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STRUCTURE OF MOLTEN SLAGS IN THE Na_2O-SiO_2-TiO_2 SYSTEM

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Synopsis: The structure of molten slags with the chemical composition of $xNa_2O+(0.8-x)SiO_2+0.2TiO_2$ ($x=0.2$, 0.3 and 0.4) has been investigated by a high temperature X-ray diffraction method. After calculating the coherent scattering intensities by the common procedure for disordered system, the radial distribution functions for three molten slags were obtained, from which structural parameters in near neighbor region were estimated. Silicon is found to be tetrahedrally coordinated by four oxygen in the composition range presently investigated. Whereas, the coordination number around titanium appears to decrease with the increment of SiO_2/Na_2O ratio. This suggests that a tetrahedral site of oxygen for titanium is rather preferred in the higher SiO_2 region. The structural analysis of glassy slags with the same chemical compositions were also carried out. The resultant structural parameters in glassy slags again follow the characteristic structural variation around titanium detected in the molten state.

Key words: radial distribution function, high temperature X-ray diffraction, Na_2O-SiO_2-TiO_2 system, molten slags, glassy slags, disordered system

1. Introduction

The molten slags in the Na_2O-SiO_2-TiO_2 system have long received much attention, by finding some characteristic variations of physical properties as a function of chemical composition. For example, the addition of TiO_2 to the Na_2O-SiO_2 system induces the decrease in viscosity [1][2][3]. This suggests that the TiO_2 behaves as a component of so-called network modifier in this silicate slags. Similar observation has been confirmed by the measurements of electrical conductivity of this slag system [4][5]. TiO_2 is known to be one of the amphoteric compounds in silicate system and the ionic radius of titanium suggests its potential variation in the environmental structure, such as 4-, 5- and 6-fold coordination of oxygen. Nakamura et al. [5] discuss the variation of electrical conductivity of Na_2O-SiO_2-TiO_2 melts by introducing the preference of octahedrally coordinated titanium in the SiO_2 rich region, although they rather suggest the predominant effect of the amount of Na_2O. Kusabiraki and Shiraishi (1981) propose a preference of octahedrally coordinated titanium in this slag system from infrared emission spectra with suggestion that any evidence for the tetrahedrally coordinated titanium was not well recognized [6]. In this context, structural investigation of molten Na_2O-SiO_2-TiO_2 slags has been strongly required, but not available yet within the best knowledge of the present authors. This prompts us to report our recent results on the melt structure of this slag system by a high temperature X-ray diffraction method.

2. Experimental procedures

Slag samples with three chemical compositions of $xNa_2O+(0.8-x)SiO_2+0.2TiO_2$ ($x=0.2$, 0.3 and 0.4) were prepared from the required amounts of sodium carbonate, silicon dioxide and titanium dioxide powders. The weighted chemical regents were melted in a platinum crucible at about 1573 K, then quenched by sandwiching the melts between two water-cooled brass plates. Repeating this procedure three times for homogenization, the flakes of glassy slag samples were successfully obtained. The color of $0.2Na_2O+0.6SiO_2+0.2TiO_2$ glass appears black brown and others tinge yellow. The chemical analysis of these three samples indicates no significant deviation from the required nominal compositions (within 2 mol%). A miniature furnace composed of four small silicon-carbide ceramic heaters and refractory brick was prepared for the present high temperature X-ray diffraction measurement. This miniature furnace was set on the two water-cooled electrodes in a high temperature chamber[7], making it possible to maintain the sample temperature within ±10 K at a desired temperature below 1673 K. Prepared slag samples were charged into a platinum container ($30x20x3\ mm^3$) settled in the center of a furnace, and the sample temperature was monitored by a Pt-Pt13%Ph thermocouple inserted into the position just below the platinum container during the course of measurements. X-ray scattering intensities from the molten slags at 1373 K ($x=0.2$), 1343 K ($x=0.3$) and 1323 K ($x=0.4$) in air were measured using a theta-theta diffractometer which allowed the sample to be held in a stationary horizontal position and the X-ray tube and detector rotated in opposite directions [7]. The scattering intensity was obtained using Mo $K\alpha$ radiation with a singly-bent pyrolytic graphite monochromator in the diffracted beam in the angular range from 2^o to 55^o, which corresponds to the wave vector $Q=4\pi\sin\theta/\lambda$ from 6 to 145 nm^{-1}, where λ is the wave length and 2θ is the angle between incident and diffracted X-ray beams. In this work, the observed intensity data at Q less than 6 nm^{-1} were smoothly extrapolated to zero at $Q=0\ nm^{-1}$. The effect of these extrapolation or truncation up to $Q=145\ nm^{-1}$ for the broad peaks observed in a liquid sample is known to make no critical contribution to the radial distribution function (RDF) calculated from the coherent scattering intensity by the Fourier transformation, if only the Q value exceeds about 70 nm^{-1} [8]. The structural analysis for glassy slags with same chemical compositions were also carried out for comparison.

