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Behaviour of Transition Metal Ions in Slag (Report II)†
—State of Titan Ion in K_2O-SiO_2-TiO_2 System—

Nobuya IWAMOTO*, Yoshiaki TSUNAWAKI and Masao FUJI*****

Abstract

The contribution of Tio_2 to the slag has not been clear. It is significant to elucidate the coordination state of Ti ion and the state of Ti-O bond. The state of Ti ion in the system K_2O-SiO_2-TiO_2 was investigated in this study with the measurements of Raman spectra, X ray absorption spectra and refractive index. Ti ions may change its coordination number in the slag and reinforce the silicate network in this composition range.

1. Introduction

It is said that TiO_2 has properties of both acidic and basic oxide. However, it has not been clear whether Ti ion is possible to change oxygen coordination number in the slag and how it contributes to the slag network, that is to say, as a network former or a modifier. The investigation on the state of Ti-O bond and coordination of Ti ion will probably support the problems mentioned above. In the previous paper, we discussed the state of Ti ion in the system CaO-SiO_2-TiO_2 with using some spectroscopic methods but it could not elucidate still clearly what role Ti ion played in this system[1].

It is supposed that a glassy slag behaves approximately like the molten state. The state of Ti ion in K_2O-SiO_2-TiO_2 system is investigated in this study. Rao claims that it is very likely in this system that both TiO_4 and TiO_6 group co-exist with an equilibrium[2]. This equilibrium shifts in favour of TiO_4 in the high silica region and in favour of TiO_6 in the low silica region. In this paper, measurements of Raman spectra, X ray absorption and refractive index were used in order to elucidate the role of Ti ion.

2. Experimental Procedures

The chemical compositions of samples are shown in **Table 1.** Two series having constant K_2O composition were investigated. Every component of analytical glade reagents was weighed correctly and mixed sufficiently. Each sample in a platinum crucible was held at 1300°C. After CO_2 was degassed completely, the molten sample was withdrawn and allowed to cool in air.

Table 1. Chemical composition of samples.

Sample	wt%			mol%		
	K_2O	SiO_2	TiO_2	K_2O	SiO_2	TiO_2
1	35	65	—	25.6	74.4	—
2	35	60	5	25.9	69.7	4.4
3	35	55	10	26.3	64.8	8.9
4	35	25	40	28.8	32.3	38.9
5	25	75	—	17.5	82.5	—
6	25	65	10	18.03	73.47	8.50
7	25	55	20	18.55	63.96	17.49
8	25	40	35	19.4	48.6	32.0

The measurements of Raman spectra were done with 6328Å He-Ne laser at a power level of average 50mW and with 5145Å Ar ion laser of average 500mW. The incident electric vector was perpendicular to the scattering plane. The scattered radiation was analyzed using a Spex Model 1400 spectrometer with a cooled photomultiplier. Since high intensity laser was used as the light source in Raman spectra measurements, the experiment was carried out with high S-N ratio.

X-ray absorption measurements were carried out with GF-3 (Rigaku Denki Co. Ltd.) and 400 multi channel analyser (Tullamore Model PIP 400).

The Bosh and Romb Abbe type refractometer (Shimadzu Seisakusho Ltd., 3L type) was used for the measurements of refractive index.

3. Experimental Results and Discussions

3.1 Raman spectra

It was verified by the X-ray diffraction measurement that each sample took amorphous state. The Raman spectra of vitreous SiO_2, 25wt.%K_2O-75wt.% SiO_2 and 35wt.%K_2O-65wt.%SiO_2 glasses were

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measured in order to understand the role of K_2O to vitreous SiO_2. The results are shown in **Fig. 1. Figs. 2** and **3** show how the addition of TiO_2 effects to the Raman spectra of potassium silicate glass. Th intensity of the scattered radiation decreased in increasing the amount of SiO_2. Ar ion laser was selected for the samples having high silica content.

The density of vibrational states of vitreous SiO_2 are calculated by Bell et al[3]. The bond stretching vibration mode exists at 1100 cm^{-1}, that is to say, the bridging oxygens move in opposite directions to their Si neighbours. This mode is not Raman active. The bending mode appears at 710 cm^{-1}. It is caused by the movement of oxygens perpendicular to the Si-Si lines and in the Si-O-Si planes. There exists the bond rocking motion at 410 cm^{-1} that the oxygen move at right angles to the Si-O-Si planes. At frequency lower than about 600 cm^{-1} the bonds are not well defined because of the lack of the mode localization.

