THE ELECTRICAL CONDUCTIVITY OF SOLID/MELT COEXISTING SYSTEMS

Shigehito Deki, Masako Taira, Masako Takase, Akihiko Kajinami, Yukio Kanaji and Minoru Mizuhata*

Department of Chemical Science & Engineering, Faculty of Engineering, Kobe University
Rokkodai-cho, Nada-ku, Kobe 657, Japan

*Department of Energy & Environment, Osaka National Research Institute, AIST
1-8-31, Midorigaoka, Ikeda, Osaka 563, Japan

ABSTRACT

The electrical conductivity and its temperature dependence were investigated for \( \alpha\)-Al\(_2\)O\(_3\) powder / molten KNO\(_3\) coexisting system by ac impedance method with LF impedance analyzer. The electrical conductivity of the system decreased with increasing of the volume fraction of the solid phase following Archie’s equation. The activation energy of the electrical conductivity, \( \Delta E_a \), determined from the temperature dependence by using Arrhenius equation, was correlated with an apparent average thickness of the melt phase on the surface of the \( \alpha\)-Al\(_2\)O\(_3\) particle, and it suggested that the nature of the melt changes in the vicinal liquid layer on the solid phase owing to the interaction between the melt and the solid surface.

INTRODUCTION

Molten salt / powder coexisting system is a very important and attractive system not only in the applied field of molten salt chemistry such as a metal refining process or a fuel cell technology, but also general technology such as a crystal growth, composite materials or liquid-phase sintering process of ceramics and powder metallurgy. Recently, it is also suggested that molten salts inserted in Al\(_2\)O\(_3\) powders can be used as one of solid electrolytes.

Regarding with the interfacial phenomena in the solid/liquid coexisting systems, many researches have been done. However, most of them were dealt with systems ranging in the low concentration of solid phase, which are called a suspension or colloidal solution. Whereas, few researches on the system ranging in the higher concentration of solid phase, which is called a paste, have been done.

We have already reported that in coexisting systems of the aqueous electrolyte solution and inorganic powders, the physicochemical properties of the liquid phase near the solid phase is different from those of bulk.\(^{[1-5]}\)

In the present paper, molten KNO\(_3\) was used as a liquid phase and \( \alpha\)-Al\(_2\)O\(_3\) powder was used as a solid phase. For this system, electrical conductivity was measured by the ac...
impedance method and melting behavior of KNO$_3$ was investigated with a differential scanning calorimeter.

**EXPERIMENTAL**

Various kinds of high-purity $\alpha$-Al$_2$O$_3$ powder for the ceramics, which were supplied by Showa Denko Co.Ltd. and had various specific surface areas of 1.08 - 17.7 m$^2$/g, was used. The $\alpha$-Al$_2$O$_3$ powder, after annealed at 1000°C in the air for 3hr, and solid KNO$_3$ were mixed thoroughly in an agate mortar under N$_2$ gas atmosphere and molded into a tablet with a diameter of 20mm under the pressure of 52 MPa for 30 min. Then the tablet was annealed again at 400°C in N$_2$ gas flow for 3hr, so that KNO$_3$ in the tablet melted and wetted well the surface of $\alpha$-Al$_2$O$_3$ particles.

After molding, the ac impedance for the composite samples with various melt contents was measured in the frequency range from 5Hz to 13 MHz with a Hewlett-Packard 4192A LF impedance analyzer at 160-440°C in N$_2$ atmosphere.

The sample tablet was set in an alumina ceramic inner cell, and was put closely in Pt electrodes with diameters of 10mmφ. The inner cell was held in a quartz glass tube in which N$_2$ gas was flowed, and the silica glass tube was kept in a furnace to be temperature-controlled. (Fig.1)

The resistance was determined from Z' value at the intercept of the semicircular arc to Z'-axis on the complex impedance plane and the electrical conductivity of the tablet sample was calculated from the resistance, sample thickness and the area of the electrode.

