

Molecular Dynamics Simulations of Silicate Slags and Slag-Solid Interfaces

Ling Zhang, Shouyi Sun and Sharif Jahanshahi
G K Williams CRC for Extractive Metallurgy
CSIRO-Division of Minerals,
Box 312, Clayton South, Vic. 3169, Australia
Fax: 61-3-95628919
Email: ling.zhang@minerals.csiro.au

Abstract

Molecular dynamics simulations of silicate melts and melt-solid interfaces were carried out by using ionic force field in the form of the Born-Mayer-Huggins pair potential. The study includes structural properties of the binary CaO-SiO₂ and ternary CaO-Al₂O₃-SiO₂ melts, with particular focus on the structural role played by Al₂O₃ in the silicate melts. Structural properties such as the fractions of different type of oxygen atoms have been obtained. Approaches have been developed for simulating slag/MgO interface. Information obtained, such as interfacial energy and distribution of elements at the interface are useful in understanding the relationship between structure and properties of the interface.

Introduction

Molecular simulations using empirical potential, i.e., force field approach are being increasingly used in the study of structural, dynamic, surface and interfacial properties of various materials. This is due partly to the fast improvement in computer power and the advances in theory, algorithm and procedures of the simulation technique in recent years. Such approaches are particularly useful to obtain structural information on the systems under investigation. More importantly, the relationships between structure and various properties can be examined at the atomic level. However, the reliability of the simulation results is subject to the accuracy of the force field which describes the interactions between atoms.

Since the success of molecular dynamics (MD) simulation of silica carried out by Woodcock et al [1] in the middle 70's by using the Born-Mayer-Huggins pair potential, there have been many attempts at MD simulations of silicate systems in the form of crystals, glasses and melts [2-5]. These studies together with experimental techniques, such as XRD, Raman and NMR have contributed to our advanced understanding on the structure of silicate glasses and melts in recent years.

A detailed discussion on the experimental findings on the structure of the silicate and aluminosilicate melts and glasses can be found in an article by Gaskell [6] at the previous Slag Conference. It is generally accepted that due to the strong bonding between Si and O atoms, the silicon atoms in silicate melts are almost always associated with four oxygen atoms and exist as SiO_4^{4-} , which link up to form different size of anion groups. Other singly or doubly charged metal ions surround these anions to maintain local neutrality. The degree of polymerization in the melts increases with increasing silica content. The notion of three types of oxygen, namely, free (O^{2-}), non-bridging (O^- , bonded to one Si) and bridging oxygen (O^0 , bonded to two Si) has been used to indicate the degree of polymerization.

Alumina in the melt is generally regarded as amphoteric. This is partly based on the observations of extrema in viscosity and other physical properties of aluminosilicate glasses and melts as functions of the ratio of R ($\text{Al}_2\text{O}_3/\text{M}_x\text{O}$, where M denotes metal cations, such as Na and Ca) [5,7]. Such an effect is attributed to the structural changes brought about by alumina. A paper by Zirl and Garofalini [5] discussed three structural models proposed based on different experimental data to explain the changes in physical properties. The paper also presented the results from their MD simulation study of sodium aluminosilicate glass. Their findings are consistent with one of the proposed structural models [8-9]. This model introduced triclusters which are formed by connecting three tetrahedra to the fourth type of oxygen, i.e., the three coordinated oxygen (O^3). They also found that the fraction of tricluster in the system increased with the R ratio.

A good understanding of the interaction between oxide melts and refractory materials is useful both to the design and improvement of processes in metallurgical industry, and to the optimisation of sintering of oxide ceramics involving liquid phase.

Some attempts have been made at the G K Williams Cooperative Research Centre for Extractive Metallurgy to explore the potential of the simulation technique to metallurgical slags and related systems. The studies carried out include the structure of the CaO-SiO_2 and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melts and the properties of slag/solid interfaces [10-13]. A summary of the findings and discussions on the approaches are presented in this paper.

