Electrical Conductivity Measurement of CaO-Al_2O_3-CaF_2 slags by van der Pauw-Ohta Method

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ABSTRACT

Electro slag remelting (ESR) is one of the methods used to produce high-cleanliness steel. In the ESR method, the product steel electrode is immersed in flux, and the electrode is melted by the Joule heat of the flux generated by high current. CaF_2-based melts are mainly used as fluxes, but the electrical conductivity of CaF_2-based melts varies widely among researchers and measurement methods. Therefore, this experiment aims to measure the electrical conductivity of CaF_2-based melts based on the van der Pauw-Ohta method, which does not require the cell constant that is a fundamental error factor in electrical conductivity measurement at high temperatures. The measurement temperature was set at 1450-1600 °C, and dehydrated Ar flowed through the furnace at 200 ml/min. Electrodes were fabricated by Pt-30mass%Rh alloy, and the electrodes were connected to an impedance analyzer using a four-terminal probe. The electrodes were immersed in the melt, and the impedance and phase angle were measured by AC frequency sweep (50 Hz to 200 kHz). The electrical conductivity was then calculated by utilizing the impedance's real part values when the impedance's imaginary component was zero. The electrical conductivity showed a positive temperature dependence. The electrical conductivity of $60(CaO\cdot Al_2O_3)$-$40CaF_2$ melt increased with increasing temperature but was found to be roughly one-third of those of the previous studies. In the conductivity measurement of $60(CaO\cdot Al_2O_3)$-$40CaF_2$ melt, the AC frequency with a phase angle of 0° was found to be different depending on the temperature and immersion depth. By sweeping the frequency, the impedance at the phase angle of 0° can be obtained, which enables us to measure the electrical conductivity more accurately.

INTRODUCTION

Various technologies have been developed in the field of high-grade steel production, such as vacuum technology (Koshiba, 1958; Asakuma, 1973) (vacuum melting, vacuum treatment, vacuum arc remelting, etc.), technology using new heat sources (Kato, 1984; Ono, 1993) (plasma, electron beam, etc.), and technology using the physical and chemical properties of slag (Ogino, 1979) (electroslag remelting, etc.).

The ESR (Electro Slag Remelting) method is a remelting process that effectively utilizes the electrical properties of slag. In the ESR method, the electrode metal is remelted by the resistive heat of the molten slag, and the molten metal absorbs inclusions and impurities as it falls through the slag. During this process, slag flows between the ingot and the mold, forming a slag skin that covers the surface of the ingot, resulting in ingots with excellent surface properties. Thus, in the ESR process, slag plays an extremely important role in each process of metal melting, refining, and solidification. Therefore, a thorough understanding and knowledge of the characteristics of slag is required for effective operation. The electrical conductivity of the slag is one of the most important factors controlling the operating conditions. It is known that the temperature of the slag bath, the depth of the electrodes in the slag, and the shape of the metal pool vary depending on the choice of the electrical conductivity of the slag, which in turn has a significant effect on the properties of the ingot and the power consumption (Ogino and Hara, 1979).

In addition, ESR slags are often made from systems containing fluorides such as CaF_2. Therefore, many researchers have measured the electrical conductivity of fluoride slag, but there is a large difference in the reported data. As an example, FIG. 1 shows the electrical conductivity of the CaO-CaF_2 system. Mitchell and Cameron (1971), Krauβ and Neuhof (1973), and Winterhager, Kammel and Gad (1990) reported that the electrical conductivity of the CaO-CaF_2 system decreased with the addition of CaO, while Ogino, Hara and Hashimoto (1978) and Zhmoidin (1970) reported that the conductivity increases when the CaO content is low and decreases when the CaO content is high. The electrical conductivity data of the fluoride slag varies widely among the reported data. The reason for these differences may be due to the influence of the imaginary component of impedance caused by the measurement temperature and the cell constant of the electrode. As for the effect of the imaginary component of the impedance, in the past experiments, the frequency was kept constant and the measurement was made without considering the imaginary component of the impedance.