The method for analyzing the X-ray scattering intensities of disordered systems is very common and has already been described in detail [9]. Consequently, only the essential features are given below. After applying corrections for absorption, polarization, and Compton scattering [10] to the measured intensity data in the usual manner [9], the X-ray scattering intensities were converted into electron units, by the generalized Krogh-Moe-Norman method [11] with the density values and then the reduced interference function $Qi(Q)$ was straightforwardly obtained.

The electron RDF can be readily estimated by applying the common Fourier transform to the interference function in electron units, $i(Q)$, which are defined as follows;

$$i(Q) = \frac{\left[\frac{I_{eu}(Q)}{N} - \sum_{uc} f_j^2\right]}{f_e^2} \qquad (1)$$

$$RDF_{exp.} = 2\pi^2 r \rho_e \sum_{uc} Z_j + \int_0^{Q_{max}} Qi(Q) e^{-\alpha^2 Q^2} \sin(Qr) dQ \qquad (2)$$

where I_{eu}/N is the intensity of unmodified scattering in electron units per unit of composition, f_j and f_e are the atomic scattering factor and the average scattering factor per electron, respectively. ρ_e is the average number density of electrons and Z_j is the atomic number of j-element. The term of $\exp[-\alpha^2Q^2]$ is a convergence factor, usually introduced to minimize the truncation error and weigh down the uncertainties at the higher wave vector region. However, the value of α is assumed to be zero in the present calculation of the experimental RDF. In this work, the densities of three glassy slags were measured by Archimedes' method with toluene. While those of molten slags were estimated by using the variation between the density values of glassy and molten states detected in the Na_2O-SiO_2 system. The calculated RDFs in the low r region below the nearest neighbor peak should be zero, because the atoms do not approach one another inside the atomic diameter. Therefore, the reduced interference functions given in this work include a correction term so as to remove the spurious oscillations in the low r region of calculated RDFs by the usual method [9].

On the other hand, the electron RDF can also be calculated for particular distances r_{ij} and coordination numbers N_{ij} of i-j pairs using Pair Function Distribution (PFD) equation [12].

$$RDF_{cal.} = \sum_{uc}\sum_{i}\frac{N_{ij}}{r_{ij}}\int_0^{Q_{max}}\left[\frac{f_i f_j}{f_e^2}e^{-\alpha^2Q^2}\sin(Qr_{ij})\sin(Qr)\right]dQ \quad (3)$$

The correlation distance is readily determined from the position of the corresponding peak in the experimental RDF data. In addition, the coordination numbers, can be estimated by finding the quantity of N_{ij} which will bring the calculated RDF using equation (3) to the best fit with the experimental RDF. In this process, the value of $\alpha=0.05\sim0.07$ is employed on the basis of previous studies on various oxide melts and glasses [13][14]. In this process, the variation of r_{ij} and N_{ij} in experimental RDF are ±0.002 nm and ±0.2 atom, respectively. It may be worth mentioning that the data processing using equation (3) is effective only for a few near neighbor correlations.

3. Results and Discussion

Figure 1(a) and (b) show the concentration dependence of the coherent intensity profiles for three molten slags and corresponding glassy slags, respectively. A shoulder at Q=12 nm^{-1} and a small peak at around Q=30 nm^{-1} become appreciable with increasing Na_2O content in both the molten and glassy states, although such features in X-ray intensity profiles are rather vague for the molten case. This is mainly attributed to the large amplitude of atomic variation in the molten state, compared to those in glassy state. However, it may rather be stressed here that no particular change is detected in the X-ray intensity profiles of Na_2O-SiO_2-TiO_2 slags, indicating structural similarity between these two disordered states in the composition region presently investigated.

