Raman Spectroscopic Analysis of Molten Na₂O–NaCl–SiO₂ System

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1. Introduction

Chlorine, except in the field of chloride metallurgy, is regarded as a hazardous element and is generally not welcomed in the industrial processes. Slags from high temperature incineration process were found to contain chlorine. Therefore, understanding the behavior of chlorine in slags is important for incineration process control and design.

Recently polymer plastic was injected into a blast furnace as a subsidiary of coal injection. To avoid the generation of dioxin and HCl or Cl₂, wastes that contained chlorine such as polyvinyl chloride (PVC) were not used. However, in the near future, the blast furnace may be forced to use chlorine contained waste products because of its huge ability to treat waste. In this case, slag will contain chlorine. Also in the field of steelmaking, environmental regulation required fluoride usage to decrease. Chlorine would be the first choice to replace fluorine, since both were belong to the same halogen group, chlorine is less hazardous than fluorine and fluxes containing chlorine might display similar properties to those with fluorine. However, the behavior of chlorine in slags or fluxes at high temperature is not yet well understood despite its importance. There have been a few studies on the role of chlorine in molten slags. Recently, thermodynamic study of chlorine in slag was investigated, but the structural role of chlorine in molten slags was not extensively studied. As a first step to understanding the role of chlorine in molten slags, the present study investigates the effect of chlorine on the structure of molten slags using Raman spectroscopy.

2. Experimental and Raman Spectroscopy Measurement

Detail of Raman spectroscopic measurements was essentially the same as the previous one. The mixture of appropriate portions of reagent grade Na₂CO₃, SiO₂ and NaCl powders in the Pt crucible was heated at 1 073 K for 10.8 ks for decarbonation. Then the mixture was fired in a muffle furnace at 1 473 K for 7.2 ks. The melted mixture was quenched into a water-cooled copper flat mold and then ground to form a powder. Mixtures containing more than 20 mass% of NaCl were found to be very hard to melt. Thus samples were prepared from the mixtures containing less than 20 mass% of NaCl. All melted samples were found to be glassy and transparent. The powder of about 5 mg was melted as a bead at 1 673 K on a Pt–Pt alloy hot thermocouple wire loop in air and quenched by switching off the power. The initial compositions of the samples are presented in Table 1. Na₂Cl₂ is used instead of NaCl in the table, since it is convenient to consider the substitution of 2Cl⁻ to O²⁻ (2Cl⁻ → O²⁻) with keeping total charge balance constant.

After the samples were prepared, their compositions were analyzed by using Energy dispersion X-ray method (EDX). Their compositions were found to be almost the same to the nominal compositions within the resolution of EDX (about ± 1%). Raman spectra of quenched samples were obtained with an automatic micro-Raman system. Silicate samples were excited by the 514.5 nm line of a coherent Ar⁺ laser operating at 300 mW. All the Raman spectra measurements were made at room temperature. Unpolarized spectra were measured for all samples and several spectra from each sample were measured for each composition to confirm their homogeneity.

3. Results and Discussion

The changes in Raman spectra of join Na₂O·SiO₂·Na₂Cl₂·SiO₂ system with varying Na₂O/Na₂Cl₂ ratio are shown in Fig. 1. In these measurements, total number of Si and Na cations in the melt were kept constant whereas only Cl⁻/O²⁻ ratio was changed. There was an intense band of 950 cm⁻¹ and a relatively weak band of 850 cm⁻¹ in

| Table 1. The initial compositions of the samples, in mol% |
|-------------|-----|-----|-----|
| SiO₂ | Na₂O | Na₂Cl₂ |
| 50.00 | 50.00 | 0.00 |
| 50.00 | 45.00 | 5.00 |
| 50.00 | 40.00 | 10.00 |
| 48.65 | 48.65 | 2.70 |
| 47.06 | 47.06 | 5.88 |

Fig. 1. Raman spectra of join Na₂O·SiO₂·Na₂Cl₂·SiO₂ system with varying Na₂Cl₂/Na₂O ratio.
Na2O·2SiO2 system without Cl. With an increase of Cl content, a shoulder around 1 050 cm−1 gradually developed, but the changes of 950 cm−1 and 850 cm−1 bands were not so clear. The effect of Cl on the Raman spectra of silicates can be evaluated only by their relative change of band intensities. From the result shown in Fig. 1, the relative intensity ratio of 950 cm−1 and 850 cm−1 bands, \( I_{950}/I_{850} \), was found to decrease with increasing Cl content.

