Structure Analysis of CaO–SiO₂–Al₂O₃–TiO₂ Slag by Molecular Dynamics Simulation and FT-IR Spectroscopy

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The structure information in the CaO–SiO₂–14 mass% Al₂O₃–TiO₂ slag was investigated by the molecular dynamics simulation and the FT-IR spectroscopy at 1773 K. The influence of different additions of TiO₂ and varying CaO/TiO₂ ratios on the structure was studied to clarify the role of TiO₂ in the slag. The results show that there exist three stable units, [SiO₄] tetrahedron and [AlO₄] tetrahedron as well as [TiO₆] octahedron in the CaO–SiO₂–14 mass% Al₂O₃–TiO₂ slag. The average coordination numbers, CN_{Si–Al} and CN_{Al–Al}, are all approximately equal to 1 and are barely influenced by additions of TiO₂ and varying CaO/TiO₂ ratios, which indicates that both the [SiO₄] and [AlO₄] tetrahedrons are surrounded by only one [AlO₄] tetrahedron and some other units. Nevertheless, [AlO₄] can be linked by more than one [SiO₄] tetrahedron but [SiO₄] can only be surrounded by one [AlO₄] tetrahedron. The bridging oxygen, classified into Si–O–Si, Al–O–Al and Si–O–Al, is preferentially localized in Si–O–Al. However, it is found a little violation of the so-called Al avoidance principle which states that the Al–O–Al linkage is absent have been obtained with about (less than) 5% Al–O–Al, and the bond of Al–O–Al is hardly affected by TiO₂ additions. Replacement of CaO by TiO₂ can only result in a slight change of the degree of polymerization, indicating TiO₂ has the similar role as CaO to be a basic oxide.

KEY WORDS: structure; molecular dynamics; FT-IR; CaO–SiO₂–Al₂O₃–TiO₂.

1. Introduction

There is a lot of vanadium-titanium magnetite (VTM) in Panxi region, China, in which the proven reserves is approximately 10 billion tons. The VTM is a very complex ore containing about 30.5% Fe, 10.6% TiO₂ and 0.3% V₂O₅.¹⁾ At present, in order to extract Fe, the blast furnace (BF) process is traditionally adopted to reduce the VTM, and in the process Ti is concentrated and finally enters into the slag. The slag containing about 22–25% TiO₂ has higher melting temperature and higher viscosity compared with those of the conventional BF slag without Ti-bearing.^{2–4)} The viscosity of the BF slag is an important parameter which not only affects the smelting process, but also the metal/slag reaction kinetics and the mass transfer as well as the heat transfer.^{5,6)} Thus, viscosities of various slags have been measured by steelmakers,^{7–13)} and many researchers have also tried to predict the viscosity by different modeling.^{5,14–16)}

It has been found that the structure of silicate melts is the dominant factor which influences the physicochemical properties of high temperature slag according to the research of the structures of the silicate slags using the Fourier Transform Infrared (FT-IR) spectroscopy and Raman spectrum.^{12,13,17–19)} Similarly, structure and properties of slags containing TiO₂ have also been investigated by steelmakers in order to understand the relationship between structure and

property.^{4,7–9,16–18,20–22)} It's reported that TiO₂ can increase the viscosity of the CaO–SiO₂–Al₂O₃–TiO₂ slag under reducing atmosphere indicating that it behaves as a network-former which can increase the polymerization of the network of the slag by Ohno and Ross.³⁾ However, Saito *et al.* revealed that TiO₂ decreases the viscosity in quaternary CaO–SiO₂–Al₂O₃–TiO₂ slag system.⁹⁾ Handfield *et al.* described industrial slags with high TiO₂ content are very fluid melts once completely molten.²⁾ Park *et al.*,¹⁸⁾ Sohn *et al.*¹⁷⁾ and Liao *et al.*⁷⁾ proposed that TiO₂ acts as a basic oxide resulting in the depolymerization of the slags under neutral conditions in CaO–SiO₂–MgO–TiO₂–Al₂O₃ quinary slag systems with varying basicity and TiO₂ content although the content of MgO and Al₂O₃ are different in their systems. Park *et al.*,¹⁸⁾ investigated the effect of TiO₂ on the silicate structure in CaO–SiO₂–17 mass% Al₂O₃–10 mass% MgO slags by the FT-IR and Raman spectrum contributing to the conclusion that TiO₂ act as a basic oxide.