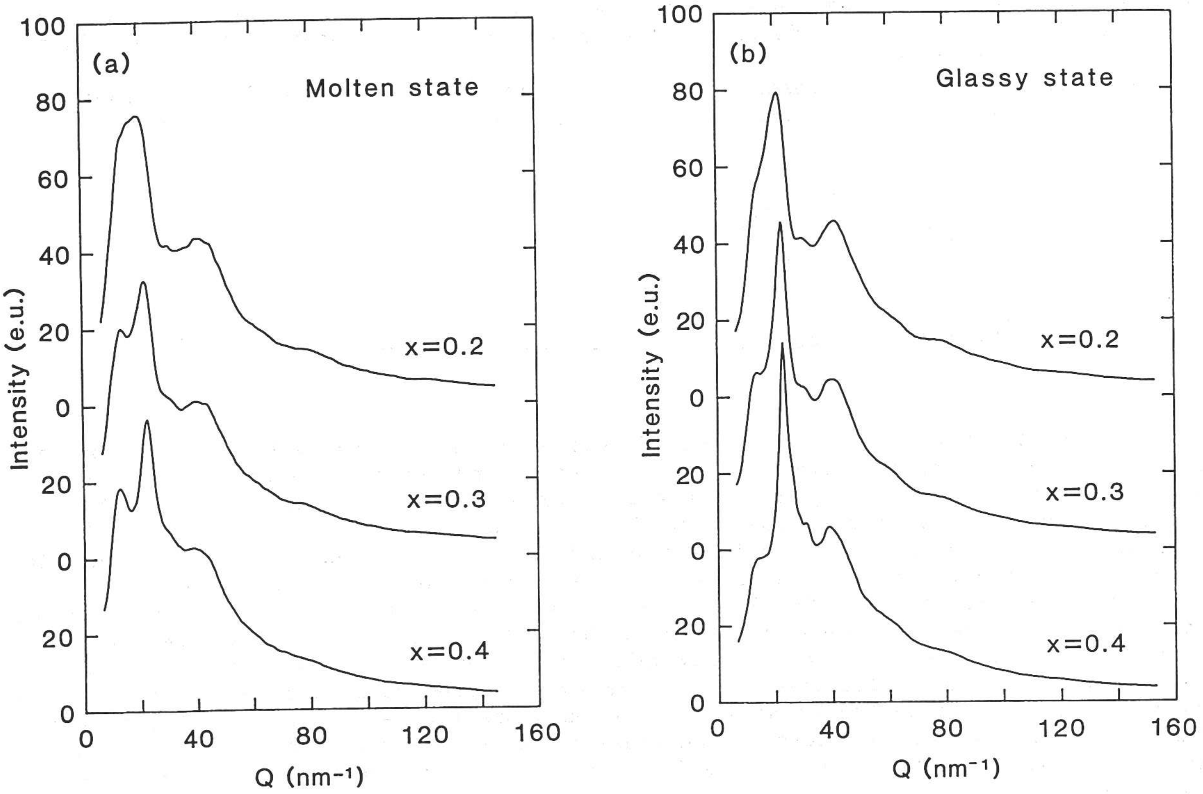

Figure 1. The coherent intensity profiles of (a)molten and (b)glassy slags of $xNa_2O+(0.8-x)SiO_2+0.2TiO_2$ (x=0.2, 0.3 and 0.4).

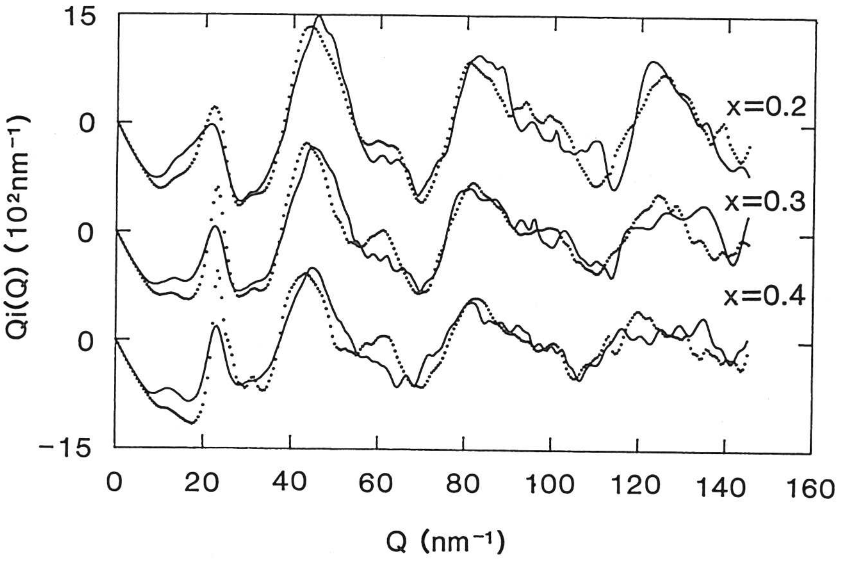

Figure 2. The reduced interference functions of molten (solid lines) and glassy (dotted lines) slags of $xNa_2O+(0.8-x)SiO_2+0.2TiO_2$ (x=0.2, 0.3 and 0.4).