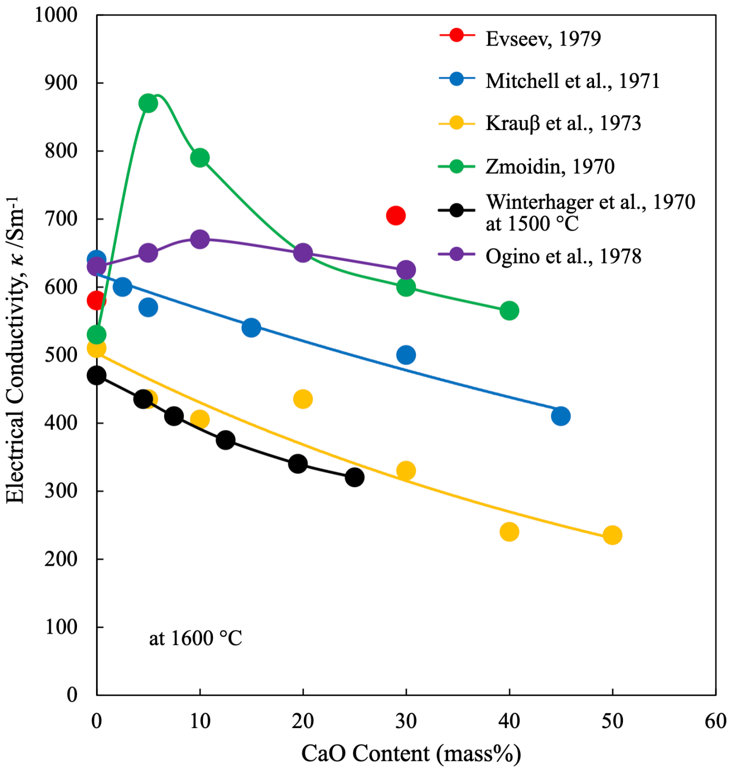

FIG 1 – Electrical conductivity of CaF_2-CaO melt at 1600 °C as a function of CaO content.

However, since the frequency at which the imaginary component of the impedance becomes zero depends on the temperature and immersion depth, it is possible that the imaginary component of the impedance is not eliminated. Therefore, the imaginary component of the impedance can be eliminated by using the value of the real component of the impedance as the resistance value when the imaginary component of the impedance becomes zero by performing a frequency sweep. Since the cell constant of the electrode differs between room temperature and high temperature, it is thought that the electrical resistance of the electrode differs. We focused on the van der Pauw method as a measurement method that does not use the cell constant, because the distance between electrodes does not affect the conductivity measurement using the van der Pauw method, and the electrodes can be regarded as points. Since the cell constant can be calculated from the distance between electrodes and the electrode area, the van der Pauw method can be applied to calculate the electrical conductivity without considering the cell constant. Therefore, the purpose of this study is to measure the electrical conductivity of fluoride slag using the van der Pauw-Ohta method.

EXPERIMENTAL

Principle of the van der Pauw method:

The two-pole and four-terminal methods (Kato and Minowa, 1965; Ogino, Hara and Hashimoto, 1978) have been mainly used to measure the electrical conductivity of melts. In the four-terminal method, on the other hand, the voltage and current measurement terminals are independent, so the internal resistance of the probe is less affected. However, both methods use cell constants for measurement, which can cause large errors at high temperatures when the electrode is easily deformed. In addition, when the resistivity of the electrode metal shows a temperature dependence, it is very difficult to exclude the effect. In this study, we applied the van der Pauw method (van der Pauw, 1958) to the measurement of the electrical conductivity of melts at high temperatures, and tried to measure the electrical conductivity without using the cell constant.

