The corrosion of molybdenum electrodes in an aluminosilicate melt was studied with the aid of electrochemical methods at temperatures up to 1600 °C. The glass melt investigated contained polyvalent ions which enabled redox reactions with the electrode material. A layer of molybdenum oxide is formed on the electrode in contact with the glass melt. The layer partially dissolves in the glass melt and eventually evaporates into the furnace atmosphere. Dissolution of the oxide layer is assumed to be the step which determines the rate of the corrosion process.

1. Introduction

The electric melting of glass is a technique with increasing importance for industrial applications. Today, molybdenum is the most commonly used electrode material. The most important problem associated with this material is the heavy corrosion in some glass melts. Over the last few years, efforts have been made to minimize the corrosion rate. One of these techniques is to superimpose a small DC potential on the AC heating voltage [1]. In this method, molybdenum electrodes are usually set on an anodic potential. Another technique is the “low-frequency passivation”, first developed in Czechoslovakia [2]. Here, the applied heating current has a frequency of 6 to 12 s⁻¹. Both techniques have already been applied to lead glass melts in Czechoslovakian industry. However, the possibility of applying the technique to other glass melt compositions, has rarely been investigated. This paper provides a study of the corrosion process of molybdenum electrodes in aluminosilicate melts using electrochemical methods.

2. Experimental

All experiments were carried out in an aluminosilicate glass melt, doped with ZnO, NiO, V₂O₅ and Sb₂O₅, the concentrations of which ranged from 0.05 to 1.5 wt.%. The corrosion experiments were carried out at temperatures up to 1600 °C. The pre-melted glass was placed in an alumina crucible, located in a large alumina muffle tube inside a MoSi₂-resistance heated furnace. Molybdenum rods (diameter: 5 mm) embedded in small alumina tubes were used for the corrosion experiments (for a more detailed description see [3]). Before the electrodes were inserted into the furnace and the glass melt, the large alumina muffle tube was rinsed with pure nitrogen to avoid the oxidation of molybdenum by oxygen in the furnace atmosphere.

For voltammetric experiments, a counter electrode (platinum plate with an area of approximately 2 cm²) and a zirconia/air reference electrode (for a detailed description see [4]) were also inserted into the glass melt. Slow voltammetric curves were recorded using a molybdenum rod as working electrode, while a platinum wire (diameter: 0.5 mm) was used as a working electrode when square-wave voltammograms were recorded. Slow potentiostatic curves were recorded with the aid of a potentiostat (Bank POS 73, G. Bank Elektronik GmbH, Göttingen (FRG)) and a scan generator; the scan rate was 5 mV/s. When square-wave voltammograms were recorded, the potentiostat was connected to a microcomputer (Apple II+, Apple Computer GmbH, München) via an analog/digital and a digital/analog converter. In the presence of polyvalent ions, square-wave voltammograms show definite peaks; the peak potentials are equal to the standard potential of the redox couple. For a detailed description of square-wave voltammetry see [5 to 8].
3. Results and discussion

Figure 1 shows a current-potential curve, recorded at a molybdenum working electrode at 1600 °C. The current was scanned slowly (5 mV/s) from a negative (−700 mV) to a positive value. At first the current increased very rapidly, then it reached a maximum at about −100 mV, slightly decreased and reached a minimum at a potential of about +150 mV, then increased again and reached a nearly constant value at about +1500 mV.

In other glasses, not reviewed here, the current decreased after reaching the maximum and became almost constant at 1/3 to 1/2 of the peak current [3, 9 and 10]. This was due to the formation of a protective layer which hindered the further dissolution of metallic molybdenum. In the aluminosilicate melt investigated here, the passivation effects are not as well pronounced. Unlike in lead glass melts, superimposing a small DC potential on the AC heating voltage does not seem to be a promising way of decreasing the corrosion rate.

Figure 2 shows square-wave voltammograms recorded in a potential region of 0 to −1400 mV at a platinum working electrode at 1600 °C. Prior to these measurements, an additional molybdenum electrode was inserted and polarized anodically at +1000 mV (versus ZrO₂/air). This procedure led to a heavy corrosion of the molybdenum electrode, and thus to a relatively high concentration of molybdenum oxide in the melt. Voltammograms were then recorded every 5 min. According to former experiments [6 to 8], polyvalent ions possess quite different standard potentials and hence peaks should appear at different potentials in the voltammograms. As large numbers of various polyvalent elements were present in the glass melt investigated, a superposition of many relatively broad peaks was observed.

