams of the Mn-Al-O system in air along with the experimental points by Dekker and Rieck [6], Bobov et al. [46] and Golikov et al. [8].

Abbreviations: L: Slag, C-Sp: Cubic Spinel, T-Sp: Tetragonal Spinel, Mono: Monoxide, Cor: Corundum, Bix: Bixbyite.
Figure 4.9²: Calculated (predicted) Mn-Al-O phase diagrams at temperatures of: (a) 1000°C, (b) 1200°C, (c) 1400°C and (d) 1600°C. Molar metal ratio versus equilibrium oxygen partial pressure.

²Abbreviations: L: Liquid, C-Sp: Cubic Spinel, T-Sp: Tetragonal Spinel, Mono: Monoxide, Cor: Corundum, AL8M: AL8MN5D810.
Chapter 5

Thermodynamic modeling of the MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-CaO system

5.1 Introduction

The thermodynamic optimization of the MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-CaO system had been carried out earlier. However, the same work has to be repeated since the MnO-Mn$_2$O$_3$-Al$_2$O$_3$ (Chapter 4) system has been reoptimized considering MnAl$_2$O$_4$ as a spinel solid solution and considering Mn$^{3+}$ species in the slag as described in Chapter 4. The optimized MnO-Mn$_2$O$_3$-Al$_2$O$_3$ (Chapter 4) system has been extended to the MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-CaO system in the present chapter by combining with the previously optimized model parameters for the system present in the FToxid database [1].

5.2 Phases and thermodynamic models

The schematic diagram of the Mn-Al-Si-Ca-O (MnO-Al$_2$O$_3$-SiO$_2$-CaO) system is shown in Fig. 5.1. The following solution phases are found in the Mn-Al-O system:

Spinel: (Mn$^{2+}$, Al$^{3+}$)$_T$ (Al$^{3+}$, Mn$^{2+}$, Mn$^{3+}$, Mn$^{4+}$, Va)$_2$O$_4$

Mullite: Al$_6$Si$_2$O$_{13}$ having a little solubility of Al$_2$O$_3$.

Corundum: (Al$^{3+}$, Mn$^{2+}$)$_2$O$_3$

Slag (molten oxide phase): MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$-CaO

Monoxide: MnO-AlO$_{1.5}$-MnO$_{1.5}$-CaO-SiO$_2$

Rhodonite: (Mn$^{2+}$, Ca$^{2+}$)[Si$^{4+}$]O$_3$

Olivine: (Mn$^{2+}$, Ca$^{2+}$)$_2$[Si$^{4+}$]O$_4$

The ternary compounds observed in the system are as follows:

Spessartite (Mn$_3$Al$_2$Si$_3$O$_{12}$)

Mn-Cordierite (Mn$_2$Al$_4$Si$_3$O$_{18}$)

No change has been made to the parameters related to any of the solid solutions present in the MnO-Al$_2$O$_3$-SiO$_2$-CaO system; all the required parameters have been obtained from the FToxid
As there is no extension of the binary or ternary solid solution toward higher order system, no thermodynamic modeling is needed for the solid solutions. In the case of liquid slag, all slag components are mixed together. So, the ternary interactions of the components can be re-optimized to reproduce all available experimental data related to liquid phase. In particular, ternary interaction parameters of the MnO-Al₂O₃-SiO₂ system were needed to be re-optimized because of the change of the model parameters for the MnO-Al₂O₃ system. In addition, the Gibbs energies of ternary compounds were also changed slightly to accommodate the change of liquid phase to reproduce the phase diagram.

5.2.1 Slag

Only the ternary parameters of MnO-Al₂O₃-SiO₂ slag were changed in the present study. No other parameter related to the slag phases was changed.

The Gibbs energy of the ternary liquid surface was calculated with the help of the Modified Quasichemical model using the “asymmetric approximation (Toop-like interpolation technique)” given by Chartrand and Pelton [2], Pelton [3] along with the binary parameters of the subsystems and ternary parameters. In the present asymmetric approximation, SiO₂ was considered as the acidic component and MnO and Al₂O₃ as the basic components. Fig. 5.2 shows the geometric model used in the current interpolations.

The optimized parameters for the previously optimized binary subsystems were used alongwith two small ternary parameters to obtain the Gibbs energy of the ternary liquid surface. All these parameters are shown in Table 5.1

5.2.2 Ternary compounds

Snow [4] observed two ternary compounds, Spessartite (Mn₃Al₂Si₃O₁₂) and Mn-cordierite (Mn₂Al₄Si₅O₁₈) in the MnO–Al₂O₃–SiO₂ system. The heat capacity and entropy were taken from
Jung et al. [5]. The enthalpy of formation at 298 K, $H^\circ_{298}$, was optimized in the present study to reproduce the experimental phase diagram data. The optimized values are shown in Table 5.1.

5.3 Critical evaluation and optimization

5.3.1 MnO-Al$_2$O$_3$-Mn$_2$O$_3$-SiO$_2$ system

This MnO-Al$_2$O$_3$-SiO$_2$ system consists of the following binary subsystems:

a. Al-Si-O system: The thermodynamic optimization of this system has already been done by Eriksson and Pelton [6].

b. Mn-Si-O system: The thermodynamic optimization of this system has already been done by Eriksson et al. [7].

c. Mn-Al-O system: The thermodynamic optimization of this system has already been shown in chapter 4.

Fig. 5.3 and 5.4 show the calculated phase diagrams of the Al$_2$O$_3$-SiO$_2$ and MnO-SiO$_2$ binary systems from the optimized model parameters stored in FToxide database [1]. All experimental data related to phase diagrams, cation distribution and thermodynamic properties were considered in the modeling. All the previous model parameters were used in the present study without any modification.

Jung et al. [5] performed all the thermodynamic optimizations related to the MnO-Al$_2$O$_3$-SiO$_2$ system. However, MnAl$_2$O$_4$ was considered as a stoichiometric compound in their study rather than a spinel solution and no Mn$^{3+}$ in the liquid was considered. In the present study, the thermodynamic calculations for the MnO-Al$_2$O$_3$-SiO$_2$ system were performed using the present revised Mn-Al-O system containing spinel solution and MnO$_{1.5}$ oxide in slag. In summary, the accuracy of the thermodynamic modeling of the present study is compatible with the previous study by Jung et al. [5]. The details of the present optimization are given below.