In our study about vitreous SiO_2, weak band at 1200 cm^{-1} and strong bands at 75, 496 and 608 cm^{-1} were observed except for the band modes calculated by Bell et al. The band at 797 cm^{-1} will probably correspond to the bending mode. When K_2O was added to vitreous silicate, such phenomena as follows were observed. (Fig. 1) The bands at 75 and 451 cm^{-1} in the vitreous SiO_2 spectrum abruptly decreased when K_2O content increased. The band at 496 cm^{-1} and the bands at 608 and 797 cm^{-1} in vitreous SiO_2 spectrum slightly moved to higher and lower frequencies, respectively. The most interesting result was that a strong band appeared at about 1100 cm^{-1} instead of the disappearance of the bands at 1061 and 1200 cm^{-1} in the vitreous SiO_2 spectrum. Increasing K_2O content, the band became sharper and stronger. At the same time the bands at 496 and 608 cm^{-1} also became sharper. They would probably be attributed to the vibration of the $Si\text{-}O^-$ nonbridging oxygen bond and to a decoupling from other modes of the random network. These results are the same as observed in soda silicate glasses by Hass[4]. However he did not observe the dissolved bands at 500 cm^{-1}

When TiO_2 was added to potassium silicate glass, the following results were observed. (Figs. 2 and 3) The bands at 500, 600 and 1100 cm^{-1} sharpened by $Si\text{-}O^-$ bond reduced with increasing TiO_2 content. This tendency was more obvious in K_2O 25wt.% series than 35wt.%. New bands appear (at 900 and 980 cm^{-1}), which do not belong to the original bands of rutile TiO_2 (280, 510, 660 and 750 cm^{-1}). The band at 980 cm^{-1} was observed apparently in the low TiO_2 composition and the band reduced in the high TiO_2 composition. With increasing TiO_2 the bands at 280 and 770 cm^{-1} became more obvious which were probably attributed to the intrinsic character of rutile TiO_2. (It, however, leaves the doubt that the band at 510 cm^{-1} is not observed which appears most strongly in rutile TiO_2 spectrum.)

These results as mentioned above may be due to TiO_4 and TiO_6 group as predicted by RaO[2]. If it is true, the band at the frequency of 980 cm^{-1} might have appeared because of the existence of TiO_4 group. The increase of TiO_6 group might correspond to the fact that the bands at 280 cm^{-1} and 770 cm^{-1} became stronger and the band at 980 cm^{-1} vanished. It is not clear what contributed the sharp band at 900 cm^{-1}.

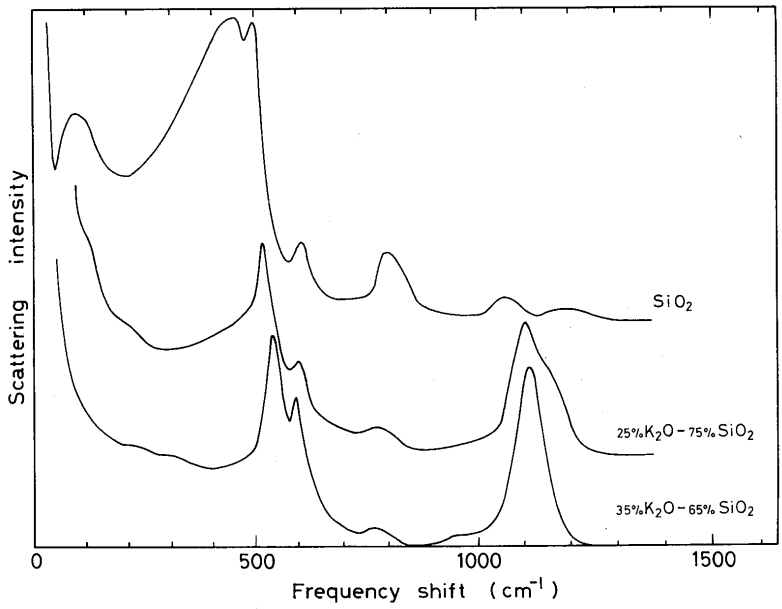

Fig. 1. Raman spectra of potassium silicate glasses.

