Mechanism of Oxygen Ion Transfer in Oxide Melts Based on V\textsubscript{2}O\textsubscript{5}

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Abstract—A model of oxygen ion transport in molten V\textsubscript{2}O\textsubscript{5} is proposed. Within the framework of this model, the values of the parabolic rate constant of the catastrophic oxidation of copper in contact with V\textsubscript{2}O\textsubscript{5} and oxygen flux through an ion transport membrane with liquid-channel grain-boundary structure on the basis of V\textsubscript{2}O\textsubscript{5} are calculated as $k'' = 2.4 \times 10^{-5}$ kg\textsuperscript{2}/(m\textsuperscript{4} s) and $J = 2.7 \times 10^{-4}$ mol/(m\textsuperscript{2} s) at 700°C. These values are in agreement with the experimental data in order of magnitude, indicating the agreement between theory and experiment.

Keywords: oxide melts based on V\textsubscript{2}O\textsubscript{5}, oxygen ions, transport mechanism.

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INTRODUCTION

Some metals and alloys in contact with low-melting V\textsubscript{2}O\textsubscript{5} oxide are susceptible to accelerated oxidation. This phenomenon is called the catastrophic oxidation of metals (COM) [1–8]. It is known that COM is caused by the formation of transverse liquid channels in oxide layers that conduct oxygen ions [7–9]. The literature also reports high conductivity of oxygen ions in molten vanadium slags [10] and in ion transport membranes (ITM) with liquid-channel grain-boundary structure (LGBS) based on molten V\textsubscript{2}O\textsubscript{5} [11–14]. Since slags and COM play an important role in the steel industry [15, 16], and the same is true for ITM in the electrochemical power sources [17] and chemical engineering [18, 19], understanding the oxygen ion transport in oxide melts is very important.

In this work, we propose a model of oxygen ion transport in molten V\textsubscript{2}O\textsubscript{5}. Using this model, we calculate the values of the parabolic rate constant for COM and oxygen flux through an ITM. Our results are compared to experimental findings.

EXPERIMENTAL

COM Kinetics

The catastrophic oxidation of copper in contact with V\textsubscript{2}O\textsubscript{5} was studied in [9]. Figure 1 shows the kinetic curves of oxidation of copper plates preliminarily coated with layers of V\textsubscript{2}O\textsubscript{5} powder of different weights at 800°C in air. The coated copper is catastrophically oxidized at 560°C (the temperature of liquid eutectic). The rate of copper oxidation increases along with the specific weight of the coating.

The dependence of the oxygen flux through partially molten V\textsubscript{2}O\textsubscript{5}–(12–18) wt % CuV\textsubscript{2}O\textsubscript{6} composites simulating an oxide layer formed on the copper surface during COM on the volume fraction of the liquid is presented in Fig. 2. The oxygen flux increases along with the volume fraction of the liquid.

The catastrophic oxidation of copper is described by a parabolic rate law [7–9]

$$\left( \frac{m}{s} \right)^2 = k'' t,$$

where $k''$ is the rate constant. The experimental values of the parabolic rate constant are shown in Table 1.

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>Uncoated</th>
<th>Coated</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>$1.0 \times 10^{-7}$</td>
<td>$4.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>700</td>
<td>$2.9 \times 10^{-7}$</td>
<td>$4.1 \times 10^{-5}$</td>
</tr>
<tr>
<td>800</td>
<td>$1.0 \times 10^{-6}$</td>
<td></td>
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</table>
Mechanism of Oxygen Ion Conductivity. Some results from the measurements are presented in Figs. 3 and 4.

Structure of Oxide Melts Based on V₂O₅

The structures of V₂O₅ melts and some binary oxide systems based on it were studied via X-ray diffraction, neutron diffraction, electron diffraction, NMR, and other methods in [20–29]. It was found that the intramolecular coordination of the atoms during melting did not change significantly. There was a loss of long-range order, due to the relative displacement of structural elements. The multi-component oxide melts had strongly expressed microinhomogeneous structures, due to the resistance of the atom groups with the structure of congruent compounds existing in the state diagrams.

The structure of solid V₂O₅ (Fig. 5a) is formed from layers of distorted trigonal bipyramids formed by oxygen anions, and in the triangular base of these are cations of vanadium. The layers are interconnected by the oxygen anions farthest from the vanadium cations. The vanadium cations are in highly distorted oxygen octahedra. When V₂O₅ melts, the weakest V−O bonds evidently break with the formation of two-dimensional layers of oxygen bipyramids (quasimolecules).