The maximum mole fraction of Mn$_2$O$_3$ in the MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ slag phase at 1600°C is as low as 0.0001 which is very low. The optimized liquidus surface of the MnO-Mn$_2$O$_3$-Al$_2$O$_3$-
SiO$_2$ system under reduced oxygen condition (Fe saturation) is shown in Fig. 5.5(b). It can be compared with the previously optimized liquidus projection which has been shown in Fig. 5.5(a). All the calculated primary phase regions of the MnO-Al$_2$O$_3$-SiO$_2$ system at Fe saturation, compared with the experimental points of Snow [4] and Roghani et al. [8], are depicted in Fig. 5.6. The primary phase boundary of mullite and corundum are slightly lower in SiO$_2$ content than the experimental data. Consequently, the primary phase field of corundum is slightly smaller than the experimental one.

The liquidus experimental data of the ternary MnO-Al$_2$O$_3$-SiO$_2$ system at reduced oxygen conditions are well reproduced between 1200 and 1600$^\circ$C, as it can be seen in Fig. 5.7. Sharma and Richardson [9] and Woo et al. [10] determined the activities of MnO in the MnO-Al$_2$O$_3$-SiO$_2$ system at 1650 and 1550$^\circ$C, respectively. The calculated iso-activity lines in Fig. 5.8 are in good agreement with experimental data. Several researchers also investigated the variation of activity of MnO and SiO$_2$ along the liquidus at 1550, 1600 and 1650$^\circ$C as presented in Fig. 5.9 and 5.10. The experimental data are well reproduced in the present calculations.

In the present work, small ternary interaction parameters for the slag have been used. Moreover, the enthalpies of the two ternary compounds have been changed in order to reproduce the experimental data. The results obtained from the present work are in very good agreement with the previously optimized results of Jung et al. [5].

The calculated ternary invariant points are listed in Table 5.2. A comparison of these calculated points with those obtained experimentally by Snow [4] shows good agreement within the experimental uncertainty.

Unfortunately, no experimental data were available for the Mn-Al-Si-O system at high oxygen potential. So, it is difficult to evaluate the ternary model parameters for the Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ system, and therefore the ternary parameters were set to be zero in the present study. Calculations based on good thermodynamic databases can be used to obtain thermodynamic information for liquid steel and their inclusions which can be helpful in obtaining inclusions of
specific compositions. All the calculations related to inclusion chemistry in the Mn₂O₃-Al₂O₃-SiO₂ system done by Jung et al. [5] have been repeated here with the updated database. The change in inclusion compositions obtained with the present study is almost identical to the previous results of Jung et al. [5] as shown in Fig. 5.11 and 5.12.

5.3.2 CaO-MnO-Mn₂O₃-Al₂O₃ system

The CaO-MnO-Al₂O₃ ternary system consists of three binary subsystems:

a. Ca-Mn-O system: The thermodynamic optimization of this system has already been done by Wu et al. [11].

b. Ca-Al-O system: The thermodynamic optimization of this system has already been done by Eriksson and Pelton [6].

c. Mn-Al-O system: The thermodynamic optimization of this system has already been shown in chapter 4.

Fig. 5.13 and 5.14 show the calculated phase diagrams of the CaO-MnO and CaO-Al₂O₃ binary systems from the optimized model parameters stored in FToxide database [1]. All experimental data related to phase diagrams and thermodynamic properties were considered in the modeling. All the previous model parameters of the subsystems were used in the present study without any modification.

The maximum mole fraction of Mn₂O₃ in the CaO-MnO-Mn₂O₃-Al₂O₃ slag phase at 1600°C is as low as 0.0001 which is very low. The optimized liquidus surface of the CaO-MnO-Al₂O₃ system under reduced oxygen condition (Fe saturation) is shown in Fig. 5.15(b). It can be compared with the previously optimized liquidus projection as shown in Fig. 5.15 (a).

Any phase diagram study of the CaO-MnO-Al₂O₃ system is yet to be reported in literature.

The Gibbs energy of the ternary liquid surface was calculated with the help of the Modified Quasichemical model using the “asymmetric approximation (Toop-like interpolation technique)”
given by Chartrand and Pelton [2], Pelton [3] along with the parameters of the binary subsystems. In the present asymmetric approximation, Al$_2$O$_3$ was considered as the asymmetric component and CaO and MnO as the symmetric components. No additional ternary parameters were considered.

The calculated activities for MnO in the ternary slags have been compared with the available experimental data and the results are depicted in fig. 5.16.

5.3.3 CaO-MnO-Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ system

The CaO-MnO-Al$_2$O$_3$-SiO$_2$ ternary system consists of three ternary subsystems:

a. Ca-Al-Si-O system: The thermodynamic optimization of this system has already been done by Eriksson and Pelton [6].

b. Mn-Al-Si-O system: The thermodynamic optimization of this system has already been shown in section 5.3.1 above.

c. Ca-Mn-Si-O system: The thermodynamic optimization of this system has already been done by Kang et al. [12].

d. Ca-Mn-Al-O system: The thermodynamic optimization of this system has already been discussed in section 5.3.2 above.

The optimized parameters of the ternary sub-systems are used to predict the thermodynamic properties of the of the phases present in the 4-component system using the recently developed approximation methods by Chartrand and Pelton [2], Pelton [3]. There was no need to use any additional model parameters.

The maximum mole fraction of Mn$_2$O$_3$ in the CaO-MnO-Al$_2$O$_3$-SiO$_2$ slag phase at 1600°C is as low as 0.00007 which is very low.

Fig. 5.17 shows the comparison between the activities of MnO (solid standard state) calculated from the present study along with the experimental data. The calculated data are in agreement
with the experimental data except for the slag with composition ‘K’. The point to be noted here is that the compositions of the slags with compositions ‘C’ and ‘K’ are similar and the agreement of the calculated values for ‘C’ with corresponding experimental values is good.

