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Molecular dynamics simulations of the structural properties of Al_2O_3-based binary systems

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ABSTRACT

In order to aid the research and development of Al_2O_3-based mold fluxes, a comprehensive study of the structural properties of Al_2O_3-based binary systems was carried out via molecular dynamics simulations. The simulation results demonstrated that the structural properties of Al_2O_3-based binary systems varied with both the Al^{3+} content and the type of metal cation. The aluminate network becomes more complex with increasing Al_2O_3 content, and for a given Al_2O_3 content in different systems, both the Al–O structural disorder and the polymerization degree of the network structure increase as the metal cations become more electronegative. For a given Al_2O_3 content, the effects of the components on stabilizing the Al–O network is sequenced as $K_2O > Na_2O > CaO > MgO$, and the polymerization degree of the structure in different systems follows the order $K_2O–Al_2O_3 < Na_2O–Al_2O_3 < CaO–Al_2O_3 < MgO–Al_2O_3$. In addition, both the metal cations and the oxygen triclusters play a role in the charge compensation of the AlO_4 tetrahedron.

1. Introduction

In the field of metallurgy, there is an old adage that says, "*Look after the slag and the metal will look after itself.*" As such, mold fluxes, a type of indispensable auxiliary material in continuous casting, play an important role in improving the quality of slag and the smooth running of the process. Traditionally, SiO_2 has been the basis of most mold fluxes, and the physical properties of mold fluxes are strongly dependent on the silicate structure developed in the molten slag. However, with the recent developments of high-Al-content steel for lightweight-automotive applications, the fact that SiO_2-based mold fluxes are easily reduced by the Al in the molten steel, leading to performance deterioration of the mold fluxes, has emerged as a significant issue [1–4]. To solve this problem, Al_2O_3 has been suggested as a substitute for SiO_2 to develop Al_2O_3-based mold fluxes with low reactivities [5]. However, up to now, there have been no reports on the successful industrial application of Al_2O_3-based mold fluxes. Previous research into Al_2O_3-based mold fluxes has mainly focused on the effects of the components and temperatures on the macro properties [5,6], while the microstructural characteristics and action mechanisms of the typical components have not been involved. Since the macroscopic properties of melts are determined by the microstructure, structural characterization of aluminate melts is central to our understanding of the structure–property relationships of Al_2O_3-based mold fluxes.

Compared to silicate melts, aluminate melts have a much more complex structure, which is unpredictable due to the amphoteric property of Al_2O_3 and the electric charge of Al^{3+}. It has been concluded that in basic melts, Al_2O_3 exists as AlO_4^{5-} ions with four coordinated oxygen that form a tetrahedral network structure, while in acidic melts, it dissociates into O^{2-} and Al^{3+} to break the Si–O covalent bond as a network modifier [7]. Although the structural information of simple aluminate melts has been studied via various techniques [8–11], there are still several aspects that have no exact explanation. Because of the electric charge of Al^{3+}, charge compensation of Al^{3+} in the tetrahedral coordination is necessary, which can be achieved with either alkali- or alkaline-earth metals. The nature of the charge-balancing cation also affects the structural behavior of Al^{3+} because the Al–O bond properties depend on the metal cations [12–14]. Mysen [15,16] demonstrated that metal cations play a role in the charge balancing of the AlO_4 tetrahedron, while additional metal cations in excess of those required act as network modifiers. However, thus far, the type of metal cation that is more likely to compensate the charge deficiency of the AlO_4 tetrahedron in alumina-based melts has not been clarified. In addition, several studies on melts that contain no sufficient charge-balancing cations, have determined that the oxygen coordinates to a mixture of three tetrahedra for this charge balancing [17,18]. Lacy originally proposed this geometry, termed as a "tricluster" [19]. A systematic study of the energetic stability of "triclusters" in aluminosilicate glasses was carried out via molecular orbital calculations, and on the basis of the results, it was predicted that all the tricluster configurations modeled to be dynamically stable except for one containing three Al^{3+} cations [20]. Although the existence, conformation, quantity, and influence on the dynamic properties of these oxygen triclusters have been widely

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investigated [21–24], the behaviors of triclusters in aluminate melts that contains no silica remain to be seen.

Because of the high melting temperatures of aluminate melts and the harsh experimental conditions, the structures of Al_2O_3-based slags have not yet been fully understood. As a very valuable technology currently used in exploration of melt atomic microstructures, molecular dynamics (MD) can overcome the obstacles in the experimental processes and offer clearer insights into these structures. Moreover, the nature of these multicomponent systems with significant topological and chemical disorders often leads to an overlap among diverse structural units, necessarily increasing the difficulty of this research. Therefore, in this study, the structural properties of Al_2O_3-based binary systems, which include Na_2O–Al_2O_3, K_2O–Al_2O_3, MgO–Al_2O_3, and CaO–Al_2O_3 systems, were studied via MD simulations to identify the components that can best contribute to stabilization of the Al–O network. The results should provide a theoretical basis for the research and development of Al_2O_3-based mold fluxes.

2. Simulation method

The key to success of MD simulations is selecting the appropriate potential function and its corresponding parameters. Since the two-body Born–Mayer–Higgins (BMH) potential function, which is composed of the long-range Coulomb interactions, short-range repulsion interactions, and van der Waals forces, has been generally and successfully used in studying the structures of slags, it was applied here as:

$$U_{ij}(r) = \frac{q_i q_j}{r_{ij}} + A_{ij}\exp(-B_{ij}r) - \frac{C_{ij}}{r_{ij}^6}, \quad (1)$$

where $U_{ij}(r)$ is the interatomic-pair potential; q_i and q_j are the selected charges that usually equal the standard valence of the atoms; r_{ij} represents the distance between atoms i and j; A_{ij} and C_{ij} are energy parameters for the pair ij describing the repulsive and van der Waals attractive forces, respectively; and B_{ij} is an e-folding length characterizing the radically symmetric decay of the electron-repulsion energy between the atom pair ij. The parameters of all the systems [25] used in this study are listed in Table 1.