Computational Method

Ionic type of force field, such as the Born-Mayer-Huggins (BMH) pair potential has been used for silicate systems. It has been shown that the main structural features of silicate

systems can be reproduced reasonably well by using the BMH potential [4]. The original form of the BMH potential between two ions i and j was expressed as

$$\Phi_{ij}(r) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r} + (1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j})b \bullet \exp(\frac{\sigma_i + \sigma_j - r}{r}), \quad (1)$$

where r is the distance between the two ions, Z_i is the valence of the ion i , e is the electron charge, ϵ_0 is the dielectric constant, n_i is the number of outer shell electrons of the ion i , σ_i is the characteristic ionic radius, and b and r are constants. The first term in Eq.(1) is the Coulombic term which describe the electrostatic interactions between charged particles. The second term is for the short range repulsion. A simplified form of the BMH potential is commonly seen in the literature as

$$\Phi_{ij}(r) = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r} + A_{ij} \exp(-\frac{r}{B_{ij}}), \quad (2)$$

where the parameters A_{ij} and B_{ij} can be obtained by fitting the crystal structure or other properties of the ionic system [2].

Two different simulation package and program [14,15] have been used for the present work during the years depending on the suitability and availability at the time. Table 1 provides details of computational methods used for the different investigations. The general procedures of simulation of amorphous phases were followed. The simulation of slag alone was performed in a cubic box of constant volume with periodical boundaries. The atoms in the simulation box were started from a random configuration at 6000 K followed by a cooling process that brought the system to a temperature at which the equilibrium data were collected. The simulation of the slag phase was performed in a constant energy and constant volume ensemble (NVE).

The simulations of slag/solid interface involves the following three steps:

- (1) preparation of slag cells – the procedure is the same as described above in which the atoms in the box were brought to equilibrium state;
- (2) preparation of solid – a unit cell of crystal MgO was taken from MSI database [15] and multiplied in three dimensions. It was then shaped into a cubic cell;
- (3) Interface simulations – a standard procedure of interface building from the instruction of the MSI package was followed. The slag and solid cells prepared in the above two steps were brought together. Figure 1 shows a schematic model interface system of slag/MgO used in the simulation. During the simulation periodical boundary conditions were used for the interface box. The coordinates of atoms in the crystal phase were fixed, while the atoms in the slag cell were allowed to relax until the interface system reached equilibrium. The simulation results in terms of interfacial energy and elemental distribution at the interface were subsequently collected.

Results and Discussion

A. Structure of CaO-SiO₂ melts at 2000 K

MD simulations were carried out at four compositions for the CaO-SiO₂ melts (X_{SiO_2} =0.2, 0.333, 0.5 and 0.667) to determine the composition dependence of the fractions of free ($\text{N}_{\text{O}^{2-}}$), bridging (N_{O^0}) and non-bridging (N_{O^-}) oxygen. The results are shown in Figure 2 where they are compared with experimental values obtained from the Raman spectra study of Tsunawaki et al [16]. The calculated values of the fractions for the three type of oxygen by using the Cell Model (a thermodynamic model) [17,18] are also shown in the figure. It can be seen that

all three sets of data are in accord and that the fraction of bridging oxygen N_O^0 increases sharply as the mole fraction of silica (X_{SiO_2}) increases beyond a value of 1/3. Note in particular that a maximum value for the fraction of non-bridging oxygen atoms is obtained at a silica mole fraction of about 1/3. According to Lin and Pelton [19], the maximum value of N_O^- in binary silicate ($MO-SiO_2$) melts at the orthosilicate composition is dependent on the relative basicity of MO , and the more basic MO , the closer N_O^- is to unity. Calcium oxide is one of the strongest basic oxides found in metallurgical melts. The maximum value of N_O^- in calcium silicate melts is about 0.9.

In Figure 3 the distributions of silicate anions of different sizes (N_{Si}) are shown as bar graphs for four calcium silicate compositions. The values of one to six used for N_{Si} represent silicate anions ranging from monomers (SiO_4^{4-}) to complex chains and rings of silicates with different numbers of Si per species. Since direct experimental data on the calcium silicate system are not available, the results from the MD simulations may only be compared with those predicted by model calculations which are based on the Cell Model and statistical treatment [19,20]. Once again good agreement between the two sets of results is apparent. According to these results, when the mole fraction of silica is 0.2, the system consists of mainly SiO_4^{4-} monomers with a small amount of dimers $Si_2O_7^{6-}$. On the other hand, when the silica mole fraction is over 0.66, large anions predominate. Between these two compositions, an increasing degree of polymerization is apparent. The results in Figure 3 show reasonable trends and good agreement with model calculations. These results demonstrate that MD simulation can be used to study long range structure in silicate melts. However, as mentioned earlier, the reliability of the results depends on the accuracy of the force field. In addition, statistical errors introduced due to the small size of the cell and short simulation time have to be considered.

