Thermal Conductivity of the Silicate Melts

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Agenda

• Introduction
  – Thermal conductivity of liquid oxide
  – Previous studies and Objectives

• Experimental
  – Apparatus, Experimental procedure, Sample preparation

• Results and Discussion
  – Temperature and Composition dependence
  – Amphoteric behavior of $\text{Al}_2\text{O}_3$
  – Relationship of thermal conductivity to silicate structure
Thermal Conductivity of Liquid Oxides

• An important physical property in material production processes
• Thermal conductivity of liquid oxide in iron- and steelmaking
  – Thermal conductivity of Na$_2$O-SiO$_2$ system (Nagata et al.)
Thermal Application of Molten Slag

- Utilization of blast furnace slag and latent heat
- Optimization of BF slag recovery process
## Previous Studies

<table>
<thead>
<tr>
<th>COMPOSITION (mass%)</th>
<th>METHOD</th>
<th>TEMPERATURE RANGE (K)</th>
<th>THERMAL CONDUCTIVITY (W/mK)</th>
<th>AUTHORS</th>
</tr>
</thead>
<tbody>
<tr>
<td>40CaO-20Al₂O₃-40SiO₂</td>
<td>hot wire method</td>
<td>373~1673</td>
<td>0.20~1.50</td>
<td>K. Nagata et al.</td>
</tr>
<tr>
<td>25CaO-15Al₂O₃-60SiO₂</td>
<td></td>
<td>373~1673</td>
<td>0.40~1.60</td>
<td>K. Nagata et al.</td>
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<td>40CaO-20Al₂O₃-40SiO₂</td>
<td></td>
<td>1573</td>
<td>0.80~1.00</td>
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<tr>
<td>40CaO-20Al₂O₃-40SiO₂</td>
<td></td>
<td>373~1673</td>
<td>0.50~1.70</td>
<td>M. Susa et al.</td>
</tr>
<tr>
<td>40CaO-20Al₂O₃-40SiO₂</td>
<td>laser flash method</td>
<td>273~1623</td>
<td>0.70~1.20</td>
<td>M. Kishimoto et al.</td>
</tr>
<tr>
<td>45CaO-15Al₂O₃-40SiO₂</td>
<td></td>
<td>273~1673</td>
<td>0.60~1.20</td>
<td>M. Kishimoto et al.</td>
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<td>50CaO-15Al₂O₃-35SiO₂</td>
<td></td>
<td>273~1673</td>
<td>0.50~1.00</td>
<td>M. Kishimoto et al.</td>
</tr>
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<td>50CaO-15Al₂O₃-35SiO₂</td>
<td></td>
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<td>T. Sakuraya et al.</td>
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</tr>
<tr>
<td>40CaO-20Al₂O₃-40SiO₂</td>
<td>radial heat flow</td>
<td>1573~1623</td>
<td>1.10~2.00</td>
<td>K. Ogino et al.</td>
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<tr>
<td>40CaO-20Al₂O₃-40SiO₂</td>
<td></td>
<td>1273~1673</td>
<td>1.00~2.00</td>
<td>T. El Gammal et al.</td>
</tr>
<tr>
<td>CaO-Al₂O₃-SiO₂ system</td>
<td>m.p.+100</td>
<td>0.70~2.80</td>
<td></td>
<td>D. Sommerville et al.</td>
</tr>
</tbody>
</table>

→ limitation in the compositions and temperature
Previous Studies

Results of thermal conductivity measurement of the CaO-Al₂O₃-SiO₂ system (left) after Slag Atlas and (right) by D.Sommerville et al, Trans. of the ISS, 1991

→ reliable thermal conductivity data in pure liquid region: insufficient
Introduction

Measurement of Thermal Conductivity

• Measurement methods for liquid oxide
  – Stationary methods
  – Non-stationary method
    • Laser flash method, Hot-wire method
Objectives

- Measurement the thermal conductivity of the CaO-Al$_2$O$_3$-SiO$_2$ system using hot-wire method from liquidus temperature to 1873K