Nevertheless, it has not been studied systematically for the detailed structure of the slags with high TiO₂ content, CaO–SiO₂–Al₂O₃–TiO₂, which occupies more than 90% in the high Ti-bearing BF slag. Thus, the fundamental information of the structure for the quaternary slag is significantly crucial. Owing to viscosity measurements are both time consuming and difficult in high temperature conditions, the molecular dynamics (MD) simulation, which is an excellent tool for studying the microstructure with classical dynamics, has been generally used in the metallurgical melt for decades. The CaO–Al₂O₃ melts were studied by Belashchenko

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et al. with the method of MD simulation with Born–Mayer pair potentials taking into account the effective dipole–dipole interaction and the thermodynamic, structural, and topological properties of the system were calculated.²³⁾ Shimoda investigated the chemical structure and dynamic properties of an amorphous slag CaO–SiO₂–MgO–Al₂O₃ using MD simulation.²⁴⁾ Zheng *et al.* have also revealed the effect of Al₂O₃/SiO₂ ratios on the structure of calcium aluminosilicate slags by MD simulation.²⁵⁾ In our previous work,²⁶⁾ the structure in CaO–SiO₂–TiO₂ system has been investigated with different additions of TiO₂ at a fixed CaO/SiO₂ ratio. In the present work, the MD simulation and FT-IR were combined to investigate the information of the structure in CaO–SiO₂–14 mass% Al₂O₃–TiO₂ slag with varying additions of TiO₂ as well as different CaO/TiO₂ ratios.

2. Simulation Method

MD simulation was performed with the Born–Mayer–Huggins (BMH) interatomic potentials which has been generally used in the research of structure of glasses or slags and has been proved successfully by the comparison with the experiment results using XRD, NMR, Raman spectrum and the simulated results from MD.^{23,27–30)} The BMH interatomic potentials function, composed of coulombic interaction, repulsion interaction and vander Waals force, was shown as follows,

$$U_{ij} = \frac{Z_i Z_j e^2}{4\pi\epsilon_0 r_{ij}} + B_{ij} \exp(-R_{ij} \cdot r_{ij}) \dots\dots\dots (1)$$

Here, U_{ij} is the interatomic potential, Z_i , Z_j the charge of the atoms corresponding to the valence of every element, e the electron charge, and r_{ij} denotes the interatomic distance between a pair of atoms. The first term on the right hand of the Eq. (1) represents the Coulombic interaction which was calculated by the Ewald method and the cutoff of the potential was set to be 10 Å in this work to simplify the computation. The second item on the right hand denotes the short-range repulsion interaction between two atoms which are determined by parameters of B_{ij} and R_{ij} . The parameters were adopted from Zheng's work²⁵⁾ as well as our previous study²⁶⁾ to insure the accuracy. The parameters B_{ij} and R_{ij} , corresponding to the short-range repulsion interaction between two atoms, were listed in **Table 1**.

In this work, the samples were simulated with different TiO₂ additions and varying ratios of CaO to TiO₂. The other components were chosen to be the same as those in the blast furnace. All samples were divided into 13 groups and the numbers of them were listed in **Table 2**. The densities were all set to be 2.95 g/cm³. The three-dimensional periodic boundary conditions were applied on the model box, in which all of the atoms were inserted randomly and the Gear integration of motion equations was used. The atoms were equilibrated at 5 000 K for 3 000 time steps with a time step $\Delta t = 1$ fs (10^{-15} s). Subsequently, it was cooled down to 1 773 K within 2 000 steps and equilibrated at 1 773 K for 15 000 time steps in order to acquire the information of the structure by statistics. More steps were conducted and there have not noticed relevant differences.

Table 1. Potential parameters used in this study.