The first attempt to determine the liquidus of the CaO-MnO-Al₂O₃-SiO₂ system was made by Rait and Olsen [13] by determining the composition of slags with Al₂O₃/SiO₂ weight ratios of 0.25 and 0.5. Preparation of the master slags was done from pure oxides. Melting of the slags was carried out in graphite crucibles under Argon atmosphere in a Balzer induction furnace. The samples were heated at 1450°C, 1500°C and 1550°C for 1.5 hours followed by quenching in water baths. The compositions of the liquid slag in the quenched samples were determined by EPMA.

Recently, Roghani et al. [14] and Kang et al. [15] carried out similar experiments with slags of Al₂O₃/SiO₂ weight ratios of approximately 0.41 at various temperatures. The Fig. 5.18 (a) and (b) show the predicted liquidus surface of the monoxide phase at 1450°C, 1500°C and 1550°C with Al₂O₃/SiO₂ weight ratios of 0.25 and 0.5 respectively. The experimental data are in good agreement with the calculated liquidus lines.

The Fig. 5.19 shows the calculated liquidus surface at an Al₂O₃/SiO₂ weight ratio of 0.41 at 1200°C and 1300°C. The experimental points from Roghani et al. [14] and Kang et al. [15] were also plotted although the Al₂O₃/SiO₂ weight ratio varied from 0.39-0.46 and 0.34-0.46 respectively. The Fig. shows that the calculations are in good agreement with the experimental points of Kang et al. [15]. However, they are only in agreement with the experimental points of Roghani et al. [14] only for the monoxide liquidus. The reported compositions of Gehlenite in equilibrium with liquid by Roghani et al. [14] deviated significantly from the stoichiometric composition, whereas those reported by Kang et al. [15] were in very good agreement with stoichiometric Ca₂SiAl₂O₇. Moreover, the Gehlenite grains obtained in the study of Roghani et al. [14] were much smaller than that obtained in the study of Kang et al. [15]. These results seem to suggest that probably full equilibrium conditions were not achieved by Roghani et al. [14] and as a result the experimental points showing the Gehlenite liquidus is not in agreement with the
calculated Gehlenite liquidus. However, the same explanation doesn’t hold for the case of Anorthite liquidus since the solid Anorthite compositions reported by Roghani et al. [14] were close to the stoichiometric composition. Hence, this discrepancy remains unsolved.

5.3.4 Other systems at oxidizing atmosphere

There is no experimental data available for any other subsystem in oxidizing condition. Hence, Factsage [1] can be used along with proper database to predict phase relationships in any system at any condition.

5.4 Summary

The previous work in the Mn-Al-O system has been extended to the MnO-Al₂O₃-SiO₂-CaO system. Except few changes in the ternary parameters for the MnO-Al₂O₃-SiO₂ system, no other change in the model parameters has been done. All the calculations in the MnO-Al₂O₃-SiO₂-CaO system which were previously done have been performed again with the newly obtained database. All the present results have been compared with the previously optimized results and they are found to show good agreement with each other and the experimental data.
References


Table 5.1: Optimized model parameters of the liquid oxide present in the MnO-MnO$_{1.5}$-AlO$_{1.5}$-SiO$_2$ system (J/mol and J/mol K).

Liquid Oxide: MnO-MnO$_{1.5}$-AlO$_{1.5}$-SiO$_2$

\[
G(\text{MnO}) = G^0(\text{MnO,liquid})
\]

\[
G(\text{MnO}_{1.5}) = 1.25G^0(\text{MnO,liquid}) + 25,731.6^a
\]

\[
G(\text{AlO}_{1.5}) = 1/2G^0(\text{Al}_2\text{O}_3,\text{liquid})
\]

\[
q_{\text{MnO,AlO}_{1.5}}^{00} = -6,694.4^b
\]

\[
q_{\text{MnO,AlO}_{1.5}}^{20} = 5,439.2^b
\]

\[
q_{\text{MnO,AlO}_{1.5}}^{01} = -39,329.6^b
\]

\[
q_{\text{MnO,AlO}_{1.5}}^{00} = -25,104^b
\]

\[
q_{\text{MnO,SiO}_2}^{00} = -79,955.3 + 20.91977T^c
\]

\[
q_{\text{MnO,SiO}_2}^{07} = 228,817.9 - 62.7598T^c
\]

\[
q_{\text{MnO}_5,\text{SiO}_2}^{05} = 41,840^c
\]

\[
q_{\text{AlO}_{1.5},\text{SiO}_2}^{00} = 4,799.866^d
\]

\[
q_{\text{AlO}_{1.5},\text{SiO}_2}^{30} = 100,783.9^d
\]

\[
q_{\text{AlO}_{1.5},\text{SiO}_2}^{50} = 142,067^d
\]

\[
q_{\text{AlO}_{1.5},\text{SiO}_2}^{20} = 78,571.06^d
\]

\[
q_{\text{MnO}_2,\text{SiO}_2(\text{AlO}_{1.5})}^{00} = -41,840^c
\]

\[
q_{\text{AlO}_{1.5},\text{SiO}_2(\text{MnO})}^{001} = -41,840
\]

Note: there is no ternary parameter for the Mn$_2$O$_3$-Al$_2$O$_3$-SiO$_2$, Mn$_2$O$_3$-MnO-SiO$_2$ and Mn$_2$O$_3$-MnO-Al$_2$O$_3$ systems.
### Stoichiometric compounds