X-ray diffraction measurement was applied to make sure of the composition for the tablet after annealed. The colorimetry was applied to determine the solubility of $\alpha$-Al$_2$O$_3$ powder in molten KNO$_3$. After annealed, the tablet was dispersed in distilled water and the salt was dissolved into the water and separated from the $\alpha$-Al$_2$O$_3$ powder with a filter. Ferron(8-hydroxy-7-iodoquinoline-5-sulfonic acid) and pH buffer solution were added to this filtrate. The absorbance measurement was carried out with a UV/VIS spectrophotometer.

DTA-TG and DSC were applied to investigate the decomposing and melting behavior for KNO$_3$ coexisting with the alumina powder in the tablet. The measurement was carried out under N$_2$ gas flow.

**RESULTS AND DISCUSSION**

SEM observation was applied in order to investigate the change of the surface morphology of the alumina particles due to some reactions with the melt during the temperature raising. The cross section of tablet before and after annealing was observed with SEM. The change in the morphology of $\alpha$-Al$_2$O$_3$ particles after annealing was not observed.

The X-ray diffraction patterns measured for composite samples were only assigned to $\alpha$-Al$_2$O$_3$ and KNO$_3$, and none of eutectic mixtures or reaction product were not detected. (Fig.2)

The solubility of the $\alpha$-Al$_2$O$_3$ powder into molten KNO$_3$ was measured for the fine $\alpha$-Al$_2$O$_3$ powder whose specific surface area of 17.7m$^2$/g was the largest in the applied alumina. As a result, ca. 150 μg of Al$^{3+}$ in 1g of molten KNO$_3$ was detected. As the solubility of $\alpha$-Al$_2$O$_3$ powder for the melt was so small, the contribution of the dissolved alumina to the electrical conductivity as a carrier might be neglected.

As a above mentioned result, $\alpha$-Al$_2$O$_3$ powder and molten KNO$_3$ were less reactive in the measuring temperature region and each sample was treated as a mixture of $\alpha$-Al$_2$O$_3$ powder and molten KNO$_3$. 

204
The complex impedance plots varied with the temperature. At higher temperature the complex impedance plots showed a linear locus, which indicated a typical Warburg impedance. It is recognized that the resistance of the composite decreased with melting of KNO$_3$. At the lower temperature, the complex impedance plots showed a semi-circular arc in the high frequency range. It is presumed that KNO$_3$ gradually froze and the resistance of the composite increased rapidly. At the lower temperature region, the complex impedance plots showed only the semi-circular arc. However, most arcs were slightly deformed and it showed that those complex impedance plots consisted of two kinds of semi-circular arcs. Such impedance plots often can be seen for solid electrolyte systems, and suggests that two different types of capacitance and resistance are contained in the equivalent circuit for these systems. And also, it indicates that the nature of molten KNO$_3$ near solid surface is different from that in the bulk of liquid phase.

The deflection point, Tt, corresponding to the phase transition of KNO$_3$ was observed on a temperature dependence of the electrical conductivity. In the higher temperature region, the plots of log $\sigma$ vs. $1/T$ showed a linear relationship, and the activation energy of the electrical conductivity was calculated from the gradient of the linear part of the plot by use of the Arrehenius equation.

The temperature hysteresis of the electrical conductivity on heating and cooling was observed. Those showed a tendency that the electrical conductivity on cooling is higher than that on heating. As a repetition of heating and cooling, the difference of the electrical conductivity decreased and the activation energy for the electrical conductivity became constant. It is assumed that the packing of KNO$_3$ and alumina particles came to be equilibrated through the repetition of melting and solidification, and a conductive path was settled in the tablet. Whereas, the hysteresis shows the tendency that the transition temperature, $T^*$, for the electrical conductivity on cooling is higher than that on heating. The temperature dependencies of the electrical conductivity for various kinds of $\alpha$-Al$_2$O$_3$ powders were measured. The coexisting system of which the specific surface area was the smallest, the electrical conductivity increased with the increase of the melt content. (Fig.3, Fig. 4) However, the activation energy in the temperature region above the transition temperature, and the transition temperature did not vary with the melt content. Besides the electrical conductivity in the temperature region below the transition temperature hardly varied. While, as the increase of the surface area, the activation energy increased and the transition temperature decreased with the increase of the melt content. (Fig. 5, Fig. 6)

The activation energy increased rapidly at a certain melt content. This behavior was observed evidently for the system containing the powder with the large surface area. However, the change of the activation energy became not so clear with the decrease of the specific surface area. This tendency was also observed for the transition temperature, also.

