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Secondary Ion Characteristics of Glasses Sputtered by Ar Ion †

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It is well known that metal ions such Al^{3+} and Ti^{4+} behave as amphoteric ions in slags.¹⁾ In order to know the basicity of slags, it is important to clarify the coordinate state of these ions in connection with the behaviours as network former or modifier.

Al^{3+} ions in slags have been studied widely with the measurements of density²⁾, refractivity²⁾, viscosity³⁾, ultra-violet absorption edge⁴⁾, infrared absorption^{2,5)} and so on. The result obtained is as follows:

For $\text{M}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ glasses having an Al/M ratio smaller than unity, aluminum ion can substitute to the position of silicon in the glass network. When Al_2O_3 content is greater than that of M_2O , the excess Al^{3+} ions in glasses are unable to participate in the glass network but take an average coordination number of six.

On the other hand, the state of Ti^{4+} ions in slag remains unclearer. Rao⁶⁾ have measured softening temperature, thermal expansion, durability to water, tensile strength, density, refractive index, dielectric constant and the degree of oxygen packing in the $\text{K}_2\text{O}-\text{SiO}_2-\text{TiO}_2$ glasses. He suggests that Ti^{4+} ions becomes a network-former in its own right and is capable of taking part in the network in tetrahedral or octahedral coordination, depending on the composition of glass. We⁷⁾ have speculated from the Raman spectra that $\text{K}_2\text{O}-\text{SiO}_2-\text{TiO}_2$ glasses show peculiar bands at about 770 and 980 cm^{-1} which might be caused by TiO_6 and TiO_4 groups according to Rao's proposal, respectively.

Turnbull and Lawrence⁸⁾, however, denied that Ti^{4+} ions becomes a network former in itself because the dependence of TiO_2 content on total molar refractivity of $\text{Na}_2\text{O}-\text{SiO}_2-\text{TiO}_2$ glasses shows the monotonical change.

Morinaga, Itoh, Suginozawa and Yanagase⁹⁾ regarded also from their infrared measurements of $\text{CaO}-\text{SiO}_2-\text{TiO}_2$ glasses that Ti^{4+} ions took tetrahedral and octahedral sites depending on the CaO/SiO_2 mole ratio but only diluted the slag network.

As above mentioned, it is difficult sufficiently to understand the behaviours of amphoteric metal ions in

glasses. It will be, therefore, necessary to study moreover on various glasses containing amphoteric ions by helps of other methods.

This note reports the secondary ion characteristics of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{SiO}_2-\text{TiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2-\text{TiO}_2$ glasses sputtered by Ar ion using an ion micro probe mass analyzer (Hitachi IMA-SS).

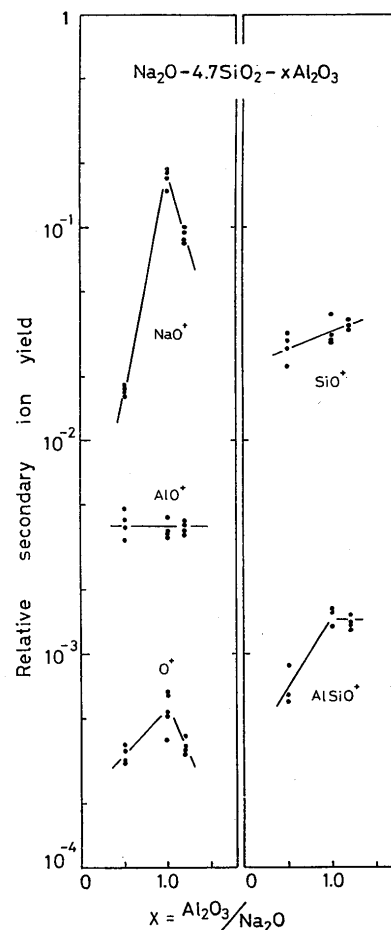


Fig. 1 O^+ ion and various molecular ions yield of $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3$ glasses sputtered by Ar ion.

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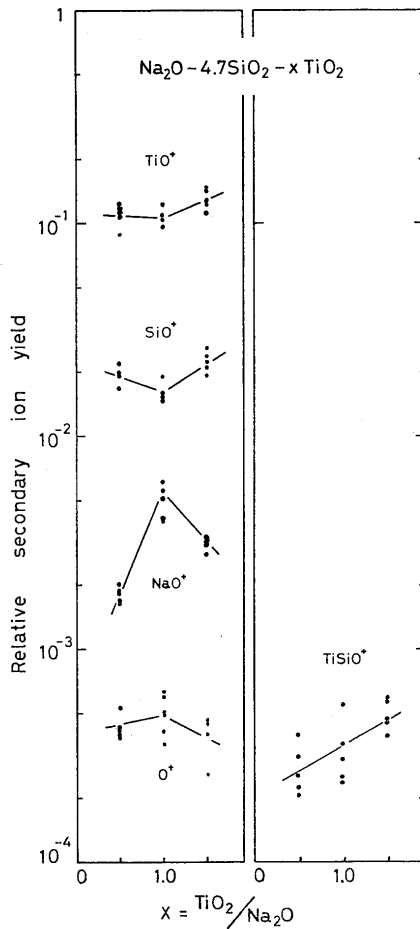


Fig. 2 O^+ ion and various molecular ions yield of $Na_2O-SiO_2-TiO_2$ glasses sputtered by Ar ion.

