

In Situ High Temperature NMR

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Abstract

It is important to analyze structure of slag and mold flux in the steel-making process with complicated multi-component systems from the viewpoint of appropriate management of the process and their effective use. Nuclear magnetic resonance (NMR), a nuclide specific method, is a powerful tool for structural analysis of slag with complicated structure. We have developed in situ high temperature NMR technique for analysis of melt structure and dynamics up to 1,500 degrees Celsius and some information have been obtained: (1) an averaged coordination number around Al increases with elevating temperature and (2) atomic-scale motion is closely related to macroscopic viscous flow.

1. Introduction

Blast furnace slag and steelmaking slag are by-products generated in large volumes in the iron-making and steelmaking processes. In order to properly control those processes and promote the utilization of those by-products, it is extremely important to analyze the composition and structure of slag. Concerning the mold flux that is used in continuous casting equipment, too, its physical properties, such as viscosity, are considered to be determined by its microscopic chemical structure. Therefore, those inorganic oxides require not only conventional composition analysis but also evaluation based on their chemical structure. However, there are very few papers that discuss in detail the chemical structure of slag or mold flux.¹⁻⁵⁾

Slag that has been cooled slowly contains a large proportion of crystal phase, and the X-ray diffraction (XRD) method is effective for identifying the mineral phases that have been crystallized. In the case of slag that has been cooled rapidly, however, ordinary XRD produces such a halo diffraction pattern that it cannot be used to obtain detailed information about the chemical structure of slag. Instead, radial distribution profile analysis using an X-ray or neutron beam and Raman spectrometry are performed to analyze the structure of such amorphous materials as rapidly cooled slag. With Raman spectrometry, it is possible to obtain useful information about the tetrahedral SiO₄ network.^{6,7)} However, the two methods mentioned above are, in principle, unsuitable for structural analysis of multi-component systems.

On the other hand, nuclear magnetic resonance (NMR), which is a nuclide-specific method, can very effectively be applied even in chemical structure analysis of amorphous materials that do not possess a long-range order, since it provides local information at a molecular level. In principle, NMR is applicable to any nuclides having nuclear spin I , that is, about 80% of all the elements in the periodic table. The elements that make up slag are no exceptions: for almost all of those elements, NMR permits multi-aspect information to be obtained regarding the chemical structure of slag. This is a major advantage of NMR. X-ray absorption spectrometry also allows for nuclide-specific analysis, but it is hardly applicable to any of the light constituent elements of slag.

As described above, NMR is an effective tool for analyzing the structure of slag and other multicomponent materials. However, since the maximum temperature that can be measured with an ordinary NMR probe is no higher than 200°C, it is impossible to directly observe molten slag with the probe. In order to observe the chemical structure of high-temperature molten slag, therefore, it is necessary to rapidly cool the hot slag and vitrify it so that it can be measured. Strictly speaking, however, the information obtained by this method concerns the structure of slag around the glass transition point (T_g). Slag structure in super-cooled liquids above T_g and in a stable liquid state above the liquidus temperature (T_{liq}) needs to be estimated from the data around T_g . Besides, when slag is cooled and solidified, its molecular motion is frozen. Therefore, in the above method, the molecular motion of molten slag cannot be analyzed either. Because

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of these restrictions, there is demand for a new analytical technique that permits direct observation of the behavior of slag in both super-cooled and stable liquid states.

In view of the above situation, our study group aimed to establish a new NMR technique that would allow for in situ observation of slag in the molten state and to directly observe the NMR spectra of inorganic oxides in the super-cooled and molten states, respectively. Specifically, we have developed an NMR probe that allows for in situ NMR measurement at temperatures up to 1,500°C. Using the newly developed probe, we have observed the temperature-dependent changes in the chemical structure and dynamics of Al in a CaO-Al₂O₃-SiO₂ glass system—a typical inorganic oxide and the principal component of slag and mold flux—and studied the mechanism of viscous flow of slag.⁸⁾