Atom i	Atom j	B_{ij} (eV)	R_{ij} (1/Å)
Ca	Ca	9 684.976	3.448
Ca	Si	1 362.401	4.492
Ca	Al	4 879.785	3.448
Ca	Ti	107 000.0	6.25
Ca	O	3 718.745	3.448
Si	Si	1.866e ¹⁹	40.00
Si	Al	2 219.246	3.448
Si	Ti	8 687.5	6.25
Si	O	223 440.54	7.018
Al	Al	2 444.136	3.650
Al	Ti	12 081.25	6.25
Al	O	1 945.759	3.546
Ti	Ti	35 187.5	6.25
Ti	O	240 000.0	6.06
O	O	15 812.842	3.846

Table 2. The composition of slags, number of atoms.

No.	Composition (mass-%)				Atomic number						Length of box (Å)
	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Ca	Si	Al	Ti	O	Total	
CSAT1-0#	45.0	41.0	14.0	0	804	683	274	0	2 581	4 342	38.12
CSAT1-1#	42.4	38.6	14.0	5	757	643	274	63	2 580	4 317	38.12
CSAT1-2#	39.8	36.2	14.0	10	711	603	274	125	2 578	4 291	38.12
CSAT1-3#	37.2	33.8	14.0	15	664	563	274	188	2 577	4 266	38.12
CSAT1-4#	34.6	31.4	14.0	20	618	523	274	250	2 575	4 240	38.11
CSAT1-5#	32.0	29.0	14.0	25	571	483	274	313	2 574	4 215	38.11
CSAT1-6#	29.3	26.7	14.0	30	523	445	274	375	2 574	4 191	38.11
CSAT2-0#	43.0	30.0	14.0	13.0	768	500	274	163	2 505	4 210	38.12
CSAT2-1#	38.0	30.0	14.0	18.0	679	500	274	225	2 540	4 218	38.12
CSAT2-2#	33.0	30.0	14.0	23.0	589	500	274	288	2 576	4 227	38.12
CSAT2-3#	28.0	30.0	14.0	28.0	500	500	274	350	2 611	4 235	38.12
CSAT2-4#	23.0	30.0	14.0	33.0	411	500	274	413	2 648	4 246	38.12
CSAT2-5#	18.0	30.0	14.0	38.0	321	500	274	475	2 682	4 252	38.10

3. Experimental Method

Samples were synthesized with analytical reagent grade chemicals of CaO, SiO₂, Al₂O₃, and TiO₂. The 100 g of slag was melted at 1 773 K under 1.0 L/min of Ar in a crucible made of molybdenum to eliminate the contamination, which was stirred by a Mo rod for 3 times within more than 2 h in order to obtain a homogeneous slag. The TiO₂ varies from 0 to 30 mass%, and the varying CaO/TiO₂ ratios were also investigated, with the chemical composition listed in Table 2, the same as the composition in MD simulation.

After 2 h, the homogenized slags were drawn from the furnace and quickly quenched by pouring it into a plate filled with cooling water. Subsequently, the slags were crushed to confirm the chemical composition of the slags by the X-ray fluorescence spectroscopy (S4 Explorer; Bruker

AXS GmbH, Karlsruhe, Germany) and no apparent variation was observed before and after the experiment. In addition, the structures of the slags were also investigated using FT-IR spectroscopy.

4. Results and Discussion

4.1. Pair Distribution Function and Coordination Number

Slags in high temperature are non-crystalline oxide systems with only short-range order, which can be described by the pair distribution function (PDF). The PDF was evaluated by means of Eq. (2), where N_i and N_j are the total numbers of ions i and j , respectively. V is the volume of the system, and the $n(r)$ denotes the average number of the ions j surrounding the ion i in a spherical shell within $r \pm \Delta r/2$. The coordination number (CN) can also be obtained from the pair distribution function $g_{ij}(r)$, which is calculated by integrating the $g_{ij}(r)$ curve to the first valley of it, and the formula is presented as Eq. (3).