As shown in FIG. 2, we placed four electrodes around a sample of thickness W, applied a voltage between two terminals to measure the current, and measured the voltage between the remaining two terminals.

$$\rho = \frac{\pi W}{ln2} \cdot \frac{R_1 + R_2}{2} \cdot f\left(\frac{R_1}{R_2}\right) \qquad \ldots(1)$$

where $R_1=V_{cd}/I_{ab}$, $R_2=V_{da}/I_{bc}$, and ρ is the electrical resistivity of the sample. Expressing equation (1) in terms of ρ, we get

$$\exp\left(-\frac{\pi R_1 W}{\rho}\right) + \exp\left(-\frac{\pi R_2 W}{\rho}\right) = 1 \qquad \ldots(2)$$

$$f\left(\frac{R_1}{R_2}\right) = 1 - (\frac{R_1 - R_2}{R_1 + R_2})^2 \cdot \frac{ln2}{2} - (\frac{R_1 - R_2}{R_1 + R_2})^4 \{\frac{(ln2)^2}{4} - \frac{(ln2)^3}{13}\} \qquad \ldots(3)$$

If the values of R_1 and R_2 are close, f (R_1/R_2) = 1 can be regarded, and the reciprocal of the electrical resistivity calculated by formula (2) becomes the electrical conductivity. In this way, the electrical conductivity can be measured by the difference between W_1 and W_2 without the need for cell constants.

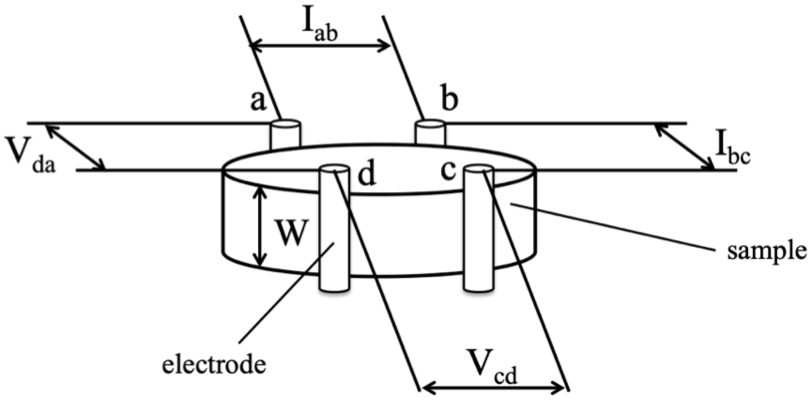

FIG 2 – Principle schematic for electric conductivity measurement based on the van der Pauw method.

Principle of the van der Pauw-Ohta method:

As shown in FIG. 3, when the van der Pauw method is applied to the melt, the measured resistance R_M is considered to be the parallel composite resistance of the resistance R_A (the immersed part of the electrode) and the spreading resistance R_B (the non-immersed part) (Ohta et al., 1981). This makes it necessary to remove the spreading resistance R_B, but since R_A and R_B cannot be separated from a single immersion depth, they cannot be removed. Therefore, the electrical conductivity is calculated using the measured resistances of two points with different immersion depths. First, for the immersed part of the electrode, the depth of immersion is W. From equation (2), the following equation is obtained

$$\rho = \frac{2\pi W}{ln2} \cdot R_A \qquad \text{…(4)}$$

If $R_M = (R_1 + R_2)/2$ and the R_Ms at W_1 and W_2 are R_{M1} and R_{M2}, respectively, then the spreading resistance R_B becomes

$$R_B = \frac{R_{M1}R_{M2}(W_1 - W_2)}{R_{M1}W_1 - R_{M2}W_2} \qquad \text{...(5)}$$

Since R_M is the parallel composite resistance of R_A and R_B

$$R_A = \frac{-R_M R_B}{R_M - R_B} \qquad \text{...(6)}$$

Organizing equations (4), (5), and (6), we obtain

$$\rho = \frac{2\pi W}{ln2} \cdot \frac{R_M R_{M1} R_{M2}(W_2 - W_1)}{R_{M1}W_1(R_M - R_{M2}) - R_{M2}W_2(R_M - R_{M1})} \qquad \text{...(7)}$$

Where W is W_1 or W_2, equation (7) is expressed as equation (8)

$$\rho = \frac{2\pi}{ln2} \cdot \frac{R_{M1}R_{M2}(W_2 - W_1)}{R_{M1} - R_{M2}}$$

...(8)

Therefore, the electrical resistivity ρ can be obtained by determining R_{M1} and R_{M2} for W_1 and W_2, and its reciprocal is the electrical conductivity.