2. Main Subject

2.1 Experiment

2.1.1 Sample

The CAS glass and melt studied here contain 43.1 mol % CaO, 12.5 mol % Al₂O₃, and 44.4 mol % SiO₂. The glass was synthesized from reagent-grade, well-dried starting materials, CaCO₃, Al₂O₃, and SiO₂, in air in a Pt crucible using the conventional melt quenching method (quenching the crucible in water). Glass produced at 1,500 °C for 1 hour was ground and re-melted until the sample became homogeneous. Typically, about 1 g of the sample was used in each high temperature NMR experiment. The melting point and glass transition point of the CAS glass were about 1,265 °C and about 810 °C, respectively.⁹⁾

2.1.2 NMR

²⁷Al MAS NMR data were collected using Varian Inova 800 (18.8 T) and 600 (14.1 T) spectrometers at Larmor frequencies of 208.40 and 156.28 MHz, respectively. Varian/Chemagnetics 3.2 mm MAS probes were used with spinning rates of 20 kHz. A pulse sequence with single pulse excitation was applied as shown in Fig. 1.

The in-situ high temperature ²⁷Al NMR experiments were performed using a Varian Infinity plus 400 (9.4 T) spectrometer operating at 104.17 MHz with a home-built static probe.¹⁰⁾ A Mo solenoidal radio frequency coil was designed to fit closely around hexagonal boron nitride sample containers. Dried 98 %-N₂/2 %-H₂ mixed gas was flowed through the space exposed to high temperature in the probe to avoid oxidation of the boron nitride capsule and the Mo coil and heater. Longitudinal relaxation time T₁ was measured by a saturation-recovery pulse sequence.

2.2 Results and discussion

Using the newly-developed, in-situ, high-temperature NMR probe (measurement range: room temperature to 1,500 °C), we observed the changes in chemical structure and dynamics of Al in the CAS glass with the rise of temperature and studied the mechanism of vis-

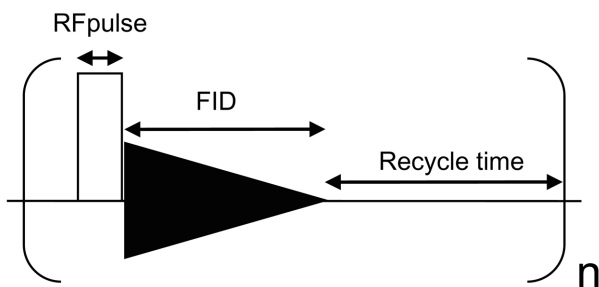


Fig. 1 Pulse sequence of ²⁷Al MAS spectra

cus flow.

2.2.1 Local structure of Al in CAS glass

Fig. 2 shows ²⁷Al MAS spectra at room temperature collected at 14.1 and 18.8 T. A featureless, asymmetric line shape with a tail to lower frequency has been observed. With increasing the external magnetic field from 14.1 T to 18.8 T, the line width becomes narrower due to the decrease in the second-order quadrupolar broadening. As a result, pentacoordinated Al was more clearly resolved around 30 ppm in addition to tetrahedral Al at 18.8 T.

The quadrupolar coupling constant C_Q and the isotropic chemical shift δ_{iso} of ²⁷Al can be obtained from the centers of gravity at two different magnetic fields as in the following Eqs. (1) and (2):¹¹⁾

$$C_Q \text{ (MHz)} = \left\{ (\delta_{cg(1)} - \delta_{cg(2)}) \left[\frac{\nu_{0(1)}^2 \nu_{0(2)}^2}{\nu_{0(1)}^2 - \nu_{0(2)}^2} \right] (1/6000) (1 + \eta^2/3)^{-1} \right\}^{1/2} \quad (1)$$

$$\delta_{iso} \text{ (ppm)} = \delta_{cg(1)} + 6000 (C_Q / \nu_{0(1)})^2 (1 + \eta^2 / 3) \quad (2)$$

where δ_{cg(1)} and δ_{cg(2)} are the centers of gravity at the two different magnetic fields, ν₀₍₁₎ and ν₀₍₂₎ are the Larmor frequencies, and η is the asymmetry parameter in the quadrupolar interaction tensor. For disordered materials such as glasses, the derived parameters are estimates of the means of the distributions of parameters represented by the peaks or peaks included in the center of gravity determination. Assuming η = 0 and using δ_{cg(1)} = 54.6 ppm (at 14.1 T), δ_{cg(2)} = 60.2 ppm (at 18.8 T), C_Q and δ_{iso} of ²⁷Al were estimated to be 7.2 MHz and 67.4 ppm, respectively. These values are relatively close to those of previous data in which C_Q and δ_{iso} of tetrahedral Al sites in a CAS glass with the composition of 44 mol % CaO, 14 mol % Al₂O₃, and 42 mol % SiO₂ were 6.6 MHz and 68.9 ppm, respectively.¹²⁾ Because our estimation of δ_{iso} included the shoulder for pentacoordinated Al, it should give a slightly lower chemical shift compared with the previous value, which was for tetrahedral Al only.