As given in equation (2), a knowledge of the function *Qi(Q)* is useful in the RDF analysis for disordered systems. Consequently, Fig.2 shows the reduced interference functions *Qi(Q)* of Na_2O-SiO_2-TiO_2 slags, where those of glassy slags are indicated by dotted lines. It may be noted that the reason for the introduction of a factor of *Q* is to supplement the observation of the small oscillating behavior in the high *Q* region. The general features of the reduced interference function *Qi(Q)* for all samples are similar to that of typical oxide melts and glasses. Namely, the profiles of *Qi(Q)* are composed of the first peak at *Q*=22 nm^{-1} followed by a number of peaks, which contrast to the cases of metallic glasses where the damping behavior of the function *Qi(Q)* is rapid and monotonic [9]. If species having definite bond lengths and angles exist, persistence of the oscillation in *Qi(Q)* would be clearly detected in the high *Q* region [11]. Therefore, the oscillations observed in these molten and glassy slags imply that a considerable fraction of the local ordering unit structure remains although its distribution appears to be random.

It is worth mentioning from the results of Fig.2 that a comparison of the *Qi(Q)* function in the molten state with that of the glassy one shows only minor difference. This is particularly true in the high *Q* region. Using the characteristics of the Fourier transformation, such behavior suggests no significant difference, at least, in the local ordering structure near neighbor region between two disordered states of Na_2O-SiO_2-TiO_2 slags. However, it should be remembered in mind that there may be a certain difference in the slag structure over long distances.

The RDFs of molten and glassy slags are shown in Fig.3(a) and (b), which correspond to the Fourier transform of the *Qi(Q)* functions in Fig.2. The first peak at around 0.16 nm in the RDFs of all samples appear almost completely resolved and the subsequent oscillations are reduced so as to converge to the average number density value at the larger distance of *r*. Information of local ordering unit structures could be obtained by fitting the respective peaks with the pair function method. The arrows in Figs.3(a) and (b) denote the distances of some pairs expected from the information on ionic radii of constituent elements. It may feasible to consider the peak at around 0.16 nm and 0.27 nm as Si-O and O-O pairs, respectively. Whereas the resolution around 0.20 nm in the RDF for both the molten and glassy slags is not enough for separating two expected pairs of Ti-O and Na-O. Therefore, the interatomic distances and coordination numbers of first four correlations were estimated by means of the pair function method so as to maintain the most feasible values with physical meaning for interatomic distance around sodium and titanium. The results are summarized in Table 1 along with the density values used in the present analysis. The calculated RDF with structural parameters listed in Table 1 is given using the result of a sample of x=0.4 as an example. These results lead to give the following remarks.