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature Range (K)</th>
<th>( H^0_{298.15} )</th>
<th>( S^0_{298.15} )</th>
<th>( C_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spessartite</strong></td>
<td>298 to 1475</td>
<td>-5,662,394.485</td>
<td>( S^0_{298.15} = 3S^0_{298.15} (\text{MnO}(s)) + S^0_{298.15} (\text{Al}_2\text{O}_3(s)) )</td>
<td>( +3S^0_{298.15} (\text{SiO}_2(\text{tr})) )</td>
</tr>
<tr>
<td>((\text{Mn}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12}))</td>
<td></td>
<td></td>
<td></td>
<td>( C_p = 3C_p (\text{MnO}(s)) + C_p (\text{Al}_2\text{O}_3(s)) )</td>
</tr>
<tr>
<td><strong>Mn-Cordierite</strong></td>
<td>298 to 1453</td>
<td>-8,747,113.142</td>
<td>( S^0_{298.15} = 2S^0_{298.15} (\text{MnO}(s)) + 5S^0_{298.15} (\text{SiO}_2(\text{tr})) )</td>
<td>( +2S^0_{298.15} (\text{Al}_2\text{O}_3(s)) )</td>
</tr>
<tr>
<td>((\text{Mn}_2\text{Al}_4\text{Si}<em>5\text{O}</em>{18}))</td>
<td></td>
<td></td>
<td></td>
<td>( C_p = 2C_p (\text{MnO}(s)) + 2C_p (\text{Al}_2\text{O}_3(s)) )</td>
</tr>
</tbody>
</table>

---

a The model parameters for the Mn-O system were optimized previously by Kang *et al.* [16].
b The model parameters for the Mn-Al-O system have been obtained from Chapter 4.
c The model parameters for the Mn-Si-O system were optimized previously by Eriksson *et al.* [7].
d The model parameters for the Al-Si-O were optimized previously by Eriksson and Pelton [6].
e The model parameters for the Mn-Al-Si-O system were optimized previously by Jung *et al.* [5].

Table 5.2: Comparison of calculated ternary invariant points (not in parentheses) with reported values of Snow [4] (in parentheses).

<table>
<thead>
<tr>
<th>Invariant reaction(^1)</th>
<th>Composition (wt. %)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MnO</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>Reaction</td>
<td>L → Sp + Tr + Mn-Crd</td>
<td>L + Tr + Mu → Mn-Crd</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td></td>
<td>33.123(30)</td>
<td>17.34(19)</td>
</tr>
<tr>
<td></td>
<td>28.48(24)</td>
<td>20.122(23)</td>
</tr>
<tr>
<td></td>
<td>39.669(40)</td>
<td>23.623(24)</td>
</tr>
<tr>
<td></td>
<td>41.617(38)</td>
<td>11.155(13)</td>
</tr>
<tr>
<td></td>
<td>51.22(50)</td>
<td>9.43(11)</td>
</tr>
<tr>
<td></td>
<td>53.638</td>
<td>14.748</td>
</tr>
<tr>
<td></td>
<td>63.06</td>
<td>12.417</td>
</tr>
<tr>
<td></td>
<td>34.773</td>
<td>21.073</td>
</tr>
<tr>
<td></td>
<td>38.897</td>
<td>23.555</td>
</tr>
<tr>
<td>(L + Crd → Sps + Mn-Crd)</td>
<td>(33)</td>
<td>(24)</td>
</tr>
<tr>
<td>(L + Mu → Crd + Mn-Crd)</td>
<td>(32)</td>
<td>(25)</td>
</tr>
</tbody>
</table>

1Abbreviations: Crd: Cordierite, Ga: Galaxite, Mu: Mullite, Rh: Rhodonite, Sps: Spessartite, Te: tephorite, Tr: tridymite.
Figure 5.1: Schematic representation of phases in the MnO-Al₂O₃-SiO₂-CaO system under reducing condition.

Figure 5.2: Geometric representation of asymmetric Kohler/Toop model (Toop-like model) given by Chartrand and Pelton [2].
Figure 5.3: Phase Diagram for the Al$_2$O$_3$-SiO$_2$ system [6].

Figure 5.4: Phase Diagram for the MnO-SiO$_2$ system [7].
Figure 5.5: Optimized liquidus surface of the MnO-Al₂O₃-SiO₂ system at Fe saturation (Temperatures in °C): (a) From Jung et al. [5] and (b) Present work
Figure 5.6: Optimized primary phase fields of the MnO-Al₂O₃-SiO₂ system at Fe saturation along with the experimental points by Snow [4] and Roghani et al. [8]: (a) From Jung et al. [5] and (b) Present work.

Figure 5.7: Calculated liquidus surface of the MnO-Al₂O₃-SiO₂ system at temperatures between 1200 and 1600°C compared with experimental data by Sakao [17], Fujisawa and Sakao [18], Ohta and Suito [19], Roghani et al. [8] and Kang and Lee [20]: (a) From Jung et al. [5] and (b) Present work.
(i) at 1650°C with experimental data from Sharma and Richardson [9].

(ii) at 1550°C with experimental data from Woo et al. [10].

Figure 5.8 (i) and (ii): Calculated activities of MnO (solid standard state) in MnO-Al₂O₃-SiO₂ slag: (a) From Jung et al. [5] and (b) Present work.
Figure 5.9: Calculated activities of MnO (solid standard state) in MnO-Al$_2$O$_3$-SiO$_2$ liquids at 1550, 1600 and 1650$^\circ$C at saturation with solid MnAl$_2$O$_4$, Al$_2$O$_3$ or mullite along with the experimental points by Sharma and Richardson [9], Fujisawa and Sakao [18], Ohta and Suito [19] and Woo et al. [10]: (a) From Jung et al. [5] and (b) Present work.

Figure 5.10: Calculated activities of SiO$_2$ (solid cristobalite standard state) in MnO-Al$_2$O$_3$-SiO$_2$ slags at 1550 and 1600$^\circ$C at saturation with solid MnAl$_2$O$_4$, Al$_2$O$_3$ or mullite along with the experimental points by Fujisawa and Sakao [18] and Ohta and Suito [19]: (a) From Jung et al. [5] and (b) Present work.
(a) total dissolved (Mn + Si) contents of 0.5

(b) total dissolved (Mn + Si) contents of 1.0
Figure 5.11 (i), (ii) and (iii): Calculated compositional trajectories of MnO-Al₂O₃-SiO₂ inclusions in equilibrium with liquid Fe containing various Mn/Si weight ratios at 1600°C. Experimental Mn/Si ratios at Al₂O₃ or mullite saturation are shown beside all experimental points which are obtained from Ohta and Suito [19] and Kang and Lee [20]. The calculated liquidus curves at 1600 and 1200°C are also shown. All calculations are: (a) From Jung et al. [5] and (b) Present work.

