

## Mixed Alkali Effect on Structure of Al<sub>2</sub>O<sub>3</sub>-based Slags

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## INTRODUCTION

Designing and optimizing industrial slag, flux, and salt based on a detailed understanding of the atomic-scale structure of supercooled liquids is necessary to effectively control their physicochemical properties. However, the structural analysis of the industrial multi-oxide system is challenging due to the interaction between multiple network formers, intermediate oxides, and network modifiers. In particular, the  $\text{Al}_2\text{O}_3$ -based multi-oxide system presents additional complications due to the amphoteric nature of aluminate and the easy conversion of boron between the three- and four-coordinated states depending on the alkali composition. Furthermore, maintaining charge compensation between  $\text{AlO}_4$  and alkali cation is very difficult at high temperatures.

Baek *et al.* (2018) have reported that the  $\text{AlO}_4$  structure preferentially bonded with Na ion is drastically decreased by increasing temperature in the sodium aluminoborosilicate system. If the alkali does not play a charge-compensating role for Al, the aluminum coordination increases to  $\text{AlO}_5$  or  $\text{AlO}_6$ , which can act as network modifiers. In addition, the released alkali ions can reduce network connectivity by generating non-bridging oxygen.

However, establishing a highly stable network structure in the melt state at high temperatures is crucial for designing chemically stable slag that does not react with high aluminum molten steel and prevents the formation of undesirable crystal phases. The chemical reaction between Al of molten steel and  $\text{SiO}_2$  of mold flux occurs very rapidly during the continuous casting of high Al steel. The chemical reaction of  $3(\text{SiO}_2) + 4[\text{Al}] = 3[\text{Si}] + 2(\text{Al}_2\text{O}_3)$  changes the composition of the designed lime silica-mold flux and varies physical and chemical properties, eventually yielding problems with the essential functions. Permanent changes in the chemical composition of the mold flux will cause unexpected problems in the casting process, resulting in inadequate lubrication and severe product defects. Thus,  $\text{Al}_2\text{O}_3$ -based mold flux is an excellent alternative to prevent chemical reactions. However, controlling the size or morphology of crystals of an  $\text{Al}_2\text{O}_3$ -based system is difficult due to their thermodynamic characteristics.

Therefore, an innovative design method of  $\text{Al}_2\text{O}_3$ -based glass-forming liquid with a very stable network structure at high temperatures to retard chemical reactions with proper lubrication is essential. This work proposes exploiting the mixed alkali effect (MAE), which exhibits non-linear changes in chemical and physical properties such as ionic conductivity, viscosity, chemical durability, and glass transition temperature ( $T_g$ ), as a key to enhancing the charge compensation stability at high temperatures. The mechanism of MAE has yet to be well understood, despite various physical and phenomenological models proposed over the past several decades. The main aim of this study is to develop the industrial composition with enhanced structural stability by MAE. To determine the MAE, we analysed the structure by changing the chemical composition and examined the relative bond stability between  $\text{AlO}_4$  and alkali cation by increasing the temperature to 1550 °C from 1350 °C. The structure analysis was performed using solid-state MAS NMR and Raman spectroscopy to assess the structural changes of aluminate and borate according to temperature and composition.

## EXPERIMENTAL

Table 1 gives the sample names and alkali oxide ratios of six  $\text{Al}_2\text{O}_3$ -rich glassy slag samples prepared for the present study. The relative proportions of the alkali oxides are changed to find the composition that maximizes the stability of the  $\text{AlO}_4$  structure by MAE. The molar ratio of the total alkali oxides to  $\text{Al}_2\text{O}_3$  is designed to be 1:1 for all samples. The samples were prepared from reagent-grade  $\text{SiO}_2$ ,  $\text{CaCO}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{B}_2\text{O}_3$ , and  $\text{CaF}_2$ . The starting materials were well mixed by a mixing machine for an hour, followed by homogenization and melting in a graphite crucible using a box furnace at 1350 °C and an induction furnace at 1550 °C, respectively, with an air atmosphere. Then the melts were poured into a steel plate at room temperature to obtain twelve glass samples. After the conventional melting-quenching method, all glass sample was crushed to make powder for the NMR spectroscopy.

A solid-state  $^{27}\text{Al}$  magic angle spinning (MAS) NMR (Advance III HD, Bruker, Germany) analysis was performed using a 4 mm CP MAS (Triple Resonance) probe operating at 130.32 MHz. The  $^{27}\text{Al}$  spectra were recorded at a 10 kHz spinning rate.  $\text{AlCl}_3$ , as a reference, was set at 0 ppm.  $^{11}\text{B}$  MAS NMR spectra were obtained with the same solid-state MAS NMR operated at 160.46 MHz and 10 kHz spinning rate with a 4 mm CP MAS probe. Boric acid in  $\text{H}_2\text{O}$ , as a reference, was set at 0 ppm.