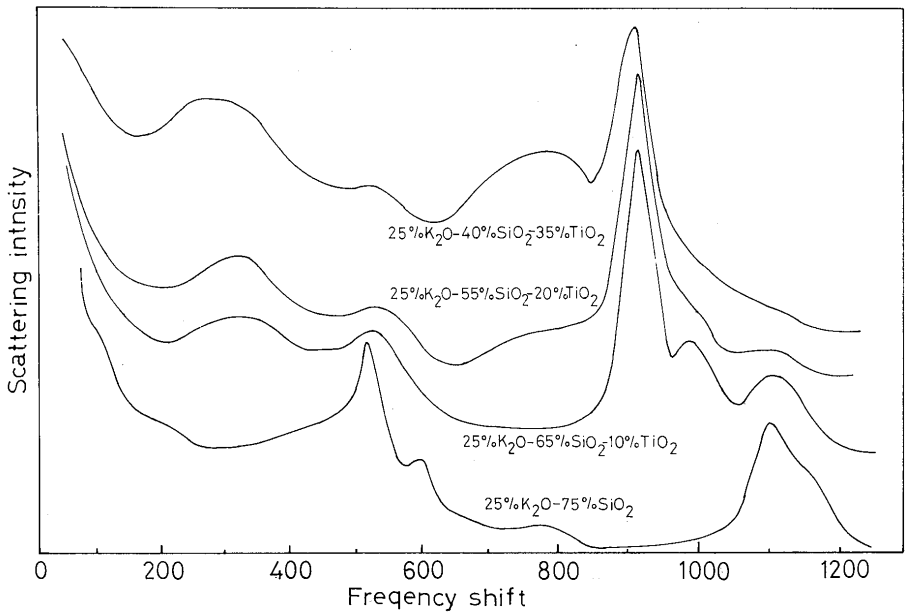

Fig. 2. Raman spectra of potassium titanosilicate glasses (K_2O 25wt.% series).

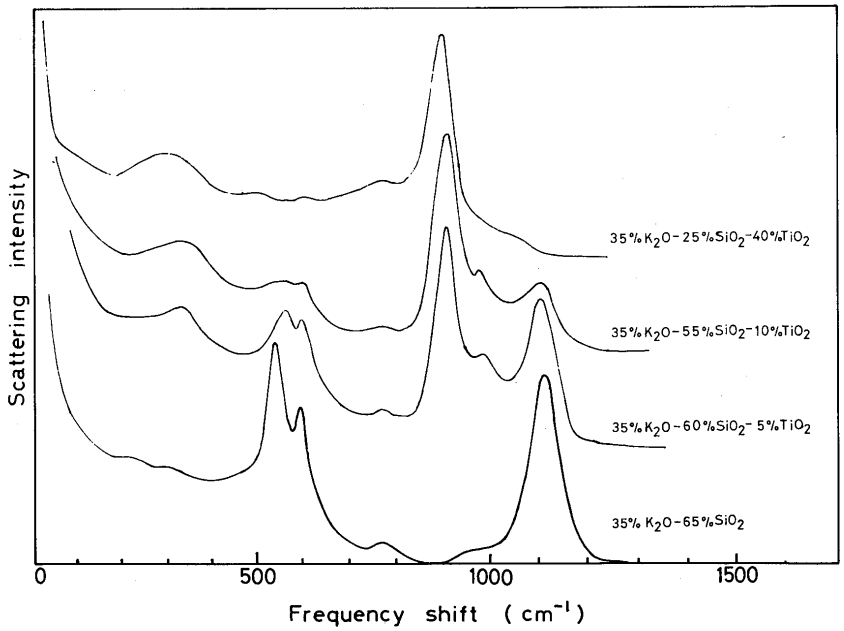

Fig. 3. Raman spectra of potassium titanosilicate glasses (K_2O 35wt.% series).