2.2.2 Change in structure of CAS glass and melt with increasing temperature

The temperature dependence of the ²⁷Al static spectra is shown

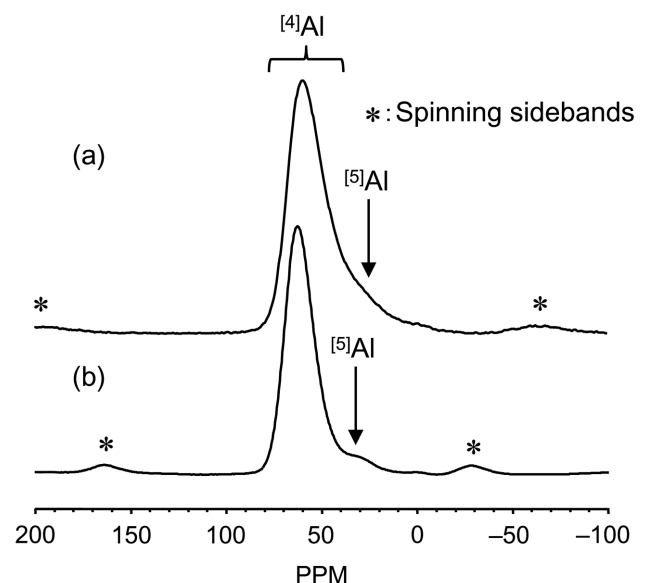


Fig. 2 ²⁷Al MAS spectra for the CAS glass at 14.1 T (a) and 18.8 T (b)

in **Fig. 3**. The peak maxima changed very little in frequency from room temperature to about 850 °C. Careful inspection of the spectra in this temperature range revealed that the decrease in the line width from ambient temperature to 850 °C is about 960 Hz, indicating the ^{27}Al – ^{27}Al dipole-dipole interaction is considered to be partly averaged at this temperature by small local motions.

In contrast, from 850 to 1,000 °C, large effects of temperature on peak shape and position were observed. The peak maximum dropped rapidly in frequency by about 30 ppm. However, since the center of gravity was nearly the same as that for the glass at room temperature, this rapid shift to lower frequency of the apparent δ_{cg} with increasing temperature up to 1,000 °C is probably not primarily caused by a change in the actual mean δ_{iso} (a structural effect), but instead represents the approach to the true δ_{cg} caused by a decrease in the line widths due to motional averaging, which allows more accurate determination of the true line shape. The apparent δ_{cg} at 1,000 °C is observed at 33.5 ppm, which is lower in frequency than the calculated δ_{cg} (38.7 ppm) from equations (1) and (2) and the MAS data, suggesting some increase in the mean coordination number above T_g .

The signal at 1,000 °C had the narrowest peak, which was almost Lorentzian in shape. Motion at 1,000 °C was insufficient to average the full static quadrupolar powder spectrum of the satellite transition ($\pm 3/2$, $\pm 5/2$), which would require reorientation and/or exchange at frequencies of at least 10's of MHz. Therefore, such a marked narrowing with a resulting Lorentzian-shaped peak is probably due primarily to motional averaging of the anisotropic effects on the central transition alone, caused by reorientation of tetrahedral groups and/or chemical exchange between neighboring Si^{4+} and Al^{3+} ions involving Al–O bond breaking.