B. Structure of CaO-Al₂O₃-SiO₂ melts at 2000 K

In the present study MD simulation of the CaO-Al₂O₃-SiO₂ melts were performed with a fixed mole fraction of silica, i.e. $X_{SiO_2} = 0.4$. The R ratio, (Al_2O_3/CaO) took the values of 0.2, 0.5 1.0 and 2.0 so that the structural changes with increasing alumina could be investigated. The results are shown in Figures 4 and 5. It is evident (Figure 4) that the degree of polymerisation (fraction of bridging oxygen) of these melts increases with increasing mole fraction of Al_2O_3 or R . The bridging oxygen can be one of three bonding situations, i.e., Al-O-Al, Al-O-Si and Si-O-Si.

Existence of triclusters or a fourth type of oxygen, i.e., the three coordinated oxygen O_3 was also found, though they are only a few percent of the total oxygen. As shown in Figure 5, the majority of the triclusters are three tetrahedra of AlO_4^{5-} . Triclusters of three SiO_4^{4-} or two SiO_4^{4-} and one AlO_4^{5-} were not found. Furthermore, the O_3 -Al bond was found to be about 2.5% longer than other O-Al bonds of 1.74 Å. Because of this the stability of the connections of the tetrahedra is expected to be lower than normal connection of two tetrahedra. It may be inferred that the increase in the number of triclusters in the melts with increasing R may create weak points between the linkage of the anions which cause the extreme value in viscosity in the melts found by experiments.

C. Slag/MgO Interface at 2400 K

The current work was an attempt in examining the interfacial contact between solid MgO and silicate melts. Two orientations of the crystal were chosen such that the (100) or the

(111) crystal plane was in contact with the melt. The distribution of the elements, particularly the cation species, was analysed for the liquid layer ($\sim 20 \text{ \AA}$) by dividing it into 20 thin slices. The results shown in Figure 6 are the ratio of the real number of atoms over the average number of atoms in each slice. In other words, if the atoms are evenly distributed in each slice, the ratio should be unity throughout the liquid layer. It was found that Mg and Si tend to enrich near the melt/MgO(100) interface and Mg and Ca near the melt/MgO(111) interface (oxygen surface). Such re-arrangement of elements is driven by energy requirement of the system. For both the (100) and (111) crystal orientations, a decrease in energy was found which is mainly due to the formation of chemical bonds established between the ions in the melt and the MgO surface.

The interfacial energy $\gamma_{L/S}$ has been calculated by

$$g_{L/S} = (E_{total} - E_{MgO} - E_{melt}) / 2A, \quad (3)$$

where E_{total} is total energy of the interface cell, E_{MgO} is energy of bulk MgO crystal cell, E_{melt} is energy for the bulk silicate melt and A is the cross section area of the interface. The calculated values are -0.58 and -8.0 (N/m) for (100) and (111) crystal plane respectively. The absolute values from the MD simulation may not agree with the measured values as the model systems used here may be over simplified which was limited by the methods used. The factors such as the small size of the system and the unrelaxed surface atoms of the MgO block will have influence on the accuracy of the results. However, the structural information obtained for a model interface at the atomic level which can not be obtained otherwise is considered to be useful.

D. Limitations and Potential of Molecular Simulations

The MD simulations of model systems using the BMH potential described above have demonstrated the great potential of the technique, i.e., structural information and its relation to the other properties can be obtained. Such information at the atomic level is difficult or sometime impossible to obtain by any other means. However, the technique is still at its early stage in the application to practical problems. One frequently encountered problem is the availability and the reliability of the force field used for the simulations. This is due to (1) the force field parameters for some common elements, such as Fe, in metallurgical melts are not readily available, and (2) the available force field parameters in the current form may not adequately describe some effects, such as polarization of the ions and crystal field effect for transition metals. Better representation of the real systems will come about with refinement and improvement in the quality of the force field and computational aspects of the simulation technique, such as algorithm used and speed of the computer.