3.2 X ray absorption spectra

It is said that the profile of X ray absorption edge depends on valence, bond type, interatomic distance, crystal structure and so on. The typical X ray absorption spectrum is shown in **Fig. 4.** White et al.[5] showed the change of absorption edge due to the coordination number in the case of GeO_2. The position of the absorption edge in rutile GeO_2 (six fold coordination) shifts to lower energy than that in quartz GeO_2 (four fold coordination). The intensity of band E increases in the state of the larger number coordination.

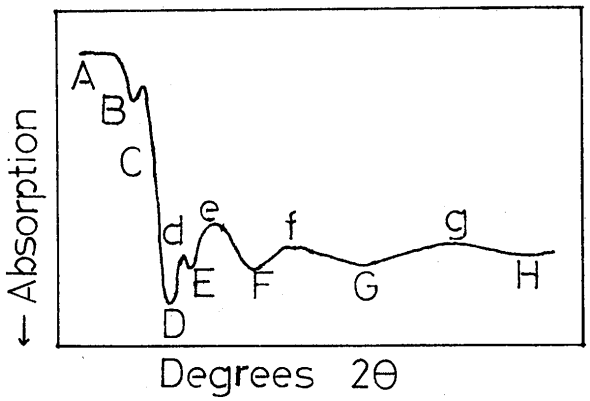

Fig. 4. A typical profile of X ray absorption spectra.

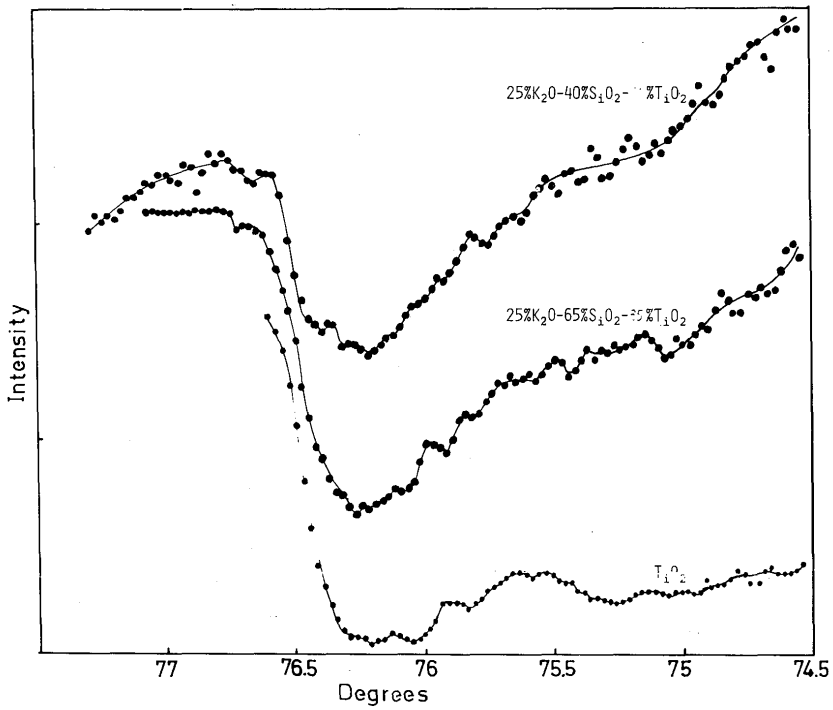

Fig. 5. X ray absorption spectra of TiK in glasses and rutile.

The X ray absorption spectra of TiK_α of rutile TiO_2 and potassium titanosilicate glasses are shown in **Fig. 5.** According to RaO[2], Ti ion forms dominantly TiO_4 group in the sample containing 10 wt% TiO_2 and TiO_6 group in 35 wt% TiO_2 sample. The spectrum of the latter sample was relatively similar to that of TiO_2. The band E vanishes in the former sample. When these results are compared with the spectra of rutile and quartz GeO_2, they might support the conclusions predicted by RaO. However, the shift of absorption edge was not observed in this study.

3.3 Refractive indices

A refractive index for visible light correlates with the distortion on the deformation of electronic shell in a structure unit of the slag. The change of the refractive index is caused by the deformation of a large oxygen ion i. e., the change of polarization, since a small cation with a high charge is hardly deformable.