Assignments of main Raman bands in silicate melts have been basically established. Namely, the bands near 1 100, 950 and 850 cm−1 are due to symmetric O–Si–O (e.g., sheet structural unit), O–Si–O− (e.g., chain structural unit) and Si–O2− (monomer unit) stretch vibration respectively. Thus, the developing of 1 100 cm−1 band due to the Cl substitution simply means that the number of sheet structural unit (1 100 cm−1) was increased. The decrease of \( I_{850}/I_{950} \) with increasing Cl showed that the amount of monomer unit (850 cm−1) were decreased and/or that of chain unit may increased. Based on these results, it can be said that the substitution of Cl for O enhanced the degree of the polymerization of melts.

In the previous study, the role of F in molten Na2O–NaF–SiO2 system was investigated. It was confirmed that F substitution enhanced the degree of the polymerization of silicate melts and also NaF was found to work as a dilutant. The detail of the mechanism that F substitution enhanced the degree of the polymerization was well discussed by Luth. And the same mechanism was adopted for the molten Na2O–NaF–SiO2 system. Previously measured Raman spectra of join Na2O·SiO2–Na2F2·SiO2 system with varying Na2O/Na2F2 ratio are reproduced in Fig. 2.

Compared with the results shown in Figs. 1 and 2, the change of Raman spectra due to the substitution of Cl is strikingly the same to that due to F substitution. This similarity strongly indicates that the role of Cl in silicate melts can be the same as F. Thus, the same mechanism to enhance the polymerization proposed by Luth can also be applicable to the Na2O–NaCl–SiO2 system. Namely, the mechanism that is consistent with polymerization accompanying the substitution of Cl for O was the formation of loosely bounded Na–Cl complexes. Formation of such complexes would remove Na+ ion from a network-modifying role so that the degree of polymerization was enhanced.

As a convenient parameter of the degree of the polymerization, the intensity ratio of 1 100 and 950 cm−1 bands (\( I_{1100}/I_{950} \)) was used to compare the ability of Cl and F for the enhancement of the polymerization. The values of \( I_{1100}/I_{950} \) in the Na2O–NaCl–SiO2 and Na2O–NaF–SiO2 systems are plotted as a function of Na2Cl or Na2F2 contents in Fig. 3 respectively. The ratio of \( I_{1100}/I_{950} \) increased almost proportionally with increasing Na2Cl or Na2F2 content in both systems within the experimental scatters. Comparing the two lines, it can be said that F has a slightly stronger ability to enhance the polymerization of melt than that of Cl.

If NaCl in the sodium silicate melts worked just as a diluent, the existence of NaCl does not influence the relative distribution of the complex silicate anions of silicate melts. Then, this mechanism predicts that melts along a join from NaCl to a point on the Na2O–SiO2 join has the same distribution ratio of the silicate network units although the relative amounts of Na–Cl complexes were different. If so, the Raman spectra of the melts along this line will be able to be the same. In other words, the distribution
of the silicate complex units will be solely determined by
the Na<sub>2</sub>O/SiO<sub>2</sub> ratio but the NaCl content will have no ef-
ficent on that. The change in Raman spectra of join
Na<sub>2</sub>O·SiO<sub>2</sub>–NaCl with NaCl content is shown in Fig. 4.
Although the relative band intensities were a little bit different
from each other, it could be said that they were basically
the same. Namely, NaCl worked as a dilutant just as expected.
This result confirms the previously mentioned polymer-
ization mechanism.
Based these results, it was confirmed that the structural
role of Cl ions in silicate melts was found to be basically
the same as that of F ions.

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REFERENCES
3) B. O. Mysen: Structure and Properties of Silicate Melts, Elsevier,