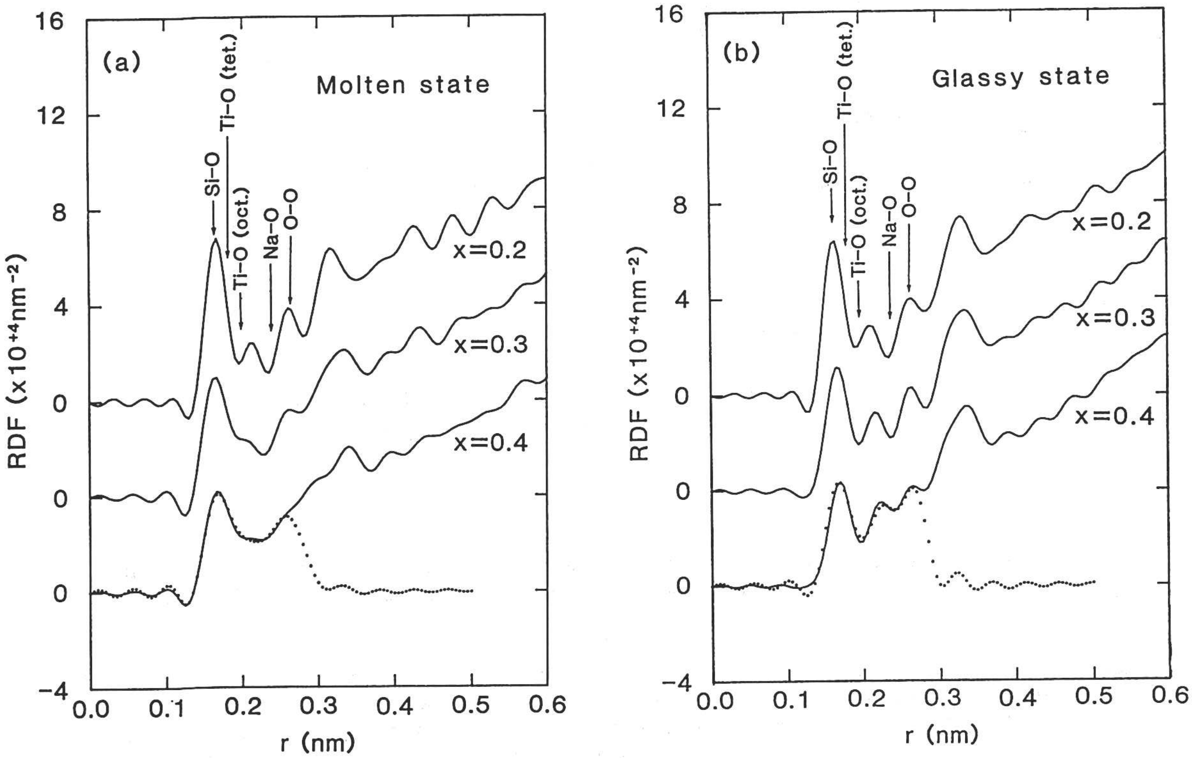

Figure 3. The radial distribution functions of (a)molten and (b) glassy slags of $xNa_2O+(0.8-x)SiO_2+0.2TiO_2$ (x=0.2, 0.3 and 0.4). Dotted line is an example of calculated RDF using the structural parameters listed in Table 1.

Table 1. Structural parameters of molten and glassy slags of $xNa_2O+(0.8-x)SiO_2+0.2TiO_2$ (x=0.2, 0.3 and 0.4).

	x	Density (Mg/m^3)	Si-O nm (atom)	Ti-O nm (atom)	Na-O nm (atom)	O-O nm (atom)
Molten	0.2	2.47	0.162(4.0)	0.192(4.6)	0.237(3.0)	0.265(5.5)
	0.3	2.46	0.161(4.0)	0.194(5.2)	0.239(3.1)	0.269(5.3)
	0.4	2.40	0.163(4.0)	0.194(5.3)	0.239(2.9)	0.271(4.9)
Glassy	0.2	2.71	0.162(4.1)	0.194(4.7)	0.233(3.4)	0.266(6.6)
	0.3	2.75	0.163(4.0)	0.194(5.0)	0.232(3.4)	0.267(7.0)
	0.4	2.75	0.162(4.0)	0.194(5.2)	0.234(3.4)	0.268(7.0)

The number of oxygen around silicon in the present slag samples is estimated to be four. Thus, the SiO_4 tetrahedra exist as the local ordering unit structures in these samples. As for Na-O pair, the interatomic distance agrees well with the values reported in the molten Na_2O-SiO_2 system [15] and shows little variation upon the chemical composition. Whereas, the coordination number of Ti-O pairs estimated here appears to decrease with the increment of SiO_2/Na_2O ratio. This suggests that a tetrahedral site of oxygen for titanium is rather preferred in the SiO_2 rich region of present slag system. As for glassy slag in this system, several information have been available [16][17], where the tetrahedral coordination of titanium is rather suggested by neutron diffraction results of $0.1Na_2O+(0.9-x)SiO_2+xTiO_2$ (x=0, 0.05, and 0.20) glasses [17]. The present results are compatible with these previous experimental data.

4. Concluding remarks

The present RDF analysis for Na_2O-SiO_2-TiO_2 slags in both molten and glassy states confirms the tetrahedrally coordinated silicon as a fundamental local ordering unit. The titanium is suggested to occur preferably the tetrahedral site of oxygen in the higher SiO_2 region. No significant difference could be detected in the structural features of this slag system between the molten and glassy states. The definite comments on the role of TiO_2 in the variation of viscosity and electrical conductivity of Na_2O-SiO_2-TiO_2 slags can not be obtained from the present structural information alone. Nevertheless, the present authors maintain the view that the change in the coordination number around titanium has one of the origins for the unusual behavior detected in the measurements of these physical properties for this molten slags. It would be useful to carry out some further structural studies of Na_2O-SiO_2-TiO_2 slags using the energy-dispersive X-ray diffraction method, in order to get more high-resolution RDFs compared to those obtained by the conventional technique.

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