The cation-anion distance for the six-fold coordination is relatively greater than that for the four-fold coordination. The fewer is the ions of opposite charge surrounding the Ti ion, the more intense is its field. Therefore the deformation of oxygen ions is greater in the four-fold coordination than the six-fold coordination. According to the discussion above, it is supposed that the change of the coordination number yields a notable change of the refractive index. D. E. Day and G. E. Rindone[6] measured the refractive index of soda-aluminosilicate glasses. They indicated that the refractive index increases rapidly over the ratio of Al/Na=1. E. I. Galant[7] also obtained the similar result of soda-and potassium aluminosilicate glasses. They claimed that the drastic change of the refractive index is caused by the change of the coordination of Al^{3+} ion from four to six.

In our investigation, a change of the refractive index is not so clearly observed as that of glasses containing alumina. (**Fig. 6**) However, there is a slight change of curvature near the point indicated by RaO[2] where the coordination number changes (Ti/K =0.47 in TiO_2 35 wt% series, Ti/K=0.17 in 25 wt% series). Some structure change may occur in this region. The following matters may be interested. In the aluminosilicate glasses, the refractive index shows a remarkable change always at the ratio of

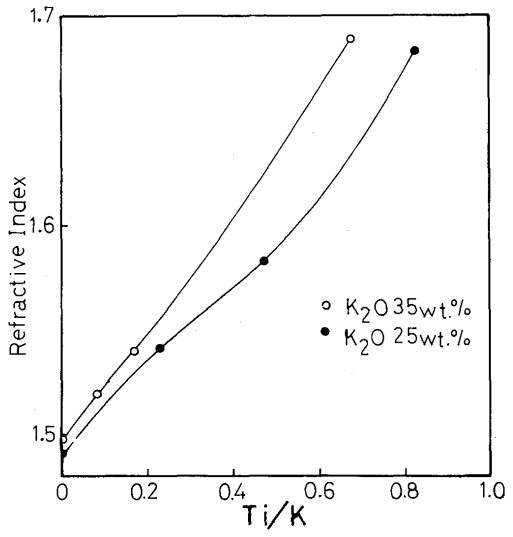

Fig. 6. Refractive index vs. Ti/K.

Al/Na=1. However, in titanosilicate glasses the refractive index does not change at the constant ratio of Ti/K. The contribution of Ti ion to the slag network may be considerably different from that of Al^{3+} ion.

4. Conclusions

It is the best way to determine the oxygen coordination number of Ti ion in slag directly with X-ray diffraction. Nowadays, it is very difficult to apply X-ray diffraction to a multicomponent amorphous system. The change of the coordination number of Ti ion was investigated in measuring Raman spectra, X-ray absorption and refractive index in this study. In the measurements of Raman spectra, the band at 980 cm^{-1} appeared in the region supposed by RaO[2] where TiO_4 group exists mainly and disappeared in the region where TiO_6 group exists mainly. This band may be the evidence of TiO_4 group existing in the slag. The profile of X-ray absorption of the sample in which a Ti ion is supposed to be in the four-fold coordination is apparantly different from that of a rutile structure. According to these results, it might be possible for Ti ion to change its coordination number in the slag.

From the view point of the ion-oxygen attraction parameter and the results of Raman spectra, TiO_2 can not be regarded as same as a typical basic oxide which dissociates in slag and Ti ions probably form anion groups in slag. The measurement of physical properties such as viscosity or surface tension must be carried out in order to elucidate the contribution of titanate anion groups to the slag network. According to the observation of molten samples, the viscosity tended to increase with the addition of TiO_2. From the Raman spectra, the sharp band caused by non-bridging oxygen bonds which increase with the addition of K_2O to the silicate network, becomes broader and disappears with increasing TiO_2. It is supposed that the addition of TiO_2 makes large silicate anion groups in the result of decreasing the number of non-bridging $Si\text{-}O^-$ bonds, or TiO_2 behaves as a network former essentially. At least, TiO_2 might have a property that protects silicate network from the attack of basic oxides.

The probability of the coordination number change of Ti ion in the slag points out that more detailed investigations are necessary to elucidate the correlation between the structure of the slag containing TiO_2 and its physical properties or its chemical reactivity.

Acknowledgement

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