A Raman spectrometer (LabRaman High Resolution, Horiba Jobin-Yvon, France) to investigate the structure of aluminate and silicate units analysed the Raman spectra of glass samples quenched at 1350 °C and 1550 °C. The Raman spectra were obtained at room temperature in 200-1600 cm<sup>-1</sup> with a wavelength of 514 nm Ar ions as the excitation laser source for 300 seconds.

TABLE 1 – Alkali oxide ratios of the Al<sub>2</sub>O<sub>3</sub>-rich glassy slag samples

Name	Alkali oxide ratio
LN	Li <sub>2</sub> O:Na <sub>2</sub> O = 1:1
L3N	Li <sub>2</sub> O:Na <sub>2</sub> O = 1:3
3LN	Li <sub>2</sub> O:Na <sub>2</sub> O = 3:1
LNK	Li <sub>2</sub> O:Na <sub>2</sub> O:K <sub>2</sub> O = 1:1:1
L2N3K	Li <sub>2</sub> O:Na <sub>2</sub> O:K <sub>2</sub> O = 3:2:1
3L2NK	Li <sub>2</sub> O:Na <sub>2</sub> O:K <sub>2</sub> O = 1:2:3

## RESULTS AND DISCUSSION

To assess the structure of aluminate and borate according to each alkali oxide ratio and temperature, the solid-state <sup>27</sup>Al and <sup>11</sup>B MAS NMR chemical shifts were analysed. Figures 1a and b show the <sup>27</sup>Al NMR data of 1350 °C and 1550 °C samples, respectively. It is well known that the <sup>27</sup>Al chemical shift depends on the coordination number of Al-O. Although this data has non-symmetric line shapes, there is almost a network former of AlO<sub>4</sub> structure rather than modifiers such as AlO<sub>5</sub> or AlO<sub>6</sub> units. This observation suggests that most of the alkali cations maintain a strong bonding with AlO<sub>4</sub> as a charge compensator even at the high temperature of 1550 °C.

Figures 2a and b show the <sup>11</sup>B MAS NMR chemical shift for the glass samples. The borate in the multi-oxide system generally exists as a BO<sub>3</sub> triangular ring or non-ring structure with a 3-coordinate boron and a BO<sub>4</sub> tetrahedron having a 4-coordinate boron. Among them, the tetrahedral borate structure can be formed only by charge compensation with alkali or alkaline earth cations, like the mechanism of AlO<sub>4</sub> formation. Moreover, both 3-coordinate boron and 4-coordinate boron can act as a glass former and do not significantly affect the glass-forming ability. Figure 2 shows a weak BO<sub>4</sub> peak compared to the BO<sub>3</sub> for all samples, which implies that most of the alkali cations are trying to achieve charge compensation with aluminate structure and not with borate. In the case of sample 3LN, it has slightly higher BO<sub>4</sub> peaks in both the 1350 °C and 1550 °C.

Alkali ions have good charge compensation ability with AlO<sub>4</sub> in the order of K>Na>Li. Therefore, due to the relatively large amount of Li<sub>2</sub>O for the 3LN sample, Li cations will actively form a little more tetrahedral BO<sub>4</sub> without charge compensation with aluminate. Finally, these <sup>11</sup>B NMR results show the bonding tendency between the network former and alkali cation, consistent with the predominant consequence of AlO<sub>4</sub> bonding from <sup>27</sup>Al spectra.

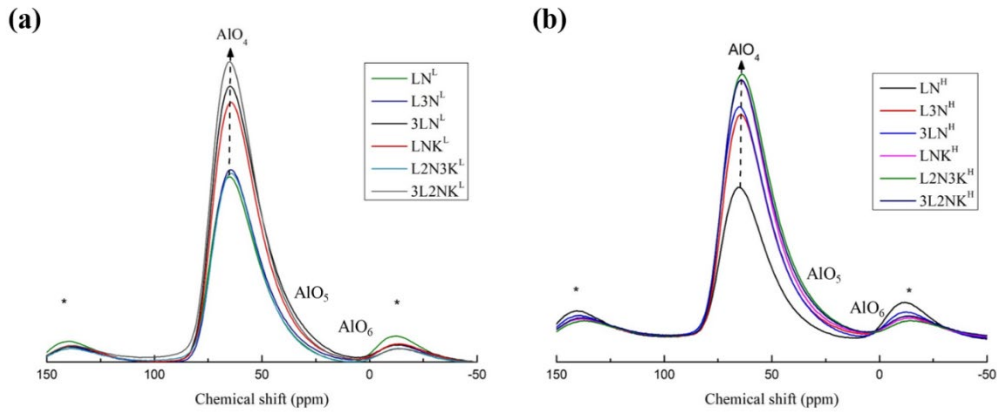


FIG 1 –  $^{27}\text{Al}$  MAS NMR spectra of samples obtained at (a) 1350 °C and (b) 1550 °C