Further increase in temperature above 1,000 °C caused a reverse shift of δ_{cg} to higher frequencies; δ_{cg} reached 65.1 ppm at 1,300 °C. The second-order quadrupolar shift $\delta_Q^{(2)}$ of solids ($I = 5/2$) propor-

tional to the square of the quadrupolar coupling constant and given as Eqs. (3):

$$\delta_Q^{(2)}(\text{ppm}) = 6000 (C_Q / \nu_0)^2 (1 + \eta^2 / 3) \quad (3)$$

Assuming that $\eta = 0$ and that C_Q at 1,000 °C is identical to the mean value obtained from MAS NMR at ambient temperature, $\delta_Q^{(2)}$ is 28.7 ppm, which is close to the observed increase in δ_{cg} between 1,000 and 1,400 °C ($\Delta = 29.8$ ppm). Hence, the low frequency peak position at 1,000 °C is due to the second-order quadrupolar shift of mostly tetrahedrally coordinated Al and small amount of pentacoordinated Al. With increasing temperature above 1,000 °C, the quadrupolar satellite transitions are increasingly averaged, decreasing the second-order quadrupolar shift. Observed peak positions thus approach the isotropic chemical shift at high temperature.

Observed increases in the line widths between 1,000 and 1,200 °C can also be attributed to the beginning of the motional averaging of the quadrupolar satellites, as the quadrupolar satellite spectrum (too broad to be observed directly) “collapses” into the central transition. These phenomena were also reported in NMR data for ^{23}Na ($I = 3/2$) in a variety of oxide glasses and melts.^{13,14}

At 1,300 °C (above the liquidus), δ_{cg} reached 65.1 ppm, which is close to but slightly lower than the mean isotropic chemical shift (67.4 ppm) estimated for the glass from ambient temperature MAS NMR and Eqs. (1) and (2). At this temperature, δ_{cg} should correspond to the isotropic, fully averaged chemical shift, because the sample is liquid-like and the large second-order quadrupolar coupling is fully averaged out. Therefore, this small shift to lower frequency may indicate a small increase in the proportion of pentacoordinated Al sites in the liquid. ^{27}Al MAS spectra with different cooling rates have been obtained to examine the pentacoordinated Al ratio. Fictive temperature T_f was calculated from the quench rate (**Table 1**).¹⁵

With increasing quench rate from 10^{-1} to 10^5 K/s, T_f is raised by 75 °C. ^{27}Al MAS for CAS glasses with different T_f are shown in **Fig. 4**. Signal intensity is normalized in terms of tetrahedral Al. With elevating T_f slight but apparent¹⁶ increase in the fraction of pentacoordinated Al was proved. Table 1 shows the fraction of pentacoordinated Al to total Al by peak deconvolution.

Thus, it was demonstrated that the fraction of pentacoordinated Al evidently increases with elevating temperature in super-cooled liquids. Previous studies have suggested that pentacoordinated Si species occurs as the intermediate in the Si–Si exchange reaction for $\text{K}_2\text{Si}_4\text{O}_9$ glass.¹⁷ In our study, pentacoordinated Al probably acts as the intermediate of atomic motion. The fraction of this intermediate increases with increasing temperature, which causes more active exchange between adjacent cations such as Si and Al. Formation of such pentacoordinated intermediate needs connection and cleavage of Al–O bonds. The bond strength of Al–O is weaker than that of Si–O, which indicates that pentacoordinated Al should be formed preferentially compared with pentacoordinated Si.

Above 1,200 °C, the line widths began to become narrower again. In this temperature range, the frequency of Al^{3+} motions has become so much greater (more rapid reorientation and exchange) than the total spectral width of all transitions that all anisotropic broadenings are averaged out. In such a rapid time scale regime, the NMR line widths are further reduced by the rapid jumps of Al^{3+} ions as temperature increases. At 1,300 and 1,400 °C, the peaks could be fitted by single Lorentzian line shapes, which is consistent with liquid-like, rapid reorientation and chemical exchange between the major tetrahedral and the minor pentacoordinated Al species at a rate faster