Conclusion

MD simulations of silicate melts and slag/solid interface presented in the present paper have demonstrated the usefulness and the potential of the technique in obtaining information of the structural and interfacial properties. The structural information obtained for the CaO-SiO₂ melts is in good accord with experimental data and theoretical predictions. The behaviour of the triclusters in the CaO-Al₂O₃-SiO₂ melts may be useful to understand the structural role played by alumina. The approaches developed for the interface study can be used to examine the trends in energetics and structural aspects for different slag/solid interface systems.

Acknowledgment

Financial support for this work was provided by BHP Ltd, MIM Ltd, Rio Tinto and Pasminco through the AMIRA (the Australian Mineral Industries Research Association Limited) and the Australian Government Cooperative Research Centres Program through the G. K. Williams Cooperative Research Centre for Extractive Metallurgy, a joint venture between the CSIRO-Division of Minerals and The University of Melbourne - Department of Chemical Engineering.

Reference

1. L.V. Woodcock, C.A. Angell and P. Cheeseman, *J. Chem. Phys.*, 1976, vol.65, pp. 1565-77.
2. D. K. Belashchenko, *Russian Chem. Reviews*, 1997, vol.66, pp.733-62.
3. D.K. Belashchenko, I.E. Gopengauz, A.B. Grytsenko and O.I. Ostrovskij, *ISIJ International*, 1992, vol.32, pp. 990-7.
4. H. Ogawa and Y. Waseda, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, 1991, vol.36, pp. 20-35.
5. D.M. Zirl and S.H. Garofalini, *J. Am. Ceram. Soc.*, 1990, vol73, pp. 2848-56.
6. D. R. Gaskell, "Structure Aspects of Slags", *5th International Conference on Molten Slags, Fluxes and Salts '97*, The Iron and Steel Society, 1997, Sydney, pp.11-26.
7. P. Kozakevitch, *Revue de Metallurgie*, 1960, vol.57, pp. 149-60.
8. E.D. Lacy, *Phys. Chem. Glasses*, 1963, vol.4, pp. 234-38.
9. G. Engelhardt, M. Nofz, K. Forkel, F.G. Wihsmann, M. Magi, A. Samoson and E. Lippmaa, *Phys. Chem. Glasses*, 1985, vol.26, pp. 157-65.
10. L. Zhang, A. Dockery and S. Jahanshahi, *Proceedings of the International Conference-MSMM'96*, (Ed. Z. Yu, Z. Xiao and X. Xie), The Chinese Society for Metals, 1996, Beijing, pp94-96.
11. L. Zhang, S. Sun and S. Jahanshahi, "A Molecular Dynamics Simulation of Silicate Melt/MgO Interfaces", in *Third Australian Molecular Modelling Workshop*, 1997, Melbourne, p32.
12. L. Zhang, S. Sun and S. Jahanshahi, "Structure of Alumina-Containing Silicate Melt", in *Proceedings of the 4th Australian Molecular Modelling Conference and Workshop*, 1998, Sydney, p29.
13. L. Zhang, and I. Yarovsky, "Application of Lennard-Jones Potential to simulation of Metal Oxide Melts", in *Proceedings of the 4th Australian Molecular Modelling Conference and Workshop*, 1998, Sydney, P32.
14. K. Refson, *MOLDY User's Manual*, Oxford, 1993.
15. Molecular Simulation Inc. <http://www.msi.com>.
16. Y. Tsunawaki, N. Iwamoto, T. Hattori and A. Mitsuishi, *J. Non-Cryst. Solids*, 1981, vol.44, pp.369-78.
17. M.L. Kapoor and M.G. Froberg, *Chemical Metallurgy of Iron and Steel*, The Iron and Steel Institute, London, 1971, pp.17-22.
18. L. Zhang, S. Sun and S. Jahanshahi, *Proceedings of the International Conference-MSMM'96*, (Ed. Z. Yu, Z. Xiao and X. Xie), The Chinese Society for Metals, 1996, Beijing, pp88-93.
19. P.L. Lin and A.D. Pelton, *Metall. Trans. B*, 1979, vol. 10B, pp.667-75.
20. D.R. Gaskell, *Can. Metall. Quart.*, 1981, vol.20, pp. 3-9.



