Polarization curves were obtained by using nickel electrodes in a flowing molten mixture of potassium nitrate, sodium nitrate and sodium nitrite (HTS) under transverse magnetic field or under potentiostatically imposed potential without magnetic field. It is found that the relation between the electro-magnetically induced potential and current is almost the same as that between the potentiostatically imposed potential and current. Such a relation, i.e. the polarization curve, seems to be independent of the flow velocity and to be dependent on the temperature. This view is supported by the cyclic voltammetry which was carried out by using the same electrodes and the molten-salt flow under the same temperature.

1 Introduction
In an effort to enhance the usefulness of molten salt for the blanket of fusion reactors, we noticed in the previous paper that the induced potential was observed in the molten-salt flow which crossed the magnetic field. Such an induced potential may accelerate corrosion of the conduit in which the molten salt flows. Although the conducting carrier in molten salt, i.e. ion, is quite different from that in liquid metal, i.e. electron, the current due to the transport of ion or electron gives no change of composition in the bulk molten salt or liquid metal. However, the charge transfer is inevitably accompanied with an electrode reaction at the interface between the metal wall and the molten salt while the electronic charge transfer is not accompanied with electrode reaction at the interface between the liquid metal and the metal wall. It follows from such an electrode reaction that some substances might transfer. It is the purpose of this work to measure the rate of electrode process by the induced potential and to investigate whether such electromagnetically induced potentials have the same effect on the rate of the electrode reaction as potentiostatically imposed potentials or not. The magnetic fields produce only the electromagnetically induced potential and do not give rise to special kinetic effects such as a mechanochemical effect on a ferromagnetic electrode.

2 Experimental
2.1 Forced convection loop
The same molten-salt loop as we used in the previous work was used again but its test section was replaced by that for electrochemical measurements as shown in Fig. 1.

2.2 Test section
The test section was composed of a casing and a test tube which was made of Pyrex glass as shown in Fig. 2. The polarization conductance between molten nitrates and nickel was reported by Nishikata et al., which showed the order of $10^{-2} \Omega^{-1} \text{m}^{-2}$. Having considered the dimensions of the loop and the conductivity of the molten salt, such a small value could be regarded as a conductivity low enough to neglect the effect of conductive wall. Based on this point of view, the metal pipe at the test section was replaced by a pipe made of Pyrex glass, which was good insulator at the operating temperature. The metal electrode was inserted into the molten salt through the glass wall. If a metal pipe instead of the glass pipe were used it would be necessary to...
joint the insulator with metals at both sides, which is more complicated than the jointing of the metal with glass pipe. The connecting leads of the electrodes were made of tungsten and were jointed with electrodes such as silver or nickel electrodes, the junctions of which were completely covered with uranium glass because the linear expansion coefficient being $5.5 \times 10^{-6}$ deg.$^{-1}$ for tungsten$^{31}$ was almost the same as that being $4.0 \times 10^{-6}$ deg.$^{-1}$ for Uranium glass$^{32}$. Such a sealing was very valuable for preventing the direct contact of molten salt with the junctions. A nickel wire with a diameter of 0.125 mm was stretched between each pair of nickel electrodes along the wall. These wires increased the area of electrodes without disturbing the flow and the potential distribution and at the same time they made output fluctuation due to turbulence average. Both ends of the glass pipe were supported and sealed by two pairs of o-rings made of silicon rubber, thus, the allowable upper limit of the operating temperature was set at 523 K. Cables for the current and the potential-readout were connected by pressing with the tungsten leads. The pipe was set in a parallelepiped casing made of SUS 304 to protect the pipe against the stress from the main loop at both sides and moreover the casing was also effective when the pipe was accidentally broken. The casing was equipped with a pair of viewers, which enabled us to observe the flowing molten salt directly.

2.3 Instrumentation

Electrical measurement was carried out by using the measuring setup as shown in Fig. 3. Two same potentiostats (Hokuto Denko Ltd., HA-301) were used, one of which was used as an electrometer. A strip-chart recorder with six channels (Rikadenki Co., Ltd., KB-681-L) was used to record the outputs from both potentiostats, temperature of the salt, flow rate and exciting current for the electromagnet simultaneously.

