MOLECULAR DYNAMIC INVESTIGATION OF THREE-DIMENSIONAL ANIONIC STRUCTURES OF MOLTEN Al_2O_3-Na_2O-SiO_2 SYSTEM

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Al^{3+} as well as Si^{4+} ion has been known to have a high ability to form a network in the molten slags. Since Al_2O_3 is a major constituent of iron and steelmaking slags, the effect of Al^{3+} on the physical and chemical properties of slags has been extensively studied, and several results suggest that Al^{3+} in the silicate melts may have a preference to construct a three-dimensional network structures.

However, the detail of the Al^{3+} based three-dimensional structure and the relations between Al^{3+} and Si^{4+} tetrahedral based network have not been established. Therefore, the role of Al^{3+} ions on the anionic structure of molten silicate slags was investigated by employing the Raman spectroscopy measurement and molecular dynamics simulations of Na_2O-Al_2O_3-SiO_2 system with various content of Al_2O_3.

Raman spectra measurements were carried out for the quenched Na_2O $2SiO_2$ and Na_2O SiO_2 systems contained with Al_2O_3 from about 3 to 15 mol%. Samples were excited by 515 nm line of coherent Ar+ laser operating at about 250 mW. The pair potential used in the molecular dynamics simulations is the Busing approximation of Born-Mayer-Huggins form of

$$U_{ij}(r)=Z_iZ_je^2/r + B_{ij}\exp(-r/R_{ij})$$

where r is the distance between ions *i* and *j*, Z_i is the charge of ion *i*, B_{ij} and R_{ij} are repulsive parameters that was were empirically determined to reproduce crystal structures. The evaluation of the connections between Al^{3+} and Si^{4+} tetrahedral were calculated based the average distance between them.

The measured Raman spectra of quenched sodium alumino-disilicate melts with varying Al_2O_3 content (up to 11.1 mol%) equilibrated in air at 1673K are shown in Fig.1-(b) and (c). The spectrum of Na_2O $2SiO_2$ is also shown as a reference (Fig.1-(a)). The change of the relative intensities of 1100, 950 and 600 cm^{-1} bands due to the addition of Al_2O_3 is not so significant. The most notable change with the increase of the Al_2O_3 content is the appearance of a new band near 500 cm^{-1} and its intensity increases with the Al_2O_3 content and finally becomes dominant in $2Na_2O$ Al_2O_3 $6SiO_2$ system. Compared with the previous results, the 500 cm^{-1} band will be attributed to the three-dimensional network structure involving Al^{3+} and Si^{4+} ions.

Table 1 shows the distribution of the connection between Si and Al tetrahedrals obtained from the molecular dynamic simulation for $5Na_2O$ Al_2O_3 $6SiO_2$ system. Vertical column shows the number of bridging anions to Si tetrahedral, and horizontal raw means the number of bridging anions to Al tetrahedral. It shows the number of connections of each Si^{4+} tetrahedral connect to Si and Al tetrahedral. For example, for Al tetrahedral, the number of 27.00 at column 1 and rank 3 means that the fraction of Al^{3+} tetrahedral that connected to three Si tetrahedral and one Al tetrahedral per 100 Al tetrahedral is 27.00. If all tetrahedrals construct the perfect 3-dimensional network structure, all cells can be zero except diagonal ones. The structure deviated from diagonal cells corresponds to the structures such as monomer, chain and sheet network structure.

Compared with Si and Al tetrahedral distributions in Table 1, Al tetrahedral is mainly distributed along the diagonal (61%), but Si tetrahedral is not so much (20.33 %). It simply means that Al^{3+} has a preferable tendency to construct 3-dimensional network than that of Si^{4+} ions. Si tetrahedral can form three-dimensional structure, but also chain or sheet structures. The same tendency was also obtained for the metasilicate system.

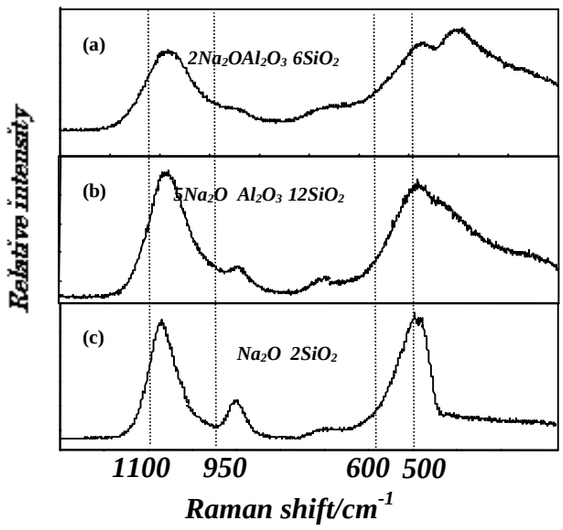

Fig.1 Raman spectra of quenched sodium alumino-disiloicate melts.

Table 1 The distribution of the connection between Si tetrahedral and Al tetrahedral.

Si	0	1	2	3	4
0	0.33	1.67	1.00	2.00	0.00
1	2.00	13.00	10.00	1.00	0.00
2	12.33	20.33	6.33	0.00	0.00
3	17.01	7.33	0.00	0.00	0.00
4	5.67	0.00	0.00	0.00	0.00
Al	**0**	**1**	**2**	**3**	**4**
0	0.00	0.00	0.00	0.00	0.00
1	0.00	0.00	7.00	4.00	0.00
2	7.00	12.00	16.00	0.00	0.00
3	13.00	27.00	0.00	0.00	0.00
4	14.00	0.00	0.00	0.00	0.00