$$g_{ij}(r) = \frac{1}{\rho} \frac{n(r)}{V} = \frac{V}{N_i N_j} \sum_j \frac{n(r)}{4\pi r^2 \Delta r} \quad \text{..... (2)}$$

$$N_{ij}(r) = \frac{4\pi N_j}{V} \int_0^r r^2 g_{ij}(r) dr \quad \text{..... (3)}$$

The PDF and the average CN curves for all cations and O^{2-} anion in CAST1-4#, which is close to the composition in typical blast furnace, were shown in Fig. 1. The bond length of them can be directly acquired from the first peaks of the PDFs in Fig. 1(a). The values of Si-O, Al-O, Ti-O and Ca-O are 1.6, 1.75, 1.9 and 2.3 Å, respectively. The bond length of Si-O, Al-O, Ti-O and Ca-O are in accordance

with previous results although in different slag systems,^{24,25,29,31} indicating that the strong stability of short-range order less than 6 Å despite of different systems. The combining capacity between cations and O^{2-} were also presented by comparing the bond length and it can be obviously seen that the rank of stability is Si-O > Al-O > Ti-O > Ca-O, which is opposite to the rank of their lengths. Correspondingly, the average CNs of Si-O, Al-O, Ti-O and Ca-O are shown in Fig. 1(b) with the values approximately equal to 4, 4, 6 and 6, respectively. It can be concluded that both Si and Al are coordinated with 4 O in a tetrahedron and Ti with 6 O in an octahedron. Nevertheless, the Ca-O has no stable structure, corresponding to the absence of a platform in the CN_{Ca-O} curve. In order to determine the CN_{Ca-O} , the cutoff distance was defined using the location of the minimum after the first peak in the PDF for Ca-O and it was set to be 3.0 Å. It can be obtained the CN_{Ca-O} is approximately 6, similar to that of Ti from Fig. 1(b), resulting in the same role on the structure in slags, which is consistent with the results in previous study by measuring the viscosity in CaO-SiO₂-Al₂O₃-TiO₂ system.^{3,9} However, the stability of Ca-O octahedron is much weaker than Ti-O octahedron resulting in the different effect on the viscosity.

4.2. Effect of TiO₂ on the Coordination Number for Si and Al

The PDF mentioned above can only describe the local structure for atomic pair, which is one of the important factors affecting the structure. Furthermore, the way in which the units are connected should be paid more attention. It can be easily found that both CN_{Si-O} and CN_{Ti-O} exhibits a decrease trend as the TiO₂ content increased from Fig. 2. In

Fig. 1. The (a) PDFs and (b) CNs of the CAST1-4# in this quaternary system.

Fig. 2. Change of CN_{Si-O} and CN_{Ti-O} with varying addition of TiO₂.

addition, the variation of CN_{Ti-O} is larger than that of CN_{Si-O} , which exhibits the same trend in the $CaO-SiO_2-TiO_2$ system in our previous work,²⁶⁾ indicating that $[SiO_4]$ has a higher stability than $[TiO_6]$. The variation of CN_{Si-Si} , CN_{Si-Al} ,

CN_{Si-Ca} and CN_{Si-Ti} with different additions of TiO_2 is graphically presented in **Fig. 3**. From the decrease of CN_{Si-Si} we can conclude that the addition of TiO_2 breaks up the 3-dimensional network formed by Si and O. Correspondingly,

Fig. 3. Variation of the coordination number for Si with addition of TiO_2 .

Fig. 4. Variation of the coordination number for Al with addition of TiO_2 .