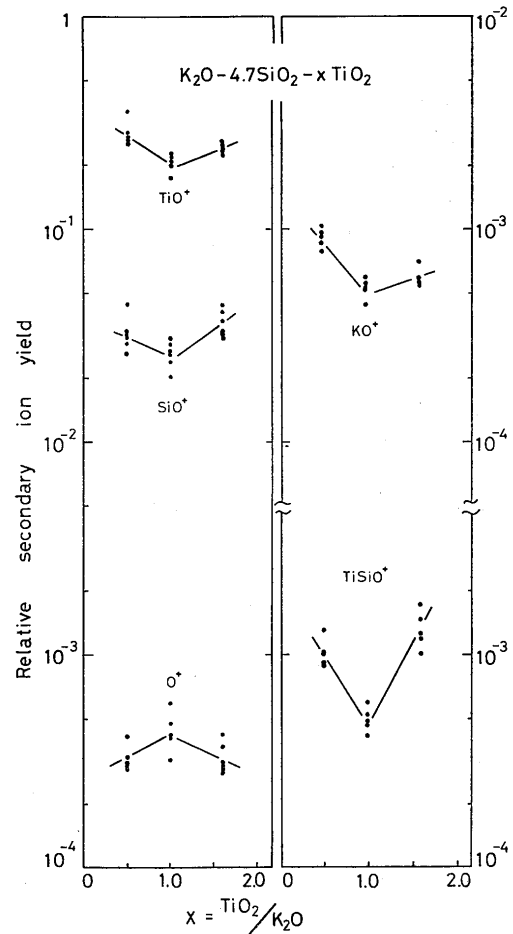


Fig. 3 O^+ ion and various molecular ions yield of $K_2O-SiO_2-TiO_2$ glasses sputtered by Ar ion.

IMA has the ability to sputter and ionize the atoms of molecular species composed of a solid surface when the atoms in the specimen accept the larger energy from the primary ion than the bonding force.¹⁰⁾ It is, therefore, expected that the quantity of secondary ion (i.e. ionized atom from the solid surface) will give an information about the bonding structure of materials to be studied. Especially, it is considered from our measurements of some oxides¹¹⁾ and intermetallic compounds¹²⁾ that matrix molecular ions or multiply charged matrix ion will be remarkably affected by the state of atoms in a solid.

Each relative molecular and oxygen ion yield of $Na_2O-4.7SiO_2-xAl_2O_3$, $Na_2O-4.7SiO_2-xTiO_2$ and $K_2O-4.7SiO_2-xTiO_2$ glasses versus to x value is shown in Figs. 1, 2 and 3, respectively. Each yield of molecular ions is normalized by the intensity of each single charged metallic ion. The change at $x=1$ of most ions might mean the change of Al^{3+} or Ti^{4+} ion state in glasses as mentioned above.

In Figs. 1 and 2, O^+ ion yield becomes maximum at

$x=1$. It was expected that SiO^+ ion yield depended strongly on the x value. However, for the glasses containing TiO_2 , SiO^+ ion yield has slightly a minimum at $x=1$, on the other hand, it becomes slightly larger with the increasing of Al_2O_3 content for the glasses containing Al_2O_3 . The yields of AlO^+ and TiO^+ ions did not show so large change that can be expected. It must be considered that NaO^+ ion yield changes extremely at $x=1$ for both glasses containing Al_2O_3 and TiO_2 . However, the value of the former is about ten times larger than that of the latter glasses. This fact might be because the bonding strength between Na and O depends strongly on the contribution of Al_2O_3 or TiO_2 to the network.

In Fig. 3, KO^+ ion yield show a minimum at $x=1$ contrary to that of NaO^+ ion in $Na_2O-SiO_2-TiO_2$ glasses. It will be difficult to interpret the results with only the difference between the polarizabilities of Na^+ and K^+ ions. Perhaps, their alkaline ions will give different contributions as modifier to glass networks.

In Figs. 1, 2 and 3, the ion yields of $AlSiO^+$ and

TiSiO⁺ show the dissimilar tendencies which will be due to the differences of behaviours of Na⁺, K⁺, Al³⁺ and Ti⁴⁺ ions in glasses.

In conclusion, it is very difficult to interpret successfully all the phenomena of various secondary ions and, furthermore, to find out some reasonable structures of glasses. However, it will be recognized that in the regions of x smaller and larger than unity, both glasses containing Al₂O₃ and TiO₂ might change the state in any way but the change are not necessarily equivalent. Moreover it seems that Na⁺ and K⁺ ions will behave differently in glasses as network modifier.

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