Figure 1. Schematic diagram of the model system for interface used in MD simulation.

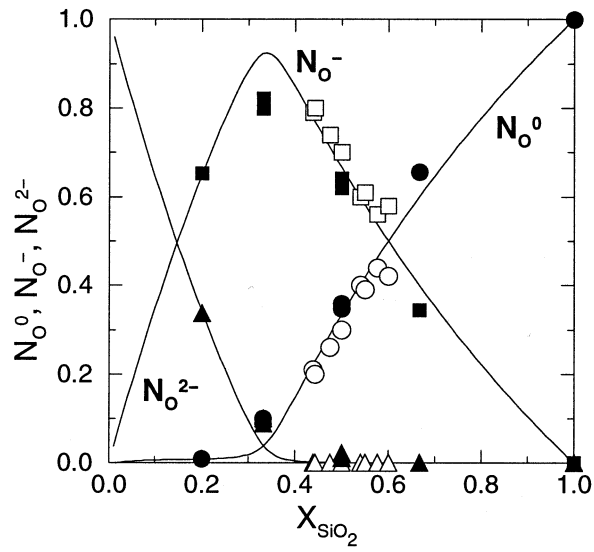


Figure 2. Comparison of the MD simulation results (solid symbols) with the data from experimental (open symbols) and thermodynamic modelling studies (solid lines) on the composition dependence of the fractions of free, non-bridging and bridging oxygen in the CaO-SiO₂ melts.

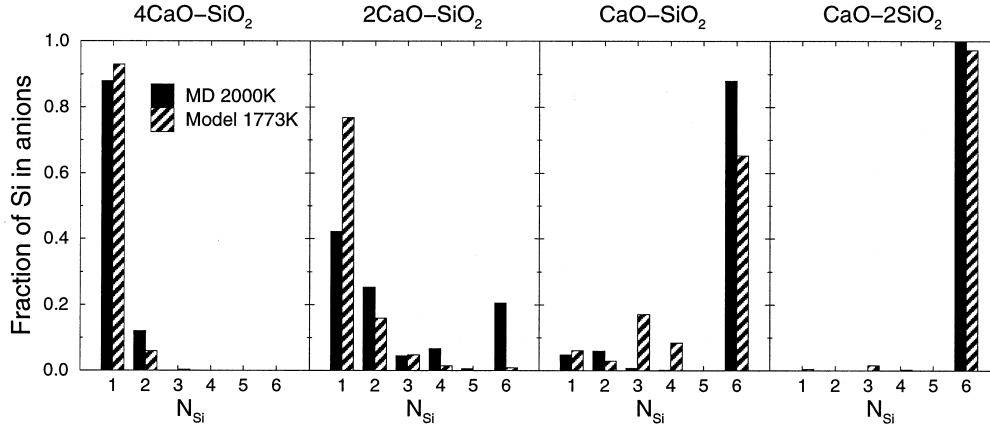


Figure 3. Comparison of the distributions of various size of anions between model calculations and MD simulations in the CaO-SiO₂ melts, where $N_{Si}=1$ represents SiO₄⁴⁻ ions, $N_{Si}=2$ is for Si₂O₇⁶⁻ ions and $N_{Si}=3$ includes both Si₃O₁₀⁶⁻ chains and Si₂O₉⁶⁻ rings. For $N_{Si}>3$ the fraction of Si includes all possible shapes of anions. The values at $N_{Si}=6$ include all Si_nO_m^{(2m-4n)-} anions with $N_{Si} \geq 6$.