CN_{Si-Ca} decreases as TiO_2 increasing while the CN_{Si-Ti} has the opposite trend, which indicate that both the Si and Ca were replaced by Ti. Nevertheless, it is worth noting that the CN_{Si-Al} which is approximately equals to 1 changes little with varying additions of TiO_2 , indicating that one $[SiO_4]$ tetrahedron is linked with only one $[AlO_4]$ tetrahedron by shared oxygen atom which was called bridging oxygen (BO). Furthermore, this linkage is barely influenced by different additions of TiO_2 in this slag system. Conclusion proposed by Park's work that the TiO_2 depolymerizes the slag by modifying the silicate structure rather than the aluminate structure in $CaO-SiO_2-MgO-Al_2O_3-TiO_2$ system,¹⁸⁾ which is in agreement with ours in terms of the unchanged CN_{Si-Al} . The detailed information will be discussed subsequently by comparing the results obtained from MD and FT-IR. The effect of TiO_2 on the CN_{Al-Si} , CN_{Al-Al} , CN_{Al-Ca} and CN_{Al-Ti} was analyzed in Fig. 4. It can be easily found that the CN_{Al-Al} has little change and about equals to 1, suggesting that one $[AlO_4]$ is linked with just one $[AlO_4]$ and unaffected by TiO_2 , too. Additionally, it can be concluded that Al tetrahedrons can be surrounded by Si tetrahedrons, but not vice versa. It's consistent with the conclusion that Al is preferentially localized in the more polymerized environments acting as the network intermediates.²⁵⁾ In addition, CN_{Al-Ti} increases dramatically along with the decreasing of CN_{Al-Si} and CN_{Al-Ca} due to the increasing TiO_2 .

4.3. Effect of CaO/TiO_2 on the Coordination Number for Si and Al

TiO_2 was regarded as a basic oxide in terms of its role on the structure, similar to that of CaO. The effect of CaO/TiO_2 ratio on the structure in the $CaO-SiO_2-14 \text{ mass\% } Al_2O_3-TiO_2$ system was investigated in order to distinguish the

influence of TiO_2 and CaO on the slag structure. Changes of the CN_{Si-O} and CN_{Al-O} with varying CaO/TiO_2 are shown in Fig. 5. It can be found that the CN_{Si-O} remains unchanged with the value equal to 4 and a platform exists indicating the

Fig. 5. Change of CN_{Si-O} and CN_{Al-O} with varying CaO/TiO_2 ratios.

Fig. 6. Effect of CaO/TiO_2 ratios on CN_{Si-Si} , CN_{Si-Al} , CN_{Al-Al} and CN_{Al-Si} .

higher stability of $[\text{SiO}_4]$ compared to $[\text{AlO}_4]$. Although the $\text{CN}_{\text{Al-O}}$ is nearly equal to 4, the stability of $[\text{AlO}_4]$ tetrahedron is weaker due to the slanting platform in the $\text{CN}_{\text{Al-O}}$ curve. Moreover, the more CaO/TiO_2 ratio, the more stability of the $[\text{AlO}_4]$ tetrahedron has. It's well known that Al_2O_3 acts as an amphoteric oxide with the composition of slags, that is, Al_2O_3 behaves as a network former in high basicity slags but a network modifier in low basicity slags.³²⁾ It's observed that the platform of $\text{CN}_{\text{Al-O}}$ curve becomes more sloped as the CaO/TiO_2 decreases, which demonstrates that more TiO_2 results in the decline of stability of $[\text{AlO}_4]$ tetrahedron, that is, Al_2O_3 transformed from a network former to a modifier. It can be also concluded that CaO possesses a higher basicity than TiO_2 . Additionally, the $\text{CN}_{\text{Si-Si}}$, $\text{CN}_{\text{Si-Al}}$, $\text{CN}_{\text{Al-Al}}$ and $\text{CN}_{\text{Al-Si}}$, corresponding to the degree of polymerization, change little with varying CaO/TiO_2 ratios, as shown in Fig. 6, indicating the similarity of CaO and TiO_2 .

4.4. Distribution of Bridging Oxygen and Nonbridging Oxygen

The oxygen ions presented in this system could be classified into BO and nonbridging oxygen (NBO) as well as free oxygen (FO) by the cations they are connected to. The BO which connects two tetrahedrons increases the degree of polymerization while the NBO which has only one network former has the contrary impact within the silicate. Moreover, FO which is connected to two modifiers exists although it's not stable with small fraction. Hence, distribution of bridging and nonbridging oxygens influenced by addition of TiO_2 and varying CaO/TiO_2 ratios are discussed in the present work, which are exhibited in Figs. 7 and 8,