(i) at 1600°C
Figure 5.12 (i), (ii) and (iii): Calculated oxygen content versus dissolved Mn/Si weight ratio at various total dissolved (Mn + Si) contents in liquid Fe in equilibrium with liquid MnO-Al₂O₃-SiO₂ inclusions saturated with MnAl₂O₄, Al₂O₃, or mullite at different temperatures. Experimental points are obtained from Fujisawa and Sakao [18], Ohta and Suito [19] and Kang and Lee [20]. All calculations are: (a) From Jung et al. [5] and (b) Present work.
Figure 5.13: Phase Diagram for the CaO-MnO system [11].

Figure 5.14: Phase Diagram for the CaO-Al₂O₃ system [6].
Figure 5.15: Calculated liquidus projection of the CaO-MnO-Al₂O₃ system: (a) From Kang et al. [12] and (b) Present work.

Figure 5.16: Calculated activities of MnO (solid standard state) in CaO-MnO-Al₂O₃ liquid solutions for different ratios of wt.% CaO / wt.% Al₂O₃. Calculated line A and data from Morita et al. represent the activity of MnO at 1600°C while others are at 1650°C. The experimental points are from Mehta and Richardson [25], Sharma and Richardson [9], Jacob [21] and Morita et al. [22]. All calculations are: (a) From Kang et al. [12] and (b) Present work.
Figure 5.17: Calculated activities of MnO (with respect to the pure solid standard state) in CaO-MnO-SiO$_2$-Al$_2$O$_3$ liquid slags along with experimental points from Abraham et al. [23], Donato and Granati [24] and Morita et al. [22]: (a) From Kang et al. [12] and (b) Present work.

(i) at Al$_2$O$_3$/SiO$_2$ weight ratios of (a) 0.25
(ii) at Al$_2$O$_3$/SiO$_2$ weight ratios of (a) 0.5

Figure 5.18 (i) and (ii): Calculated liquidus surfaces of the CaO-MnO-SiO$_2$-Al$_2$O$_3$ system at 1450°C, 1500°C and 1550°C along with experimental points from Rait and Olsen [13]: (a) From Kang et al. [12] and (b) Present work.

Figure 5.19: Calculated liquidus surfaces of the CaO-MnO-SiO$_2$-Al$_2$O$_3$ system at an Al$_2$O$_3$/SiO$_2$ weight ratio of 0.41 at 1200°C and 1300°C along with experimental points from Roghani et al. [14] and Kang et al. [15]: (a) From Kang et al. [12] and (b) Present work.
Chapter 6

**Thermodynamic modeling of the MnO-Mn$_2$O$_3$-Al$_2$O$_3$-FeO-MgO system**

6.1 Introduction

The amount of experimental data available in the present system is quite high. Since, MnO-Al$_2$O$_3$ binary system has been optimized properly now (as can be seen in chapter 4), the accuracy of the predictions for the higher order systems can be judged by comparing them with the available experimental data. The results for the MnO-Mn$_2$O$_3$-Al$_2$O$_3$-CaO-SiO$_2$ system have been compared with experimental data in chapter 5 and it was observed that the predictions are in good agreement with the experimental data. Similar to the previous system (chapter 5), we have not used any interaction parameter in the present system while performing our calculations.

6.2 Critical evaluation and optimization

6.2.1 FeO-MnO-Mn$_2$O$_3$-Al$_2$O$_3$

The FeO-MnO-Al$_2$O$_3$ ternary system consists of three binary subsystems:

a. Fe-Mn-O system: The thermodynamic optimization of this system has already been done by Wu et al. [1].

b. Fe-Al-O system: The thermodynamic optimization of this system has already been done by Eriksson et al. [2].

c. Mn-Al-O system: The thermodynamic optimization of this system has already been shown in chapter 4.

Fig. 6.1 and 6.2 show the calculated phase diagrams of the FeO-MnO and FeO-Al$_2$O$_3$ binary systems from the optimized model parameters stored in FToxide database [3]. All experimental data related to phase diagrams, cation distribution and thermodynamic properties were considered in the modeling. All the previous model parameters were used in the present study without any modification.
The maximum mole fraction of Mn$_2$O$_3$ in the FeO-MnO-Mn$_2$O$_3$-Al$_2$O$_3$ slag phase at 1600°C is as low as 0.0015 which is quite low.

The schematic diagram of the Fe-Mn-Al-O (FeO-MnO-Mn$_2$O$_3$-Al$_2$O$_3$) system under reducing condition is shown in Fig. 6.3. The following solution phases are found in the Fe-Mn-Al-O system:

- **Spinel:** $(\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Al}^{3+})\text{T} (\text{Al}^{3+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Mn}^{3+}, \text{Mn}^{4+}, \text{Va})\text{O}_4$
- **Bixbyite:** $(\text{Mn}^{2+}, \text{Al}^{3+}, \text{Fe}^{3+})_2\text{O}_3$
- **Corundum:** $(\text{Al}^{3+}, \text{Mn}^{2+}, \text{Fe}^{3+})_2\text{O}_3$
- **Slag (molten oxide phase):** FeO-MnO-MnO$_{1.5}$-AlO$_{1.5}$
- **Monoxide:** FeO-MnO-MnO$_{1.5}$-AlO$_{1.5}$

No change has been made to the parameters related to any of the solid solutions present in the FeO-MnO-Mn$_2$O$_3$-Al$_2$O$_3$ system; all the required parameters have been obtained from the FT oxid database of FactSage 6.3 software [3].