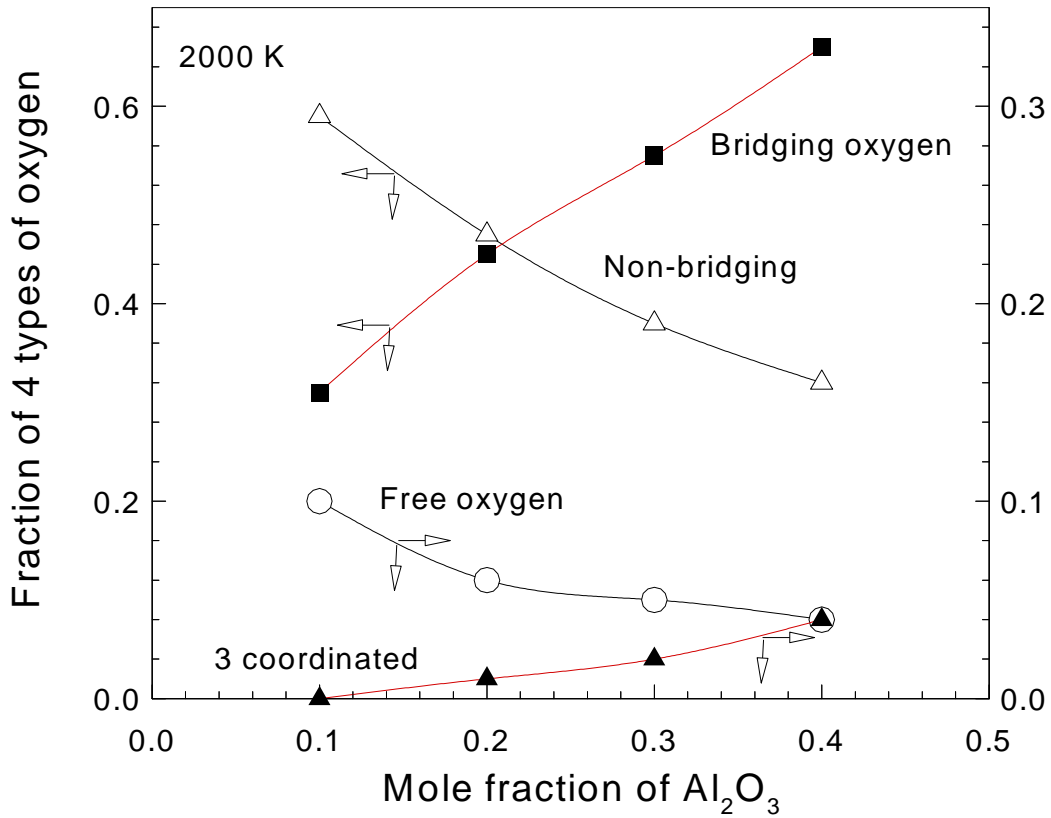


Figure 4. Variation of fraction of four types of oxygen with mole fraction of Al₂O₃ in the CaO-Al₂O₃-SiO₂ melts.