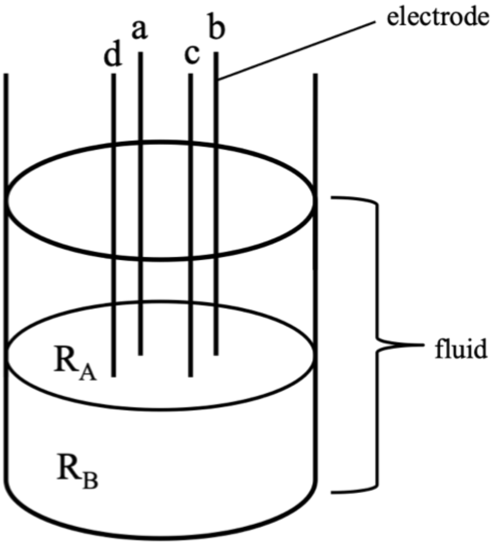

FIG 3 – Schematic of electrical conductivity measurement of liquid sample based on van der Pauw-Ohta method.

Electrical Conductivity Measurement of $15Na_2O$-$15CaO$-$70SiO_2$ Melt

The applicability of equation (8) was confirmed by measuring the electrical conductivity of $15Na_2O$-$15CaO$-$70SiO_2$ oxide melt. A square electrode was immersed in a Pt crucible filled with the sample. Four electrodes are a, b, c, and d in a clockwise direction (FIG. 3), and each electrode is connected to an impedance analyzer using a four-terminal probe. The impedance was measured by frequency sweeping at 50 mV (open circuit voltage) and 50 Hz to 200 kHz. After that, the connection terminal was rotated counterclockwise, and the impedance was measured in the same way. From the obtained data, an approximate curve was drawn with the imaginary part of the impedance near zero, and the impedance was defined as the value of the real part when the imaginary part of the approximate curve was zero. In this experiment, (W_1, W_2)=(5,10), (10,15), and (15, 20)/mm, and the electrical conductivity was calculated from equation (8) by obtaining the impedance at each immersion depth, and the average of the impedance was used as the electrical conductivity. The electrodes were immersed in the samples by raising and lowering the crucible with a lifting motor under the furnace. The samples were melted in a Pt crucible and placed in the furnace. After that, the electrical conductivity was measured by the above procedure, and then the temperature was set at 100 °C intervals and held for 30 minutes.

Electrical Conductivity Measurement of $21.3CaO$-$38.7Al_2O_3$-$40.0CaF_2$ Melt

The electrical conductivity of the $21.3CaO$-$38.7Al_2O_3$-$40.0CaF_2$ melt was measured. $CaCO_3$ was calcined at 1200 °C for 1 hour in a muffle furnace to obtain CaO. Then, various special-grade reagents were weighed and mixed to obtain the specified composition. The weighted and mixed powder samples were melted in a Pt crucible at 1550 °C in an Ar atmosphere. The experimental procedure was the same as that for the measurement of the electrical conductivity of oxide melts in the previous section. When CaF_2 is heated in air, it reacts with moisture in the air, and the reaction

$$CaF_2+H_2O \rightarrow CaO+2HF\uparrow \qquad ...(9)$$

occurs, which may cause a change in the composition of the sample and the generation of hydrogen fluoride. Therefore, the measurement was carried out in a dehydrated Ar gas atmosphere. The sample prepared in the previous section was placed in the furnace. The sample in the Pt crucible was melted in the furnace at 1600 °C and held for 1 hour. After that, the conductivity measurement was carried out according to the procedure described above, and then the conductivity measurement was carried out in the same way after holding the sample at each set temperature for 30 minutes at 50 °C intervals during the temperature decrease process.