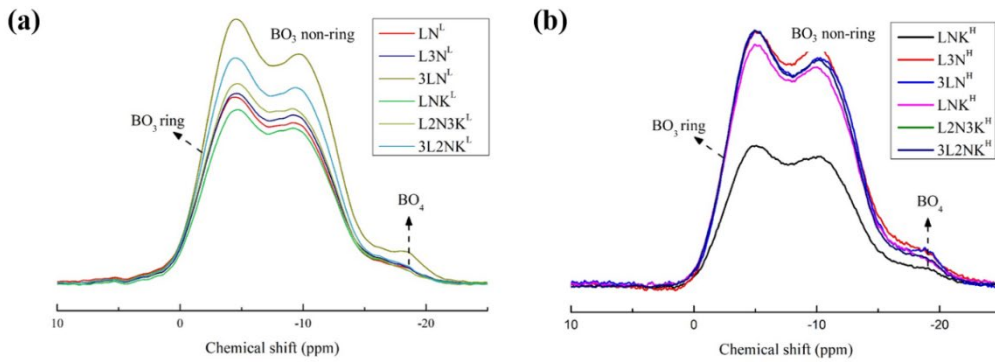


FIG 2 –  $^{11}\text{B}$  MAS NMR spectra of samples obtained at (a) 1350 °C and (b) 1550 °C

The  $^{27}\text{Al}$  NMR data show a featureless peak which indicates almost  $\text{AlO}_4$  nature, but slight differences in line width were detected. The generation of different coordination environments contributes to an increase of full width at half maximum (FWHM). To determine structure variation depending on temperature and alkali mixing ratio, FWHM values of  $^{27}\text{Al}$  NMR spectra were plotted in Figure 3. In Figure 3a, the FWHM was non-linearly decreased as the content of the stronger charge compensator Na increased due to the MAE. If the charge compensation for  $\text{AlO}_4$  is not maintained, it will transition to the 5- or 6-coordinated Al. And then, the  $^{27}\text{Al}$  spectrum broadens asymmetrically towards low chemical shift. In our previous work (Hyun, 2022), we demonstrated the new characteristic of the MAE, i.e., an increase in charge compensation stability of a small alkali when mixed with a large cation. Therefore, the non-linear variation of FWHM is due to the charge compensation stability of Li-Al being increased by the MAE. In Figure 3c, the FWHM values were nearly constant regardless of compositional changes.

However, it should be emphasized that the temperature affects the aluminum coordination environment. In Figures 3b and d, the minimum FWHM value was shown when the alkali molar ratio was equal (1:1 or 1:1:1) in the glasses quenched at a high temperature of 1550 °C. The association between alkali and aluminum weakens with increasing temperature, and finally, the alkali cation easily dissociates from aluminum. Although the Na-Al charge compensation is stronger than that of Li-Al, Na inevitably tends to release from Al at high temperatures. However, the MAE enhances the charge compensation and is finally maximized in the 1:1 composition. This observation indicates that the MAE strengthens charge compensation even from K or Na.