respectively. In this system, the BO was classified into Si-O-Si, Si-O-Al and Al-O-Al and Fig. 7(a) shows the effect on TiO_2 on the three types of BOs. It can be noticed that the BO is preferentially localized in Si-O-Al, secondly the Si-O-Si linkage. Nevertheless, it's obviously observed that the fraction of Al-O-Al linkage is much smaller than the other two BOs, which is less than 5% and it's almost unaffected by TiO_2 addition. It's a little violation of the so-called Al avoidance principle which states that two Al tetrahedrons are never found linked by an oxygen atom in aluminosilicate crystals and glasses at low Al content. However, some researchers have found that this principle is not necessarily fulfilled in amorphous aluminosilicates,³³⁾ which is consistent with our results. Both the bond of Si-O-Si and Si-O-Al exhibit a decrease trend with increasing TiO_2 , which can be observed in Fig. 7(a). However, the extent of their decreasing trends is different. The concentration of (Si-O-Al)/Si and (Si-O-Si)/Si was listed in Table 3, from which it can be seen that the change of (Si-O-Al)/Si is much smaller than that of (Si-O-Si)/Si, suggesting that the Si-O-Al has a higher stability than Si-O-Si and Si-O-Si is preferentially broken by Ti^{4+} to form Si-O-Ti.

The NBOs are divided into Si-O-Ca, Si-O-Ti, Al-O-Ca and Al-O-Ti, the distribution of which is shown in Fig. 7(b) and Table 4. In this work, Al^{3+} has the same structure like Si^{4+} , which forms a tetrahedron $[\text{AlO}_4]$ like $[\text{SiO}_4]$ and Ca^{2+} may play two roles, modifier and charge-balancing. However, it can be clearly observed that the (Al-O-Ca)/Al (average number of Ca which forms non-bridging oxygen in one $[\text{AlO}_4]$) is much smaller than (Si-O-Ca)/Si (average number of Ca which forms non-bridging oxygen in one $[\text{SiO}_4]$),

Fig. 7. Effect of TiO_2 on the distribution of three types of bridging oxygen.

Fig. 8. Effect of CaO/TiO_2 on the distribution of bridging oxygen and nonbridging oxygen.

Table 3. The concentration of (Si–O–Al)/Si and (Si–O–Si)/Si as the function of TiO₂ content.

TiO ₂ (mass-%)	0	5	10	15	20	25	30
(Si–O–Si)/Si	0.795022	0.743390	0.714760	0.653641	0.617591	0.556936	0.537079
(Si–O–Al)/Si	0.860908	0.824261	0.817579	0.772647	0.774379	0.728778	0.788764

Table 4. The concentration of nonbridging oxygen connected to tetrahedrons as the function of TiO₂ content.

TiO ₂ (mass-%)	0	5	10	15	20	25	30
(Si–O–Ca)/Si	1.409956	1.267496	1.126036	0.939609	0.860421	0.741201	0.613483
(Al–O–Ca)/Al	0.843066	0.751825	0.693431	0.576642	0.507299	0.408759	0.306569
(Si–O–Ti)/Si	...	0.26283	0.517413	0.831261	0.99044	1.26087	1.368539
(Al–O–Ti)/Al	...	0.284672	0.518248	0.649635	0.945255	1.175182	1.248175