RESULTS and DISCUSSION

FIG. 4 shows the results of electrical conductivity measurements of $15Na_2O-15CaO-70SiO_2$ melt. As shown in FIG. 4, the electrical conductivity of the $15Na_2O-15CaO-70SiO_2$ melt is close to that of the previous measurement. The reason for the lower values is that Mazurina (1967) measured the melt at a constant frequency (10 kHz) and did not consider the imaginary component of the impedance, which may have caused the error in the measured values. Therefore, we were able to measure the electrical conductivity of the oxide melt with good accuracy.

The electrical conductivity of the $15Na_2O-15CaO-70SiO_2$ melt showed a positive temperature dependence. This is because ionic conductivity plays a major role in electrical conduction in $15Na_2O-15CaO-70SiO_2$ melt, and the conductivity of the melt is determined by the ease of diffusion of ions. In the $15Na_2O-15CaO-70SiO_2$ melt, the Na^+ and Ca^{2+} cations modify the glass (melt) network, but the network deformation is caused by the Na^+ and Ca^{2+} cations. In the $15Na_2O-15CaO-70SiO_2$ melt, Na^+ and Ca^{2+} ions modify the glass network, but this requires activation energy for the network deformation. Therefore, as the temperature increases, more new diffusion paths can be created, and it is predicted that the electrical conductivity increases due to the easier diffusion of ions (Matsuoka (2017)).

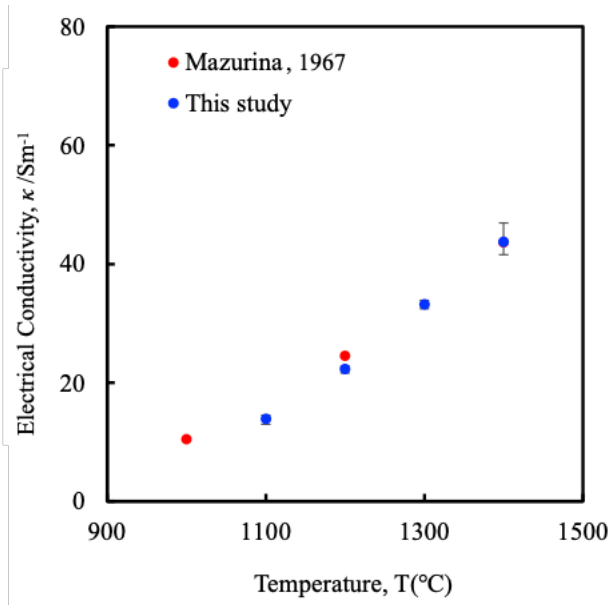

FIG 4 – Temperature dependence of electrical conductivity of $15Na_2O-15CaO-70SiO_2$ melt.

FIG. 5 shows the results of the electrical conductivity measurements of the 21.3CaO-38.7Al_2O_3-40.0CaF_2 melt. As shown in FIG. 5, the electrical conductivity of the 21.3CaO-38.7Al_2O_3-40.0CaF_2 melt showed a positive temperature dependence. Comparing the present measurements with those of Ohta et al. (1981), it was found that the electrical conductivity of the present measurements was about one-third of that of Ohta et al. (1981). The reason for the positive temperature dependence of the electrical conductivity is thought to be that the mobility of ions in the 21.3CaO-38.7Al_2O_3-40.0CaF_2 melt has become larger since ionic conduction plays a major role in the electrical conduction of the 21.3CaO-38.7Al_2O_3-40.0CaF_2 melt. Therefore, it is considered that the thermal motion of the ions (Ca^{2+}, Al^{3+}, F^-, and O^{2-}) in this system increases due to the increase in temperature, which facilitates the diffusion of the ions and increases the electrical conductivity.