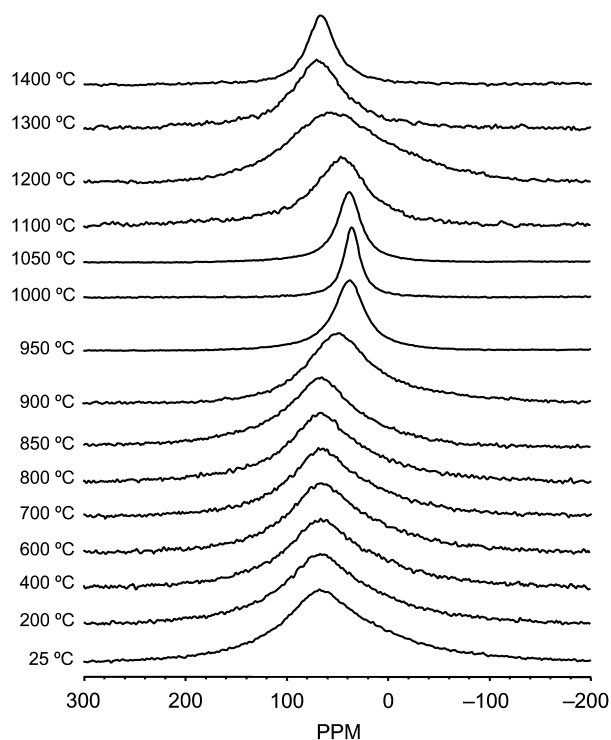


Fig. 3 ^{27}Al static spectra for the CAS glass and melt from 25 to 1400 °C

Table 1 Dependence of fictive temperature and five-coordinated Al concentrations as fractions of total Al on cooling rates

Cooling method	Cooling rate (K/s)	T_f (K)	$^{51}\text{Al}/\text{Al}_{\text{total}}$ (%)
Slow cooled	$1 \pm 0.03 \times 10^{-1}$	$1\,065 \pm 5$	6.4 ± 1.0
Water quench	$1 \pm 0.5 \times 10^2$	$1\,105 \pm 10$	7.2 ± 1.0
Fast quench	$1 \pm 0.5 \times 10^5$	$1\,140 \pm 20$	7.6 ± 1.0

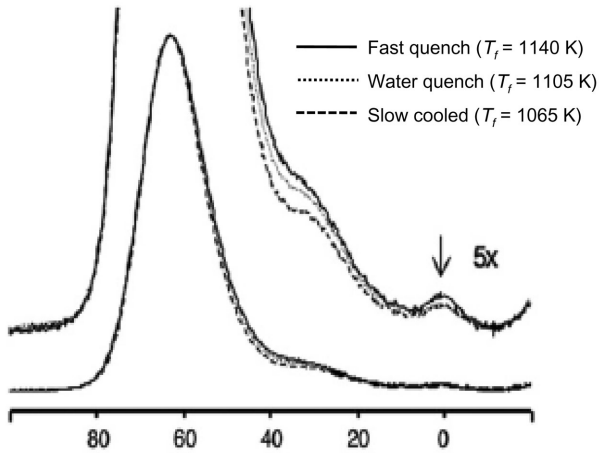


Fig. 4 ^{27}Al MAS spectra for the CAS glasses with different T_f

than their chemical shift difference.

2.2.3 Change in structure of CAS glass and melt with increasing temperature

Fig. 5 shows data for T_1 vs. reciprocal temperature for ^{27}Al in the CAS glass and melt. T_2^* values calculated from the line widths ($T_2^* = 1/\pi$ (FWHM)) are also plotted. Because such spin-lattice relaxation must be stimulated by fluctuations in the local magnetic field or electric field gradient at the Larmor frequency, it potentially carries information about atomic motion in the 100 MHz range. However, for quadrupolar nuclides such as ^{27}Al , the recovery curve generally shows non-single exponential behavior except for the very high temperature region, i.e. when $\omega \cdot \tau_c < 1$ (ω : Larmor frequency, τ_c : NMR correlation time), because all transitions are not fully excited. For a target quadrupolar spin with $I = 3/2, 5/2, 7/2$ (etc.) when the rapid correlation limit ($\omega \cdot \tau_c \ll 1$) is not satisfied, the quadrupolar interaction produces multi-exponential ($I + 1/2$ components) spin-lattice relaxation. For example, the relaxation process near room temperature in the CAS glass is actually well fitted by a tri-exponential function. However, an approximate single exponential fitting was carried out for simplicity and for ease of comparison among data from all temperatures.