Since the BMH potential function regards these melts as completely ionic solutions during the simulation process, the simulated systems should be chosen in the completely molten-composition range at a corresponding temperature. According to the phase diagrams obtained from the book [26] and the software Factsage, the molten-melt compositions were determined at 2473 K, and the total number of atoms in each sample was set at about 2000. The density of each sample at 2473 K was obtained from the experimental formula by Mills and Keene [27]. The MD simulations were performed with the Materials Explorer program in the NVT ensemble, meaning that the simulations were run maintaining a constant number of particles (N), sample volume (V), and temperature (T) of a system. The equations of motions for atoms were solved with a time step of 1 fs (10^{-15} s) via a leap-frog algorithm. As the atoms bore charges, the long-range Coulomb forces, presented in the first term of Eq. (1), were evaluated using the Ewald-sum method with a precision of 10^{-5}. When calculating the repulsive forces, the potential cutoff was set to 10 Å, a good trade-off between accuracy and computational cost. The number of atoms of each sample was placed in the primary MD cell with a random initial state, and the volume of the cell was decided by the number of atoms and the density. The composition, number of atoms, density, and box length of each sample of the Al_2O_3-based binary systems are presented in Table 2. M is presented as an alkali- or alkaline-earth cation. NA, KA, MA, and CA are abbreviations for Na_2O–Al_2O_3, K_2O–Al_2O_3, MgO–Al_2O_3, and CaO–Al_2O_3, respectively.

Through a lot of preliminary explorations, a stable simulation process was determined as follows for each sample. At the beginning of the simulation, the initial temperature was fixed at 6000 K for 24,000 steps to mix the system completely and eliminate the effects of the initial distribution. Then, the temperature was cooled to 2473 K through 96,000 steps, and the temperature reduction was accomplished via the direct velocity rescaling of each molecule. After equilibrium calculations, the system was relaxed for another 60,000 steps. Finally, the structural information of melts could be calculated and analyzed. For each sample, since the number of atoms in the real world was always far more than the quantities that the computer could support, periodic boundary conditions were applied on all sides of the model box to create an infinite system with no boundaries so that the calculated results would be more convincing.

Table 1
The potential parameters [25] of Al_2O_3-based binary systems.

Atom1	Atom2	A_{ij} (eV)	B_{ij} (1/Å)	C_{ij} (eV·Å^6)
O	O	1,497,049.00	5.88	17.34
O	Al	86,057.58	6.06	0
O	Na	282,278.80	6.06	8.67
O	K	2,149,947.00	6.06	13.00
O	Mg	154,917.90	6.06	1.73
O	Ca	717,827.00	6.06	8.67
Al	Al	4142.15	6.25	0
Al	Na	14,100.56	6.25	0
Al	K	114,430.10	6.25	0
Al	Mg	7594.81	6.25	0
Al	Ca	36,918.57	6.25	0
Na	Na	48,000.66	6.25	4.34
K	K	3,161,224.00	6.25	9.75
Mg	Mg	13,925.40	6.25	0.17
Ca	Ca	329,051.60	6.25	4.34

3. Results and discussion

3.1. Partial radial-distribution functions (RDFs) and average bond lengths

The nearest-neighbor distributions, which were determined via the statistical analyses of atomic locations using partial radial-distribution

Table 2
The composition, atom number, density [27], and box length of each sample at 2473 K.

Groups	Mole fraction,%	Atomic number				Density, g/cm^3	Box length, Å
	Al_2O_3	Al	M	O	total		
NA3	30	334	778	890	2002	2.057	32.14305
NA4	40	420	634	947	2001	2.130	31.75143
NA5	50	500	500	1000	2000	2.207	31.35890
NA6	60	572	380	1048	2000	2.303	30.90486
NA7	70	636	274	1091	2001	2.431	30.34717
NA8	80	696	174	1131	2001	2.613	29.61588
NA9	90	750	84	1167	2001	2.884	28.64913
KA3	30	334	778	890	2002	1.926	35.90136
KA4	40	420	634	947	2001	1.996	34.94027
KA5	50	500	500	1000	2000	2.076	33.97755
KA6	60	572	380	1048	2000	2.176	32.99223
KA7	70	636	274	1091	2001	2.313	31.92653
KA8	80	696	174	1131	2001	2.510	30.68654
KA9	90	750	84	1167	2001	2.811	29.21069
MA3	30	414	483	1104	2001	2.513	29.92964
MA4	40	500	375	1125	2000	2.514	29.93340
MA5	50	572	286	1144	2002	2.526	29.90639
MA6	60	632	211	1159	2002	2.563	29.77056
MA7	70	684	146	1172	2002	2.639	29.48951
MA8	80	728	91	1183	2002	2.769	29.02687
MA9	90	766	43	1192	2001	2.977	28.33507
CA3	30	414	483	1104	2001	2.608	31.30696
CA4	40	500	375	1125	2000	2.590	31.01212
CA5	50	572	286	1144	2002	2.584	30.73966
CA6	60	632	211	1159	2002	2.606	30.39140
CA7	70	684	146	1172	2002	2.667	29.92933
CA8	80	728	91	1183	2002	2.784	29.31066
CA9	90	766	43	1192	2001	2.981	28.47853