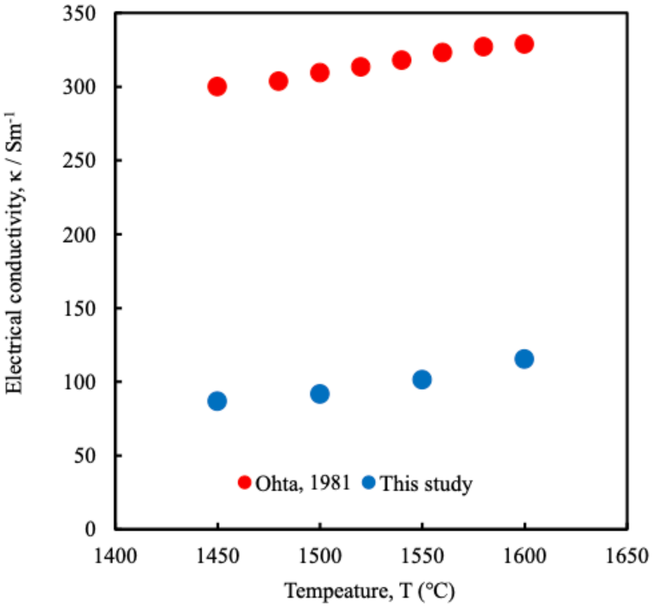

FIG 5 – Temperature dependence of electrical conductivity measurement results of 21.3CaO-38.7Al_2O_3-40.0CaF_2 melt.

TABLE 1 summarizes the measurement methods used for the past conductivity measurements of the same melts. In the present study, we used the four-terminal method, in which the current and voltage measurement terminals are independent, and we measured the electrical conductivity without using the cell constant, which is a source of error in the measurement of electrical conductivity at high temperatures. As shown in FIGS. 6 and 7, the AC frequency at which the phase angle reaches 0° varies greatly with temperature and immersion depth. These indicate that the frequency at which the phase angle is 0° was not properly selected because the frequency was kept constant regardless of the temperature and immersion depth in previous studies. Therefore, it is thought that the frequency with a phase angle of 0° was not properly selected, resulting in errors due to imaginary impedance components. In this study, on the other hand, we performed a frequency sweep to ensure the removal of the imaginary impedance component, which enabled us to measure the electrical conductivity with higher accuracy.

TABLE 1 – Experimental methods and conditions for electrical conductivity measurement in the previous studies.

Researchers	**Methods**	**Cell Constants**	**AC Frequency**
Mitchell and Cameron (1971)	two-terminals	o	1 kHz
Winterhager, Kammel and Gad (1970)	two-terminals	o	multiple Hz
Ogino, Hara and Hashimoto (1978)	four-terminals	o	1 kHz
Ohta et al. (1981)	four-terminals	x	2 kHz
present study	four-terminals	x	50 Hz ~ 200 kHz