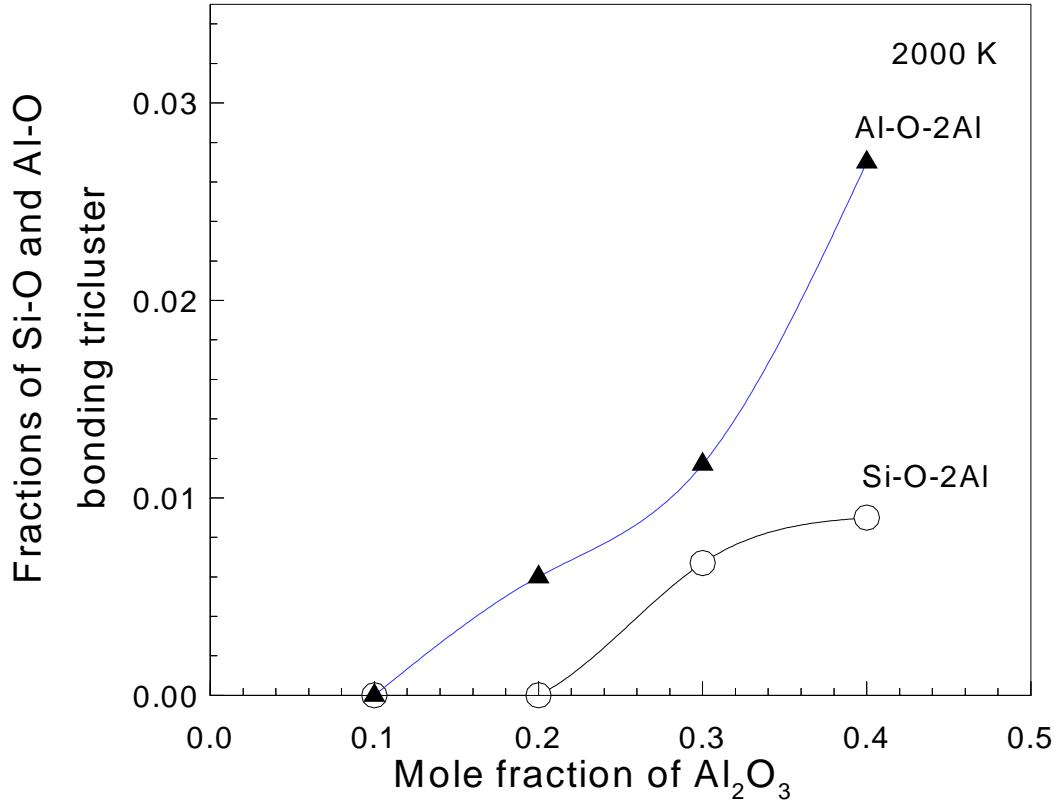


Figure 5. Variation of fraction of 4 types of tricluster with mole fraction of Al_2O_3 in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ melts. 3SiO or 2Si-O-Al types of tricluster were not found.

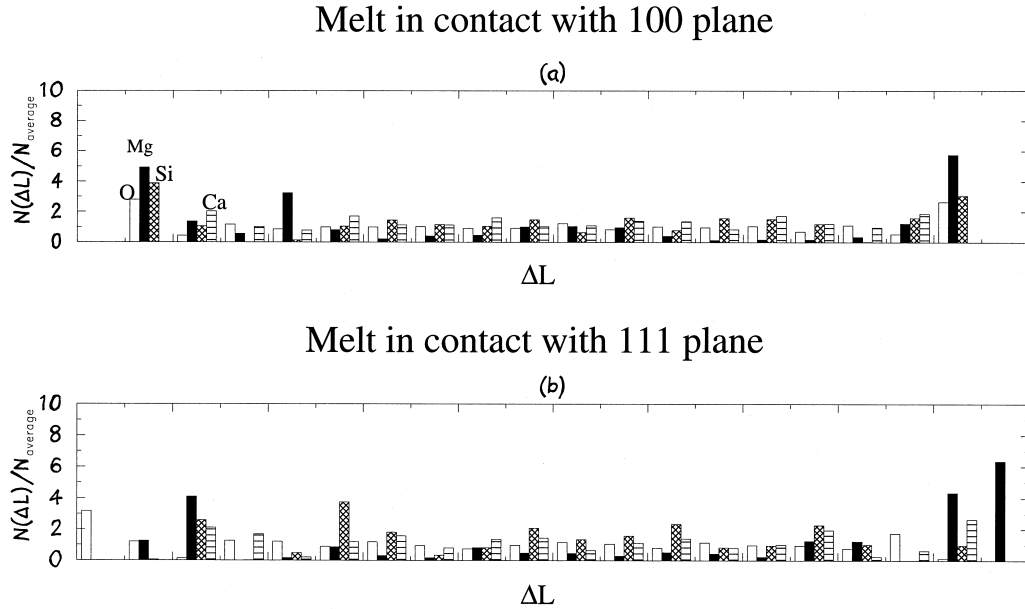


Figure 6. Distribution of each type of elements in the liquid layer (20 ΔL slices) of the slag/MgO interface. In (b) the crystal plane of Mg-(111) is on the left side of the box and O-(111) on the right.

Table 1 Summary of computational details of MD simulations

	Package /Program	Force Field	System Size (atoms)	Temperature (K)
CaO-SiO ₂	Modified MOLDY [14]	Eq.(2) (parameters from Ref.[3])	300-500	2000
CaO-Al ₂ O ₃ - SiO ₂	MSI Cerius2 [15]	glassff_1.01	~1000	2000
Slag/MgO interface	MSI Cerius2 [15]	glassff_1.01	slag: ~ 800 MgO: 500	2400