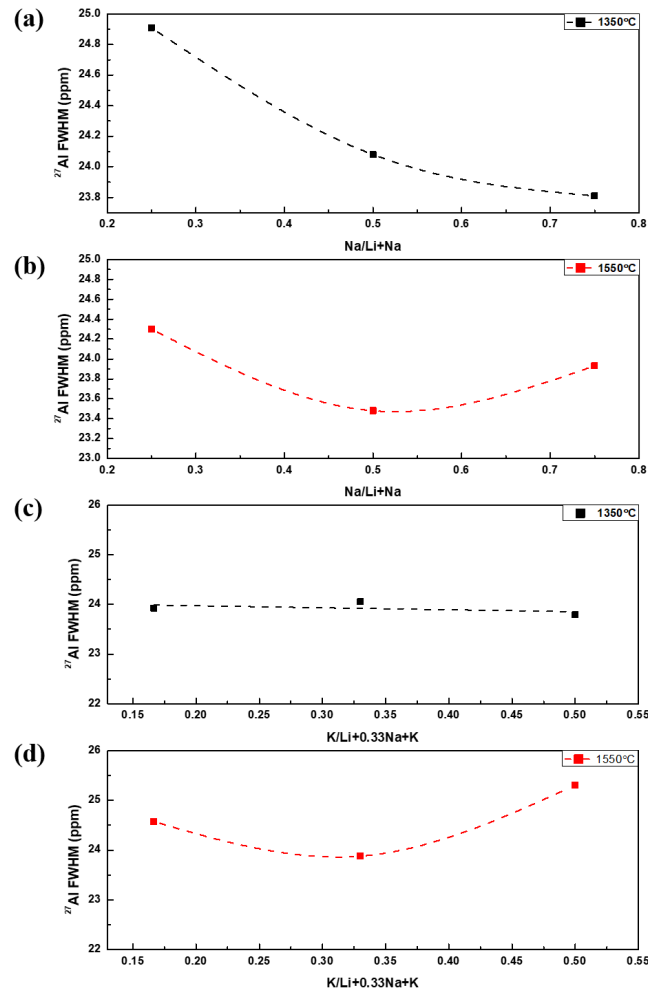


FIG 3 – FWHM values of  $^{27}\text{Al}$  MAS NMR for glasses with different homogenization holding temperatures (1350 °C and 1550 °C) and composition. (a) and (b): two types of alkalis were mixed. (c) and (d): three types of alkalis were mixed.

In Figure 4, The Raman peak at  $770\text{ cm}^{-1}$  due to the presence of the  $\text{AlO}_4$  revalidates this new knowledge. The relative intensities of the  $770\text{ cm}^{-1}$  peaks from glass quenched at two different temperatures indicate precisely the opposite trend of the NMR results. The  $\text{AlO}_4$  intensity was increased with the substitution of Na. However, the Raman feature related to  $\text{AlO}_4$  is maximized in Li: Na = 1:1 glass-forming liquid at a high temperature of 1550 °C. Therefore, the MAE is applicable to designing chemically stable  $\text{Al}_2\text{O}_3$ -rich slag systems for the continuous casting process.

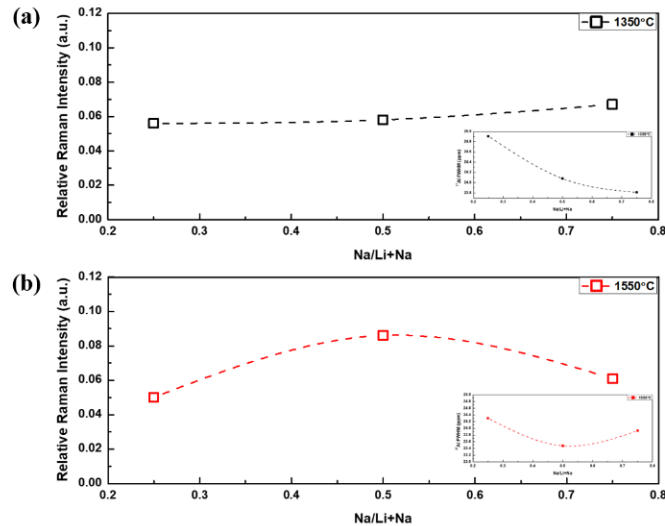


FIG 4 – Relative intensity of  $\text{AlO}_4$  peak at  $770\text{ cm}^{-1}$  in the Raman spectra for glassy slag samples obtained at (a)  $1350\text{ }^\circ\text{C}$  and (b)  $1550\text{ }^\circ\text{C}$ . Inset:  $^{27}\text{Al}$  NMR results from Figure 3.

## CONCLUSIONS

This study presents a structural study of multi-oxide systems for industrial aluminoborosilicate glassy slag systems. We provide insights into understanding complex structural changes of mixed alkali  $\text{Al}_2\text{O}_3$ -rich slag systems. To evaluate the compositional and temperature effect of the structural stability of Al,  $\text{Al}_2\text{O}_3$ -rich slags with various molar ratios of two or three alkali oxides were obtained at different temperatures of  $1350\text{ }^\circ\text{C}$  and  $1550\text{ }^\circ\text{C}$ . The stability of charge compensation between Al and alkali was significantly changed at high temperatures. Among them,  $\text{Li}:\text{Na} = 1:1$  and  $\text{Li}:\text{Na}:\text{K} = 1:1:1$  samples show the best charge compensation stability even at a high temperature which means the mixed alkali effect works most.

## ACKNOWLEDGEMENTS

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