The potentiostatic measurements were achieved as follows: When the double-throw switch $S_1$ was closed and the switch $S_2$ was kept open, we could obtain the current which flew through the nickel electrodes, the potential difference between the nickel electrode which was connected with terminal W, working electrode, and the silver electrode R which was used as a
reference one and that between the two nickel electrodes simultaneously.

On the other hand, electromagnetically induced potentials and currents were measured as follows: The potentiostat and the silver electrode was cut off by opening the switch S₁. When the potential was measured, the switch S₁ was kept open and then the magnetic field was imposed intermittently. When the current was measured, the switch S₂ was closed and then the magnetic field was imposed intermittently.

A potential difference caused by the current appeared between the terminals of the resistor R₁. R₁ was chosen so as to generate much smaller potential difference than that induced when the S₁ was open and, at the same time, was chosen so as to record it without the interference by noise, i.e. the value of small potential difference was large enough as compared with that of noise. In practice it was chosen as large as 330 Ω and 2 kΩ eventually.

2.4 Salt

The salt used in this work was a ternary mixture of nitrates and a nitrite (49 mol % NaNO₂, 44 mol % KNO₃, and 7 mol % NaNO₃) which was generally known as a heat transfer medium HTS. It was prepared from reagent-grade salts. Many kinds of chemical analysis was used for checking the impurity in molten salt before melting and during experiment. Sampling of the salt was achieved by using an evacuated glass bottle with a breakable seal. Table 1 shows the results of impurity analysis. The following six elements, Fe, Ni, Cr, Mo, W and Pt were selected since the former five elements were the constituent elements of SUS 316 and Pt was a lining material. Moisture was supposed to be removed by purified argon bubbling for half a day though it could not be determined quantitatively.

3 Results and Discussion

Two types of experiments, such as a cyclic voltammetry and polarization measurement, have been carried out by using the cell system shown in Fig. 3. The cyclic voltammetry was also used to pursue the behaviour of the individual nickel electrodes under the present condition. The nickel electrode 1, the other nickel ones and the silver one were used as a working electrode, counter ones and a reference one, respectively. Although several kinds of reference electrodes for molten salts have been proposed, the simple silver one was preferable to our loop because of is long life and simplicity. The same operating conditions as subsequent experiment, i.e. two levels of temperature at 477 K and 505 K and two levels of the mean flow velocity of 1.5 m s⁻¹ and 2.1 m s⁻¹ were chosen. Under these conditions, the Reynolds number of this molten salt flow could be calculated from published physicochemical constants as 1.4×10⁴ ~ 2.5×10⁴, indicating that the molten salt flows as a turbulent flow. The obtained cyclic voltammograms, which cover a much wider range of voltage, i.e. 500 mV, than the coverage of the subsequent experiment, i.e. 100 mV, are shown in Fig. 4. Each trace seems to consist of an anodic plateau and a cathodic slope, which may correspond to those around the zero current axis reported by

Table 1 Impurity contents in the test salt used for the operation in the loop

<table>
<thead>
<tr>
<th>Element</th>
<th>Content/ppm 10⁶</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>3</td>
<td>Oxine extraction photometry</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.5</td>
<td>Dimethylglyoxime extraction</td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td>photometry</td>
</tr>
<tr>
<td>Cr</td>
<td>1</td>
<td>2-methoxyazine extraction</td>
</tr>
<tr>
<td>Mo</td>
<td>3</td>
<td>Oxine extraction photometry</td>
</tr>
<tr>
<td>W</td>
<td>&lt;3</td>
<td>Oxine extraction photometry</td>
</tr>
<tr>
<td>Pt</td>
<td>&lt;5</td>
<td>Iodometry</td>
</tr>
</tbody>
</table>

Fig. 4 Cyclic voltammograms of nickel electrodes in the flowing molten HTS, where the traces are plotted by regarding the temperature of the salt T and the mean flow velocity V(α) as their parameters.
Zambonin and Jordan. According to their polarographic study in a molten mixture of sodium and potassium nitrate, the above-mentioned anodic plateau can be explained by the limiting current which is governed by the rate of the following charge-transfer reaction at the anode:

\[ \text{O}_3^2- \rightarrow \text{O}_2^- + e, \]  