Fig. 6.4 shows the optimized liquidus surface of the FeO-MnO-Al$_2$O$_3$ system under reduced oxygen condition (Fe saturation). The Gibbs energy of the ternary liquid surface was calculated with the help of the Modified Quasichemical model using the “asymmetric approximation (Toop-like interpolation technique)” by Chartrand and Pelton [4], Pelton [5] along with the parameters of the binary subsystems. In the present asymmetric approximation, Al$_2$O$_3$ was considered as the asymmetric component and FeO and MnO as the symmetric components. No additional ternary parameters were considered.

Hay *et al.* [6] were the first to carry out experiments to determine the phase relations in the FeO-MnO-Al$_2$O$_3$ system. They constructed the thermal diagram for the FeO-MnO-Al$_2$O$_3$ ternary system using the data from the heating, cooling curves and microscopical evidences. The partial pressure of oxygen was strictly reducing allowing no oxidation of samples. No measurement was done for mixtures exceeding 40% Al$_2$O$_3$ because of the very high temperatures required. They
also constructed a diagram showing the projection of the liquidus surface. Oelsen and Heynert [7] prepared oxide samples saturated with metal and carried out equilibration experiments by placing them in Al₂O₃ crucibles. All the experiments were done by heating the samples to either 1550, 1600 or 1650°C. Analyses were done of all the samples after quenching and this allowed them to obtain liquidus measurements in the FeO-MnO-Al₂O₃ system. Fischer and Bardenheuer [8] carried out similar experiments by equilibrating FeO-MnO-Al₂O₃ slags on FeO-MnO solid solution in sintered MnO crucibles. They carried out all their experiments in the temperature range of 1530-1700°C. The amounts of dissolved Oxygen and Manganese contents in liquid Iron along with amounts of FeO, MnO, etc. in slag were analyzed. Later, Maruhashi [9] and Ivanchev and Erinin [10] also carried out similar slag-metal equilibration experiments.

The experimental points in the Mn-O plot (Fig. 6.5) seem to follow a specific trend. The amount of dissolved O decreases slowly with increasing amounts of dissolved Mn till a certain point, after which the amount of O starts to decrease rapidly. The calculated results follow the trend and seem to trace the exact path of the experimental points.

Fig. 6.6 and 6.7 show the variation of dissolved O amount along with the variation of MnO and FeO levels in slag. The calculated amount of dissolved O at low MnO and high FeO levels in slag doesn’t seem to be as high as the experimental data. Those few experimental results could not be reproduced along with the set of data shown in Fig. 6.5. However, the trend observed in our calculations is similar to those of the experimental data. The agreement between the calculated and the experimental data improves at high MnO and low FeO levels in the slag.

Fig. 6.8 shows the effect of Mn present in molten iron on the amount of MnO in the slag. The amount of MnO in the slag increases very rapidly and reaches a plateau with initial rise in the amount of Mn in the molten iron. Its amount no more increases after a certain amount even when the Mn levels are kept increasing. Our calculated results are in excellent agreement with the observed trend of the experimental results as shown in the Fig. 6.8.
Fischer and Bardenheuer [8] carried out their experiments under FeO-MnO solid solution saturation and the variations of dissolved O and Mn along with amount of FeO in slag have been depicted in Fig. 6.9 and 6.10. Our calculated results are in excellent agreement with the findings of Fischer and Bardenheuer [8].

Fischer and Bardenheuer [8], Maruhashi [9] and Ivanchev and Erinin [10] also calculated the activities of the components of the slag (like FeO, MnO) from the measured amounts of dissolved oxygen and manganese in the liquid iron.

Fig. 6.11 to 6.13 show that the calculated activities of FeO in slag are close enough to the experimentally determined activities.

Kim and McLean [11] carried out experiments in which they equilibrated iron containing different amounts of oxygen, manganese, etc. with Al₂O₃. This resulted in the formation of aluminate solid solutions. They could obtain the activities of the components in the spinel solution from dissolved amounts of O and Mn in liquid iron (found out by chemical analyses) and composition of the deoxidation product (obtained by EPMA and Neutron analyses). Pandit and Jacob [12] also carried out equilibration experiments similar to Kim and McLean [11] and obtained similar results.

Fig. 6.14 and 6.15 show the variation of dissolved O and MnAl₂O₄ content of spinel solution along with increase of dissolved Mn content of the alloy respectively. Calculations were done with different amounts of Alumina since the exact amount of Alumina that was reacting was difficult to understand. It can be observed that the amount of dissolved O in the alloy decreases with increasing amounts of Alumina. This is because the amount of spinel formed starts to increase with increasing amounts of Alumina. So, O can no more get dissolved in the alloy as it is used up in formation of spinel. Moreover, the results in Fig. 6.15 show that amount of galaxite component in the spinel solution increases with increasing amounts of Alumina suggesting that Alumina is used up in formation of more and more of galaxite and not hercynite.
The calculated activities of the components of the spinel solid solution are in excellent agreement with the experimental results as shown in Fig. 6.16.

Fig. 6.17 shows the predicted cation distribution in the Galaxite-Hercynite spinel solid solution at 900°C. This is an example of how the optimized parameters can be used along with the software Factsage [3] to predict the phase relationships or thermodynamic property of a system at any given condition. These types of thermodynamically correct predictions are of immense help at times when there is no experimental data available.

6.2.2 MgO-MnO-Mn₂O₃-Al₂O₃

The MgO-MnO-Al₂O₃ ternary system consists of three binary subsystems:

a. Mg-Mn-O system: The thermodynamic optimization of this system has already been done by Wu et al. [1].

b. Mg-Al-O system: The thermodynamic optimization of this system has already been done by Jung et al. [13].

c. Mn-Al-O system: The thermodynamic optimization of this system has already been discussed in chapter 4.

Fig. 6.18 and 6.19 show the calculated phase diagrams of the MgO-MnO and MgO-Al₂O₃ binary systems from the optimized model parameters stored in FToxide database. All experimental data related to phase diagrams and thermodynamic properties were considered in the modeling. All the previous model parameters were used in the present study without any modification.

The maximum mole fraction of Mn₂O₃ in the MgO-MnO-Mn₂O₃-Al₂O₃ slag phase at 1600°C is as around 0.001 which is very low.