which means that Al³⁺ is surrounded by less Ca²⁺ to form NBOs compared to Si. Hence, it can be inferred part of Ca is used for compensating for [AlO₄]. In addition, NBO is preferentially connected to [SiO₄] tetrahedron rather than [AlO₄]. The reason may be that [AlO₄] needs charge-balancing but [SiO₄] does not need charge-balancing due to the different valence between Si⁴⁺ and Al³⁺, which leading to more Ca²⁺ playing the role of network modifier to form NBO (Si–O–Ca). It is furthermore interesting to note that when the TiO₂ content up to 20 mass-%, both Si–O–Ti and Al–O–Ti are in excess of Si–O–Ca and Al–O–Ca, respectively, indicating that Ti⁴⁺ is more likely to locate beside tetrahedrons than Ca²⁺ due to the higher combining capacity between Ti⁴⁺ and O²⁻. Moreover, Table 4 shows the four ratios (Si–O–Ti)/Si, (Al–O–Ti)/Al, (Si–O–Ca)/Si and (Al–O–Ca)/Al, implying the average numbers of Ca (Ti) which forms non-bridging in one [SiO₄] or [AlO₄] tetrahedron. Both the Ca²⁺ and Ti⁴⁺ may play two roles, modifier and charge-balancing, and [SiO₄] does not need charge-balancing cations. Therefore, the disparity between (Si–O–Ti)/Si and (Al–O–Ti)/Al can indirectly reflect the proportion of charge-balancing Ti⁴⁺ for [AlO₄] tetrahedron and the disparity between (Si–O–Ca)/Si and (Al–O–Ca)/Al implies the proportion of charge-balancing Ca²⁺ for [AlO₄] tetrahedron. It can be easily seen that the disparity between (Si–O–Ti)/Si and (Al–O–Ti)/Al is smaller than that between (Si–O–Ca)/Si and (Al–O–Ca)/Al from Table 4. Hence, it can be also inferred that Ti⁴⁺ barely acts as the charge-balancing atom compared to Ca²⁺. As the TiO₂ content increases, the Si⁴⁺ and Ca²⁺ are gradually replaced by Ti⁴⁺, which is described as Eqs. (4) to (6).

The relationship between CaO/TiO₂ ratios and the fraction of BO as well as NBO at a fixed sum of CaO and TiO₂ are exhibited in Fig. 8. It can be easily found that variation of three types of BOs is smaller compared with the influence by increasing TiO₂ in Fig. 8(a). Nevertheless, a slight down-trend of Si–O–Al can still be observed, which is contrary to Si–O–Si. The proportion of Al–O–Al is still less than 5%, which is discussed above. It may be inferred that the replacement of CaO by TiO₂ strengthens the linkage between [SiO₄]. The distribution of NBOs is shown in Fig.

8(b), from which it can be seen that Si–O–Ca and Si–O–Ti have a contrary trend with a symmetry axis and the same trend is found between Al–O–Ca and Al–O–Ti. Hence, it can be inferred that the varying CaO/TiO₂ ratios just result in the substitution of Ti⁴⁺ for Ca²⁺. Generally speaking, both the proportion of BO and NBO change little with varying CaO/TiO₂ ratios, indicating that the replacement of CaO by TiO₂ has little effect on the degree of polymerization in the CaO–SiO₂–Al₂O₃–TiO₂ system.

4.5. Degree of Polymerization by MD and FT-IR

The degree of polymerization is always described by the Qⁿ, which is related to the properties in slags (n means the number of bridging oxygens within a tetrahedron). The influence of TiO₂ additions on the proportion of Qⁿ for Si and Al are shown in Fig. 9. The most noticeable feature is the increase of Q¹ (Si) accompanying with the decrease of Q⁴ (Si), but both the Q¹ (Si) and Q² (Si) have a slight change. The similar trend can also be observed in Al. It can be concluded that both the degree of polymerization of Si and Al decreased with the addition of TiO₂, demonstrating that TiO₂ act as a basic oxide, which is consistent with previous studies by many investigators.^{2,4,7,17,18,26} Furthermore, it should be noted that the proportion of Q³ and Q⁴ for Al are higher compared to that of Si, which indicating that Al is inclined to form more complex units than Si. The same conclusion was proposed by Shimoda²⁴) and Lee,³⁴) by MD and NMR, respectively. The effect of CaO/TiO₂ ratios on the proportion of Qⁿ for Si and Al are also investigated and exhibited in Fig. 10. It can be noted that the Q² is the dominant unit for Si, secondly the Q¹ and Q³ while the Q⁴ and Q⁰ are less than 10%. Moreover, the distribution of these polymers is barely influenced by the CaO/TiO₂ ratios, which is contributed to the conclusion that TiO₂ acts as a basic oxide like CaO.