(1)

and similarly the cathodic slope is considered to be due to both reaction (1) and its reverse one:

\[ e + \text{O}_3^- \rightarrow \text{O}_3^2-. \]  

(2)

The peroxide and superoxide ion which appear in both reactions are equilibrated by the following reaction in the melt:

\[ 2 \text{NO}_3^- + \text{O}_2^2- \rightleftharpoons 2 \text{NO}_2^- + 2 \text{O}_3^- \]  

(3)

If the reaction (1) and (2) are applicable to our present experiment, the reaction rate in consideration is determined by the charge-transfer process. This view is also supported by the cyclic voltammograms obtained by Miles et al.

In the subsequent experiment, two types of electromotive forces (emf) were applied to the nickel electrode pair in Fig. 3, one was that potentiostatically supplied by the external circuit, i.e. the potentiostat, and the other was the electromagnetically induced one in the molten salt flow. The magnitude of which can be determined by measuring the open circuit voltage between both nickel electrodes. Obtained potential-current curves are shown in Fig. 5, where the current through both nickel electrodes \( I_n \) was taken as the anodic current of the nickel electrode 1 in positive direction. These curves are somewhat scattered but seem to be symmetric with respect to the origin. This symmetry will be explained as follows: When the ir-drop is negligible as in the present experiment, the potential difference \( \phi_{12}(I_a) \) between both nickel electrodes can be described as a function of the anodic current \( I_a \) and cathodic one \( I_c \) for each electrode:

\[ \phi_{12}(I_a) = \phi_1(I_a) - \phi_2(I_c) \text{ for } I_a = I_c \geq 0, \]

\[ = \phi_1(I_c) - \phi_2(I_a) \text{ for } I_a = I_c < 0, \]  

(4)

where \( \phi_1(I) \) and \( \phi_2(I) \) denote the potential for the electrode 1 and that for the electrode 2 with reference to a common reference electrode, respectively and the relationship, \( I_a = -I_c \), is naturally given by Kirchhoff’s current law. If the function \( \phi_1(I) \) is identical to \( \phi_2(I) \) in the equation (4), the potential-current curves corresponding to \( \phi_{12}(I) \) are naturally symmetric with respect to the origin and such equality can be practically kept as far as both electrodes are equally made and both their arrangement and the molten salt flow are axisymmetric. The symmetry of the observed potential-current curves should be attributed to such equality of the electrodes. Other two important facts are shown in Fig. 5, one is that a strong dependence of the current \( I_n \) on the temperature of the molten salt and a weak dependence of the current on the mean flow velocity became evident and the other is that no difference between the current due to potentiostatically applied potentials without magnetic field and that due to electromagnetically induced ones was observed. Both dependencies of the current \( I_n \) had...
been also seen in the narrow range of the cyclic voltammograms obtained by the previous experiment as shown in Fig. 4. Especially the weak dependence of the current on the mean flow velocity should be attributed to that at the anodic plateau shown in Fig. 4 because the circulating current $I_a$ in the closed circuit is mainly controlled by the large resistance, i.e. the anodic plateau. The latter result that the current $I_a$ flowed owing to both $emf$'s without difference suggests that the applied magnetic field, the magnitude of which was 0.72 T at the maximum, gives little additional effects, e.g. mechanochemical ones on the ferromagnetic electrodes, other than the effect of $emf$. This result enables us to investigate a corrosion process of this kind by using a voltage generator externally connected with the test cell in place of the magnetic field, indicating the effectiveness of application of Kelly's experiment\(^{12}\) for aqueous solutions to that for molten salts.

4 Concluding Remarks

A test section made of pyrex glass with silver electrodes and those made from a nickel wire has been designed and is used. By using this section polarization curves were obtained under two kinds of electromotive forces. One of them is electromagnetic induction caused by the flowing molten salt in the magnetic field and the other is the externally applied potential by a potentiostat.

It is shown that, in both cases, the obtained results under induced potential are comparable with those under the externally applied potential. Accordingly the study of corrosion in the molten-salt flow under magnetic field can be substituted by a potentiostatic measurement without magnetic field. In addition, we obtained the result that the polarization curve depends not on the flow rate but on the temperature under the condition of present work.

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References:


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