- Better understanding on the relationship between the thermal conductivity and silicate structure from its temperature and composition dependences
Experimental

Hot-wire Method

- Equation for thermal conductivity

\[
\lambda = \frac{Q}{4\pi} \frac{\partial (\Delta T)}{\partial (\ln t)}
\]

\( Q \): Heat generation of unit length of hot-wire
\( \gamma \): Euler constant

- slope \( \Delta T \) against \( \ln t \)

- Minimization of the effects of convection and radiation
Experimental

Sample Preparation

weighing, mixing  →  pre-melting at 1873K for 20min.  →  crushing to powder

Phase diagram of Na$_2$O-SiO$_2$ system and measurement range

ternary phase diagram of the CaO-Al$_2$O$_3$-SiO$_2$ system
Experimental

Experimental Procedure

**Measurement**

Supply constant power (1.5A) to hot-wire
Measure temperature change of hot-wire
Plot $\Delta T$ against $\ln t$
Calculate thermal conductivity

**Analysis**

$\text{SiO}_2$: gravimetry., Others: ICP-AES

<table>
<thead>
<tr>
<th>Crucible</th>
<th>Alumina or Pt-10%Rh</th>
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<tbody>
<tr>
<td><strong>Temp.</strong></td>
<td>L.T.$\sim$1873K, every 50K</td>
</tr>
</tbody>
</table>
Results and Discussion

Thermal Conductivity and Temperature

• The Na$_2$O-SiO$_2$ system

*Thermal conductivities of the Na$_2$O-SiO$_2$ system as a function of temperature*
Results and Discussion

Thermal Conductivity and Temperature

- The CaO-Al$_2$O$_3$-SiO$_2$ system
Results and Discussion

Thermal Conductivity and Basicity

Relationship between thermal conductivity and CaO/SiO$_2$ ratio

mass%CaO
mass%SiO$_2$ : basicity

acid-side: basicity $\propto$ thermal conductivity

basic-side: relatively high thermal conductivity

$\Rightarrow$ influence of Al$_2$O$_3$?
Results and Discussion

Amphoteric Behavior of Al$_2$O$_3$

- Maximum value in thermal conductivity with Al$_2$O$_3$ addition
- Change in the role of Al$_2$O$_3$ between network former and network modifier

**Dependence of thermal conductivity on Al$_2$O$_3$ content at constant CaO/SiO$_2$ ratios**
Silicate Structure and Temperature

• Debye’s expression for thermal conductivity

\[ \lambda = \frac{C_v l}{3} \]

- \( C_v \): heat capacity
- \( v \): sound velocity
- \( l \): phonon mean free path

in crystalline materials

\[ l \propto \frac{1}{T}, \quad \lambda \propto \frac{1}{T} \]

Reciprocal Absolute Temperature (K\(^{-1}\))

Thermal Conductivity (W/mK)
Results and Discussion

Silicate Structure and Temperature

\[ \lambda \propto \frac{1}{T} \]

Dependence of thermal conductivity of 30\%CaO-18\%Al_2O_3-52\%SiO_2 on the inverse absolute temperature.

change in silicate structure
Results and Discussion

Silicate Structure and Temperature

IR transmittance of 30%CaO-18%Al₂O₃-52%SiO₂
Silicate Structure and Temperature

Results and Discussion

- Bond breakage depends the bonding energy
- A broken bond divides the interaction volume

$\lambda \propto \exp\left(\frac{1}{T}\right)$
Results and Discussion

Silicate Structure and Temperature

Dependence of logarithm of thermal conductivity of 30%CaO-18%Al₂O₃-52%SiO₂ on the reciprocal absolute temperature
Conclusions

• The thermal conductivity of the Na$_2$O-SiO$_2$ and CaO-Al$_2$O$_3$-SiO$_2$ system was measured by hot-wire method in their pure liquid region.

• The thermal conductivity decrease in more basic silicate, and as temperature rises. And amphoteric behavior of Al$_2$O$_3$ was observed in the ternary system.

• Temperature dependence deviates from the linearity at higher temperature than liquidus temperature. The change in silicate structure may cause this disagreement.