At temperatures below 200 °C, T_1 was nearly constant, then decreased with increasing temperature from 200 to 1,200 °C. Around 800 °C, an abrupt change in the slope was seen, suggesting a change in the relaxation mechanism near T_g . A rough T_1 minimum was observed about 1,200 °C, at which point the correlation time for the motion responsible for relaxation is equal to reciprocal Larmor frequency ($\omega \cdot \tau_c = 1$) and the most efficient spin-lattice relaxation takes place. Above 1,200 °C, T_1 increased with increasing temperature.

According to theory, T_1 should be longer than T_2^* for $\omega \cdot \tau_c > 1$ (low temperatures) and be equal to T_2^* for $\omega \cdot \tau_c < 1$ (high temperatures).¹⁸⁾ In the relatively low temperature range (25 - 1,000 °C), the measured T_1 and T_2^* data follow this expectation. However, the meas-

ured T_1 values were in fact somewhat shorter than estimated T_2^* values above 1,100 °C, indicating large experimental uncertainties due to the quite short T_1 (e.g. 12.1 μs at 1,100 °C), probably related to the difficulty in completely saturating the magnetization. In previous high temperature experiments on ^{23}Na in silicate and aluminosilicate melts, T_1 was longer than T_2^* by about 0.5 natural log units above the T_1 minimum.¹³⁾ If the same extra line broadening effect is assumed in the present experiment, error bars above 1,000 °C can be defined as shown Fig. 5.

Apparent activation energies E_a of 10 and 229 kJ/mol were estimated by the linear slopes from 200 to 700 °C and from 800 to 1,000 °C respectively using the Arrhenius relationship. E_a above T_g is much larger than that at lower temperature.

On the basis of the above experimental results, the mechanism of relaxation was considered for each temperature region. In the low temperature range below T_g , ^{27}Al spin-lattice relaxation occurs mainly via the coupling with small-step acoustic lattice vibrations. Such local motions are of low amplitude and infrequent, but seem to be sufficient to cause relaxation even in solid glass. The very low apparent E_a (10 kJ/mol) at low temperature suggests small local motions of Al^{3+} ions within AlO_4 tetrahedra, which do not need to surmount high energy barriers. With increasing temperature (still below T_g), T_1 gradually decreases because the motions causing the fluctuation of the electric field gradient become faster and spin relaxation becomes more efficient. Near to T_g , translational (through-going) motions begin to occur in addition to local fluctuations.

As at some point most local fluctuations should be too fast to cause effective spin-lattice relaxation, translational motions may instead become predominant for spin-lattice relaxation. Furthermore, the relaxation process caused by translational motions, which is strongly temperature dependent, could account for the large T_1 drop between T_g (≈ 810 °C) and the temperature at T_1 minimum (probably $\approx 1,200$ °C). The much higher E_a at this temperature (229 kJ/mol) also supports this conclusion; translational motions involving site exchanges of Al^{3+} ions would need more energy to overcome the

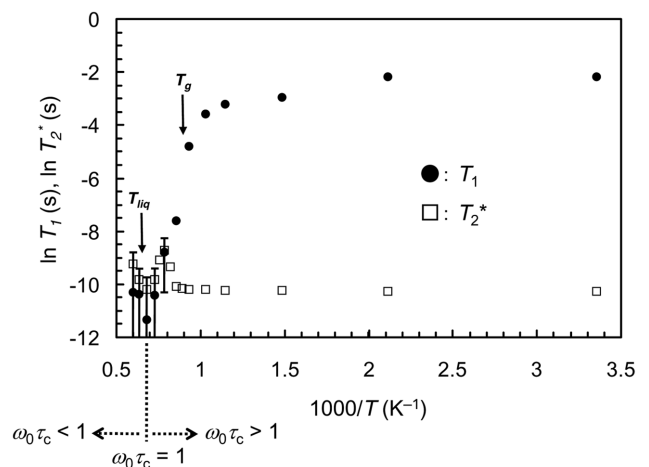


Fig. 5 T_1 and T_2^* for ^{27}Al in the CAS glass and melt from 25 to 1,400 °C

transition barrier.

T_2^* data calculated from line widths of the ^{27}Al static spectra show no dramatic changes up to 900 °C at least on a logarithmic scale, whereas the marked change in T_1 relaxation behavior occurs around 800 °C. In other words, spin-lattice relaxation data for this nuclide are more sensitive to changes in the type of motions around T_g than line width measurements.