The FT-IR results of the same composition are shown in Fig. 11. According to the previous work,^{12,13,18}) the symmetric stretching vibration of [SiO₄] tetrahedron and [AlO₄] tetrahedron are observed at about 1100–850 cm⁻¹ and 750–590 cm⁻¹, respectively. The several kinds of band groups for Si corresponding to Q⁰ (850–880 cm⁻¹), Q¹ (900–920 cm⁻¹), Q² (950–980 cm⁻¹) and Q³ (1050–1100 cm⁻¹) are marked in Fig. 11, respectively. It's obviously found that the network is depolymerized with increasing TiO₂ from the dampened trough of [SiO₄] in CAST1 system. The trough depth

Fig. 9. Proportion of Q^n for Si and Al as a function of TiO_2 additions in CAST1.

Fig. 10. Proportion of Q^n for Si and Al as a function of TiO_2 additions in CAST2.

for Q^0 and Q^1 are less than others in the slag without TiO_2 and gradually increases with more TiO_2 addition which is in agreement with the results mentioned above by MD. It can be also noted that the trough depth of Q^3 and Q^1 are almost the same for CAST1-6# which agrees with the values approximately equal to 25% by MD. The polymerization of

Fig. 11. FT-IR transmittance of the $CaO-SiO_2-Al_2O_3-TiO_2$ system as a function of wavenumber at different composition.

$[AlO_4]$ changes little when TiO_2 up to 10%, but above 10% it decreases with TiO_2 content, which agrees with Park's work that the $[AlO_4]$ tetrahedron is barely affected by TiO_2 in $CaO-SiO_2-MgO-TiO_2-Al_2O_3$ quinary slag with the TiO_2 up to 10%. In addition, the trough of Si-O-Al is detected near 500 cm^{-1} and the depth of trough dampens with increasing TiO_2 , which is in accordance with the result by MD. The influence of CaO/TiO_2 on the structure is also exhibited in Fig. 11, from which it can be noted that the distribution of Q^n for Si changes little while that for Al is more prominent. The same trend can be also found in the MD result in Figs. 5 and 10, which indicates that the $[AlO_4]$ tetrahedron is preferentially influenced with varying CaO/TiO_2 ratios. The overall degree of polymerization is barely affected when the CaO is replaced by TiO_2 , contributing to the conclusion that TiO_2 plays the same role as CaO to be a basic oxide.^{2,9,17,18)}

5. Conclusion

The structure information of the quaternary system was studied by MD simulation with different additions of TiO_2 and varying CaO/TiO_2 ratios. Additionally, the slag of same composition was also investigated by FT-IR spectroscopic analysis and was compared with the results with MD. The results of the present work can be summarized as follows,

(1) In the $CaO-SiO_2-Al_2O_3-TiO_2$ quaternary system, three stable units exist, which are $[SiO_4]$, $[AlO_4]$ tetrahedrons and $[TiO_6]$ octahedron, respectively. The attracting capability with O is $Si > Al > Ti > Ca$, the corresponding bond length are 1.6, 1.76, 1.9 and $2.3\text{ \AA}$, respectively.

(2) The average coordination number CN_{Si-Al} and CN_{Al-Al}

are all approximately equal to 1 and barely influenced by addition of TiO_2 and varying CaO/TiO_2 ratios. Correspondingly, both the $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedrons are surrounded by only one $[\text{AlO}_4]$ tetrahedron and some other units. Nevertheless, $[\text{AlO}_4]$ can be linked by more than one $[\text{SiO}_4]$ tetrahedrons but $[\text{SiO}_4]$ can be only be surrounded by one $[\text{AlO}_4]$ tetrahedron.

(3) The BO is classified into Si-O-Si , Al-O-Al and Si-O-Al and BO is preferentially localized in Si-O-Al . A little violation of the so-called Al avoidance principle which states that the Al-O-Al linkage is absent can be obtained with about (less than) 5% Al-O-Al and it's almost unaffected by TiO_2 addition.

(4) Both the results from MD and FT-IR all suggest that TiO_2 can decrease the polymerization in this system and the replacement of CaO by TiO_2 results in a slight change of the degree of polymerization, indicating the TiO_2 has the similar role as CaO .

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