It is assumed that these results is correlative with a thickness of the molten salt existing near the surface of $\alpha$-Al$_2$O$_3$ powder. Here, the apparent average thickness was defined as follows.

\[
[\text{apparent average thickness}] = \frac{[\text{total volume of molten salt}]}{[\text{total surface area of } \alpha\text{-Al}_2\text{O}_3]}
\]

This value has a length dimension and means, as a parameter, a distance from the surface of the solid phase. Therefore, it can be known that how far the influence of the solid surface extends to the melt phase. The variations of the activation energy and the transition temperature for electrical conductivity with the apparent average thickness showed good correlative. The value of the activation energy decreased and the value of the transition temperature increased with the increase of the apparent average thickness.
temperature increased with the thickness up to ca. 5-10nm. As a result, it is suggested that the ion interaction of KNO₃ is affected in the range of ca. 5-10nm as the apparent average thickness from the surface of solid phase, owing to the interaction between ionic species in the melt and the surface of α-Al₂O₃ powder. (Fig. 7, Fig. 8)

REFERENCES

1. S. Deki, M. Mizuhata, K. Nakamura, A. Kajinami and Y. Kanaji  J. Electrochem. Soc., 139(6), 1544(1992)

2. S. Deki, M. Mizuhata, S. Nakamura, K. Nakamura, A. Kajinami and Y. Kanaji  J. Electrochem. Soc., 139(4), 996(1992)

3. S. Deki, M. Mizuhata, S. Nakamura, A. Kajinami and Y. Kanaji  J. Chem. Soc., Faraday Trans., 89(20), 3805(1993)

4. S. Deki, M. Mizuhata, A. Kajinami and Y. Kanaji  J. Chem. Soc., Faraday Trans., 89(20), 3811(1993)

5. S. Deki, M. Mizuhata, S. Nakamura, K. Nakamura, A. Kajinami and Y. Kanaji  J. Colloid Interface Sci., 159, 444(1993)
Fig. 1. Apparatus for electric conductivity measurements.

Fig. 2. X-ray diffraction pattern of $\alpha$-$\text{Al}_2\text{O}_3(17.7\text{m}^2/\text{g})$ powder / KNO$_3$ coexisting system.
Melt content ; 35vol%.
Fig. 3. Temperature dependence of the electrical conductivity for various kinds of $\alpha$-Al$_2$O$_3$ (17.7 m$^2$/g) powder / KNO$_3$ coexisting system.

Fig. 4. Temperature dependence of the electrical conductivity for various kinds of $\alpha$-Al$_2$O$_3$ powders / KNO$_3$ coexisting system.

Melt content; 10vol%.
Fig. 5. Variations of $\Delta E_a$ with the melt content for various kinds of $\alpha$-$\text{Al}_2\text{O}_3$ powders / KNO$_3$ coexisting systems.

Fig. 6. Variations of the transition temperature for the electrical conductivity with the melt content for various kinds of $\alpha$-$\text{Al}_2\text{O}_3$ powders / KNO$_3$ coexisting systems.
Fig. 7. Variation of $\Delta E_a$ with the apparent average thickness of the liquid layer for various kinds of $\alpha$-$\text{Al}_2\text{O}_3$ powders / KNO$_3$ melt coexisting systems.

Fig. 8. Variation of the transition temperature for the electrical conductivity with the apparent average thickness of the liquid layer for various kinds of $\alpha$-$\text{Al}_2\text{O}_3$ powders / KNO$_3$ melt coexisting systems.