The schematic diagram of the Mg-Mn-Al-O (MgO-MnO-Mn₂O₃-Al₂O₃) system under reducing condition is shown in Fig. 6.20. The following solution phases are found in the Mg-Mn-Al-O system:
Spinel: \((\text{Mn}^{2+}, \text{Mg}^{2+}, \text{Al}^{3+})_4 \{\text{Al}^{3+}, \text{Mg}^{2+}, \text{Mn}^{2+}, \text{Mn}^{3+}, \text{Mn}^{4+}, \text{Va}\}_2 \}_2 \text{O}_4\)

Bixbyite: \((\text{Mn}^{2+}, \text{Al}^{3+}, \text{Mg}^{2+})_2 \text{O}_3\)

Corundum: \((\text{Al}^{3+}, \text{Mn}^{2+}, \text{Mg}^{2+})_2 \text{O}_3\)

Slag (molten oxide phase): \(\text{MgO-MnO-MnO}_{1.5}-\text{AlO}_{1.5}\)

Monoxide: \(\text{MgO-MnO-MnO}_{1.5}-\text{AlO}_{1.5}\)

No change has been made to the parameters related to any of the solid solutions present in the \(\text{MgO-MnO-Al}_2\text{O}_3\) system; all the required parameters have been obtained from the FToxid database of FactSage 6.3 software [3].

The Gibbs energy of the ternary liquid surface was calculated with the help of the Modified Quasichemical model using the “asymmetric approximation (Toop-like interpolation technique)” by Chartrand and Pelton [4], Pelton [5] along with the parameters of the binary subsystems. In the present asymmetric approximation, \(\text{Al}_2\text{O}_3\) was considered as the asymmetric component and \(\text{MgO}\) and \(\text{MnO}\) as the symmetric components. No additional ternary parameters were considered.

The experimental data in the system have been mainly obtained by the equilibration of the slag and spinel solution with liquid iron. Balakirev et al. [14] carried out experiments to expose the presence of spinel phases of the system in the temperature ranging between 900 and 1200°C in air. They used \(\text{Mn}_2\text{O}_3\), \(\text{MgO}\), \(\text{Al(OH)}_3\) as the starting materials for their experiments. The prepared cylindrical samples were annealed at 900, 1000, 1100 and 1200°C followed by quenching in water. Annealing was done for 100-300 hours to ensure equilibration, i.e., achievement of phase equilibrium and equilibrium cation distribution. However, X-ray data showed that equilibrium was reached within 30-50 hours of heat treatment.

They carried out XRD studies on all the samples to obtain the c/a ratios, from where they could predict the phase/phases present in that specific sample. They used all the c/a ratio measurements in order to construct phase stability regions since the initial composition of the samples were known. Their predicted phase diagrams focussed mainly on the spinel part of the \(\text{Mg-Mn-Al-O}\) system after quenching. Hence, one may acquire the knowledge of the stability of the phases
present at temperatures between 900 and 1200°C from this study. However, the phase diagram data from this work was mainly restricted to the spinel phases and according to our evaluation it was not possible to perform any calculations related to phase diagram based on this scarce data.

The Fig. 6.21 shows the calculated activities of the components of the MnAl$_2$O$_4$- MgAl$_2$O$_4$ spinel solid solution along with the experimental data. Zhao et al. [15] equilibrated mixtures of MnAl$_2$O$_4$ and Al$_2$O$_3$ using molten Ag-Mn solutions. They obtained the Gibbs energy of formation of MnAl$_2$O$_4$ by making use of some data from previous literature in a manner already discussed in section 4.3.1.2. Then, the activity of MnAl$_2$O$_4$ in a solid solution of MnAl$_2$O$_4$-MgAl$_2$O$_4$ was calculated by Zhao et al. [15] from knowledge of Gibbs energy, temperature, activity coefficient and mole fraction of Mn in solid solution and partial pressure of O$_2$. The activity of MgAl$_2$O$_4$ could, then, be calculated using the Gibbs-Duhem equation. Zhao et al. [15] carried out many equilibration experiments to determine the activity-composition relations in the MnO-MgO-Al$_2$O$_3$ solid solutions at 1550 and 1600°C. However, we have used the newly evaluated data related to Gibbs energy of formation of MnAl$_2$O$_4$ in order to increase the accuracy of thermodynamic modeling. The comparison of the experimental data with the calculated data shows that the two sets of data follow the same trend.

The Fig. 6.22 shows the calculated distribution of cations in the tetrahedral and octahedral sites of the spinel solution as a function of the composition of components of the MnAl$_2$O$_4$-MgAl$_2$O$_4$ spinel solid solution along with the experimental data.

Halenius [16] prepared single crystals of the type (Mg$_{1-x}$Mn$_x$)Al$_2$O$_4$ in a flux-growth method. The partial pressure of Oxygen was maintained in the range of 10$^{-12}$ to 10$^{-17}$ bars during the preparation of the samples. The samples were heated at first to 1200°C where they were kept for 24 hours for complete homogenization. Then, they were cooled to 900°C at the rate of 4°C/min, followed by fast cooling to room temperature. EPMA of the products gave their composition. Then, single crystal structural refinements were performed in which cation distribution in the products was calculated from an optimization program applying a minimization function in which both structural and chemical data of the products were taken into account.
The calculated results show the same trend as shown by the experimental results.

6.2.3 Other systems at oxidizing condition

There is no experimental data available for any other subsystem in oxidizing condition. Hence, Factsage [3] can be used along with proper database to predict phase relationships in any system at any condition.

6.3 Summary

The previous work in the Mn-Al-O system has been extended to the MnO-Al₂O₃-FeO-MgO system. No change in the model parameters of the ternary systems has been done. All the calculations in the MnO-Al₂O₃-FeO-MgO system have been performed with the newly obtained database. The present results show good agreement with the experimental data. This proves that the optimized model parameters for the binary MnO-Al₂O₃ system are reasonable and they can be extended to even higher order systems.
References


Figure 6.1: Phase Diagram for the FeO-MnO system under reducing condition by Wu et al. [1].