2.2.4 Relationship between microscopic motions and macroscopic viscous flow

The correlation time τ_c can be estimated from the NMR relaxation data to compare microscopic motions with macroscopic viscous flow. Although nuclear spin relaxation of quadrupolar nuclides in solid-like materials (e.g. viscous melts) can be difficult to interpret, T_1 of such nuclides in the high temperature, rapid correlation regime ($\omega_0 \tau_c \ll 1$) may be relatively simply expressed as follows:

$$1/T_1 = (3/40)[(2I+3)/I^2(2I-1)](1+\eta^2/3)[e^2qQ/h]^2\tau_c \quad (4)$$

Again, the mean value for e^2qQ/h ($= C_Q$) was estimated to be 7.2 MHz from the MAS NMR data on the glass. Assuming that the actual T_1 equals the measured T_2^* above the T_1 minimum, and that $\eta = 0$, the microscopic correlation time τ_c was estimated. These data were plotted in Fig. 6, and show good agreement with shear relaxation time τ_s as estimated from viscosity (Vogel-Fulcher-Tamman equation). These results clearly show that NMR and shear relaxation are controlled by the same type of atomic motion, in both supercooled liquids ($T_g < T < T_{liquid}$) and stable liquids ($T_{liquid} < T$). Thus, atomic-scale motions reflected by nuclear spin relaxation are directly related to macroscopic viscous flow above T_g .

3. Conclusions

In the present study, we established a new in situ high temperature NMR technique that allows for observation of slag in a molten state. The structure and dynamics of the aluminum cation and their changes with increasing temperature were elucidated for the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass and melt. The mechanism of viscous flow was also discussed.

- (1) Below T_g , the chemical structure and atomic motion of Al do not change noticeably.
- (2) Above T_g , the proportion of pentacoordinated Al increases with elevating temperature. Since the Al coordination number still increases above T_{liq} , pentacoordinated Al probably acts as the

- intermediate of atomic motion.
- (3) Above T_g , the mechanism of atomic motion changes. Translational (through-going) motions begin to occur in addition to small local motions of Al^{3+} ions within AlO_4 tetrahedra.
- (4) In the high temperature region in which $\omega_0 \tau_c \ll 1$ is satisfied, τ_c is in good agreement with shear relaxation time τ_s as estimated from viscosity, indicating that atomic-scale motions reflected by nuclear spin relaxation are directly related to macroscopic viscous flow.

In situ high temperature NMR provides information on the chemical structure and dynamics in a molten state. Such information cannot be obtained by NMR at ambient temperature for glass synthesized by melt-quench methods. It should be noted, however, that it is difficult to obtain useful structural information from the static NMR spectra below T_g because the molecular motion is considerably constrained. Therefore, in order to obtain detailed information about the structure of glass, high resolution solid-state NMR techniques at ambient temperature are more effective. The key to successful analysis is to select the most suitable technique according to purpose.

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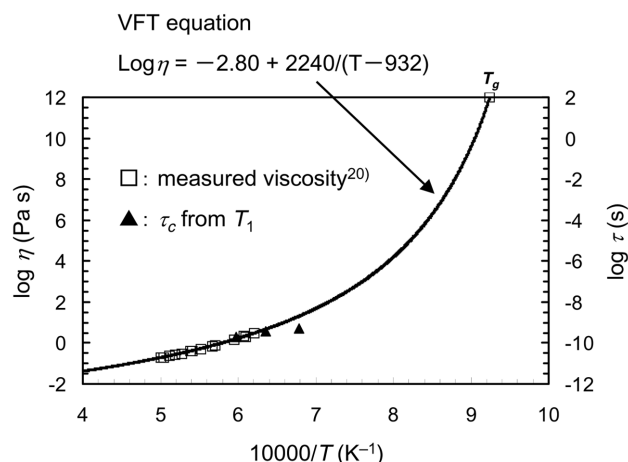


Fig. 6 Plot of \log_{10} of viscosity η , \log_{10} of shear relaxation time τ_s , and \log_{10} of NMR correlation time τ_c for the CAS glass and melt versus inverse temperature



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