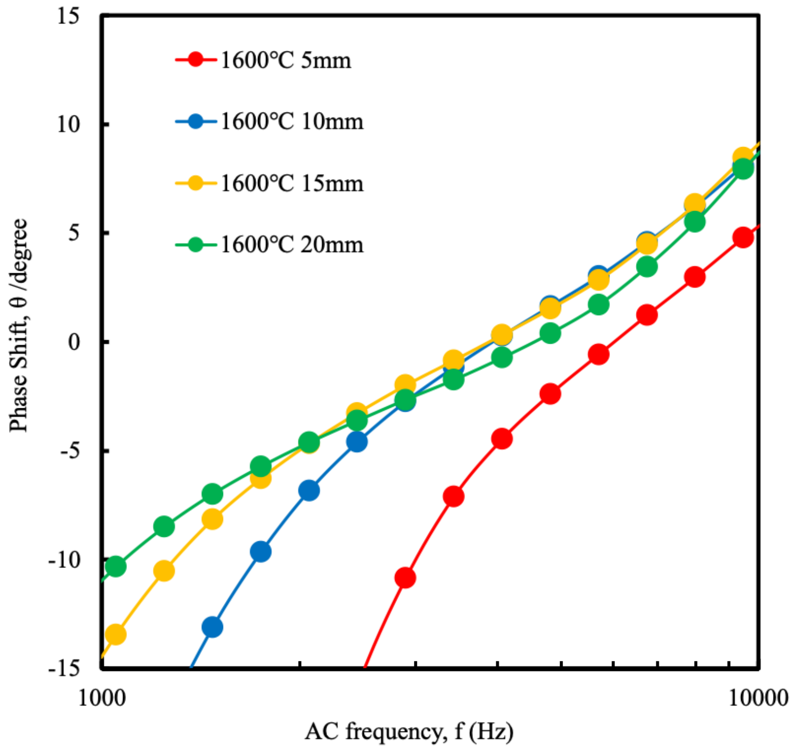

FIG 6 – Phase shifts of $CaO-Al_2O_3-CaF_2$ melts at 1600 °C as a function of AC frequency and immersion depth of electrodes.

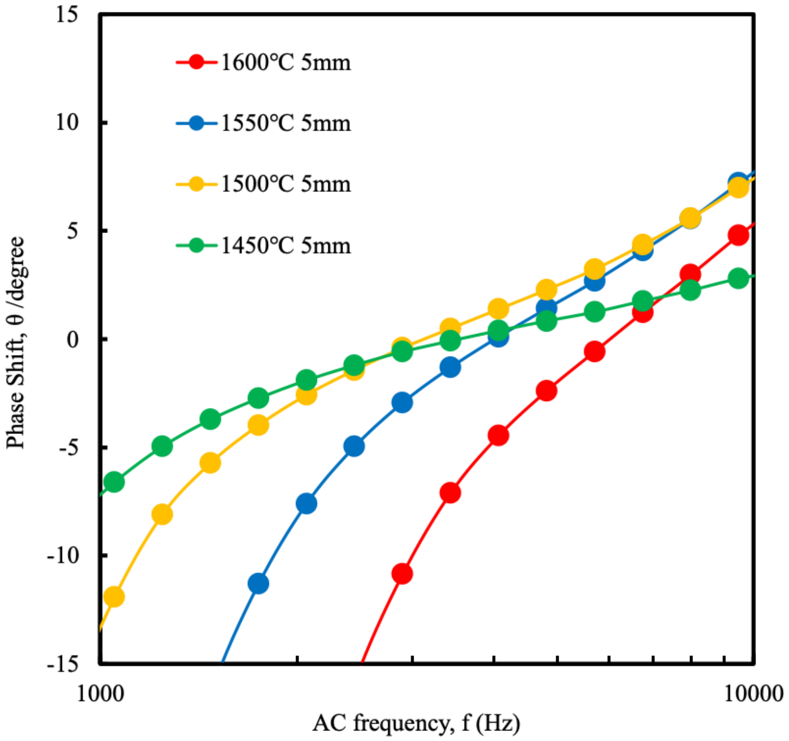

FIG 7 – Phase shifts of $CaO\text{-}Al_2O_3\text{-}CaF_2$ melts as a function of AC frequency and temperature.

CONCLUSIONS

In the present study, we quantitatively measured the high-temperature electrical conductivity of ESR flux by the van der Pauw-Ohta method and obtained the following findings.

1. A method for measuring the electrical conductivity of melts at high temperatures using a four-terminal method based on the van der Pauw method has been established.

2. The electrical conductivity of the $15Na_2O\text{-}15CaO\text{-}70SiO_2$ melt was close to that of previous measurements.

3. The electrical conductivity of $15Na_2O\text{-}15CaO\text{-}70SiO_2$ melt increased with increasing temperature.

4. The electrical conductivity of $60(CaO{\cdot}Al_2O_3)\text{-}40CaF_2$ melt increased with increasing temperature but was found to be roughly one-third of those of the previous studies.

5. In the conductivity measurement of $60(CaO{\cdot}Al_2O_3)\text{-}40CaF_2$ melt, the AC frequency with a phase angle of 0° was found to be different depending on the temperature and immersion depth.

6. By sweeping the frequency, the impedance at the phase angle of 0° can be obtained, which enables us to measure the electrical conductivity more accurately.

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