Figure 6.2: Phase Diagram for the FeO-Al₂O₃ system under reducing condition by Eriksson et al. [2].

Figure 6.3: Schematic representation of phases in the FeO-MnO-Al₂O₃ system under reducing condition.
Figure 6.4: Calculated phase diagram for the FeO-MnO-Al₂O₃ system under reducing condition. The experimental points of Oelsen and Heynert [7] and Fischer and Bardenheuer [8] are also shown for comparison with calculated results.
Figure 6.5: Calculated Mn-O equilibrium in liquid iron under FeO-MnO-Al₂O₃ slags at different conditions along with the experimental data by Oelsen and Heynert [7], Maruhashi [9] and Ivanchev and Erinin [10].

Figure 6.6: Calculated solubility of oxygen in molten iron as a function of mole fraction of MnO in FeO-MnO-Al₂O₃ slags at different conditions along with the experimental data by Oelsen and Heynert [7], Maruhashi [9] and Ivanchev and Erinin [10].
Figure 6.7: Calculated solubility of oxygen in molten iron as a function of mole fraction of FeO in FeO-MnO-Al₂O₃ slags at different conditions along with the experimental data by Oelsen and Heynert [7], Maruhashi [9] and Ivanchev and Erinin [10].

Figure 6.8: Calculated effect of manganese in molten iron as a function of mole fraction of MnO in FeO-MnO-Al₂O₃ slags at different conditions along with the experimental data by Oelsen and Heynert [7] and Maruhashi [9].
Figure 6.9: Calculated solubility of oxygen in molten iron as a function of mole fraction of FeO in FeO-MnO-Al₂O₃ slags at different temperatures along with the experimental data by Fischer and Bardenheuer [8].

Figure 6.10: Calculated effect of manganese in molten iron as a function of mole fraction of FeO in FeO-MnO-Al₂O₃ slags at different temperatures along with the experimental data by Fischer and Bardenheuer [8].
Figure 6.11: Calculated activities of FeO (liquid standard state) as a function of mole fraction of FeO in FeO-MnO-Al$_2$O$_3$ slags at different conditions along with the experimental data by Maruhashi [9] and Ivanchev and Erinin [10].

Figure 6.12: Calculated activities of MnO (liquid standard state) as a function of mole fraction of FeO in FeO-MnO-Al$_2$O$_3$ slags at different conditions along with the experimental data by Maruhashi [9] and Ivanchev and Erinin [10].
Figure 6.13: Calculated activities of FeO (liquid standard state) as a function of mole fraction of FeO in FeO-MnO-Al$_2$O$_3$ slags at different temperatures along with the experimental data by Fischer and Bardenheuer [8].
Figure 6.14: Calculated Mn-O equilibrium in liquid iron at equilibrium with spinel solid solution and (a) 0.1 moles of Alumina, (b) 0.5 moles of Alumina, (c) 1 moles of Alumina and (d) 2 moles of Alumina at different temperatures along with the experimental data by Kim and McLean [11] and Pandit and Jacob [12].

Figure 6.15: Calculated variation of the equilibrium composition of the spinel solid solution with manganese content of the alloy. The alloy and the spinel solid solutions are in equilibrium with (a) 0.1 moles of Alumina, (b) 0.5 moles of Alumina, (c) 1 moles of Alumina and (d) 2 moles of Alumina at different temperatures along with the experimental data by Kim and McLean [11] and Pandit and Jacob [12].
Figure 6.16: Calculated variation of activities with the composition of the components of the spinel solid solution at 1600°C along with the experimental data by Kim and McLean [11].

Figure 6.17: Predicted cation distribution in the (a) Tetrahedral sites and (b) Octahedral sites of the spinel solid solution at 900°C.
Figure 6.18: Phase Diagram for the MgO-MnO system by Wu et al. [1].

Figure 6.19: Phase Diagram for the MgO-Al₂O₃ system Jung et al. [13].

Figure 6.20: Schematic representation of phases in the MgO-MnO-Al₂O₃ system under reducing condition.
Figure 6.21: Calculated variation of activities of $\text{MnAl}_2\text{O}_4$ (in blue) and $\text{MgAl}_2\text{O}_4$ (in red) with their compositions at 1400°C and 1550°C along with the experimental data by Zhao et al. [15].

Figure 6.22: Calculated cation distribution in the (a) Tetrahedral sites and (b) Octahedral sites of the spinel solid solution at 900°C along with the experimental data by Halenius [16].
CHAPTER 7

Conclusion

All the experimental data in the systems MnO-Al₂O₃, MnO-Al₂O₃-SiO₂, CaO-MnO-Al₂O₃, FeO-MnO-Al₂O₃, MgO-MnO-Al₂O₃ and CaO-MnO-Al₂O₃-SiO₂ have been critically assessed and the discrepancies in the available data have been resolved based on thermodynamically consistent way. All the models used in the present study were based on the structure of the solutions so that their configurational entropy was properly taken into account in the Gibbs energy of the solution. A set of optimized model parameters have been obtained which could reproduce all reliable thermodynamic and structural data as well as phase diagrams within the experimental error limits. Two spinel solid solutions (cubic and tetragonal) have been modeled separately in the study related to the binary MnO-Al₂O₃ system. The molten oxide and the bixbyite phases were also optimized in the course of the present work. Asymmetric Toop interpolation techniques were then used in order to predict the Gibbs energies of the ternary liquid solution present in the MnO-Al₂O₃-SiO₂ system with SiO₂ as an asymmetric component and two small ternary parameters were added. In case of the CaO-MnO-Al₂O₃, FeO-MnO-Al₂O₃ and MgO-MnO-Al₂O₃ systems, asymmetric Toop interpolation technique was used with Al₂O₃ as the asymmetric component without any ternary parameters. The calculations in the ternary systems were in good agreement with the available experimental data within the experimental error.

As an application to industrial processes, the thermodynamic databases developed in this study were used to carry out calculations related to inclusion engineering in the steelmaking process. The results obtained from these calculations reiterate the usefulness of the optimized databases.