By comparison with voltammetric studies in soda-lime-silica glass melts [6 to 8], three potential regions could be distinguished:

a) The peak at −150 mV is due to the reduction of Sb³⁺ to Sb⁰ ions.

b) The peak at −800 mV is related to the reduction of molybdenum oxide.

c) The increasing current at <−750 mV is due to the reduction of Zn²⁺ and V⁴⁺ ions.

The peak at −800 mV which is related to the reduction of molybdenum oxide, decreases with time. It can be assumed that this is due to the evaporation of molybdenum compounds from the glass melt.

Over the whole potential region the currents were relatively high. Thermodynamically, metallic molybdenum can be oxidized by various multivalent ions present in this glass melt, mainly by arsenic oxide and nickel oxide, which are reduced to the metallic state (see equations (1 to 4) with A ∋ As,Ni):

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\begin{align*}
\text{Mo}^0 & \rightarrow \text{Mo}^{3+} + 3\text{e}^-, & (1) \\
\text{Mo}^{3+} & \rightarrow \text{Mo}^{6+} + 3\text{e}^-, & (2) \\
\text{A}^2 + z\text{e}^- & \rightarrow \text{A}^0, & (3) \\
\text{Mo}^{0} + 6/z\text{A}^2 & \rightarrow \text{Mo}^{6+} + 6/z\text{A}^0. & (4)
\end{align*}
\]

In further experiments, molybdenum electrodes were corroded in the aluminosilicate melt. The experiments were carried out at temperatures of 1550 and 1590 °C. The electrodes remained in the glass melt for 1 to 20 h and were then removed and rapidly cooled to room temperature (≈ 5 min). The electrodes were then embedded in an organic polymer, cut perpendicular to the electrode surface and polished.
Corrosion of molybdenum electrodes in an aluminosilicate glass melt

Figures 3a and b. SEM micrographs of a molybdenum electrode in an aluminosilicate glass melt corroded a) 4 h at 1550 °C, b) 10 h at 1590 °C.

Figure 3a shows a SEM micrograph of a molybdenum electrode which was corroded for 4 h at a temperature of 1550 °C. Between the electrode (upper part) and the glass melt (dark) a well-separated layer with a thickness of about 8 µm could be observed. Energy Dispersive X-ray spectroscopy (EDX) and Wavelength Dispersive X-ray spectroscopy (WDX) point analyses proved the layer composed of molybdenum oxide. Within this layer, some spherical particles to be consisting of an antimony/nickel alloy, could be noticed. In all corrosion experiments, both molybdenum layers and metallic particles were observed, but the thickness of this layer was strongly influenced by the experimental conditions. At some electrodes, regions possessing quite different structures could be seen as shown by the SEM micrograph in figure 3b. At the electrode, an obviously strongly adhesive layer could be identified. This layer consists of an antimony/nickel alloy; the dark and light regions within this layer are due to different chemical compositions and can be shown by EDX to be due to high nickel and high antimony concentrations, respectively. The electrode shown in figure 3b was corroded for 10 h at 1590 °C, but fairly similar regions could also be observed when the experimental conditions were altered. Only in the upper part of figure 3b, a thin layer between the antimony/nickel alloy and the glass melt can be seen. This layer consists of molybdenum oxide. In some other SEM micrographs, particles consisting of an antimony/nickel alloy could be seen within the glass melt, which were completely loosen from the electrode surface.

The thickness of the surface layer as a function of the corrosion time at 1550 and 1590 °C is shown in figure 4. For both temperatures, the layer thickness increases with the corrosion time in a parabolic fashion. The upper curve was obtained from experiments carried out at 1550 °C. Surprisingly, the layer thickness was greater at lower temperature. As rate constants of chemical reactions almost always increase with increasing temperatures, due to positive activation energies, the quantity of oxidized metallic molybdenum must also increase with temperature. Thus, the thickness of the surface layer cannot be used as measure of the corrosion.

This behaviour can be explained by the dissolution of the molybdenum oxide layer in the glass melt. This process is controlled by the solubility of molybdenum oxide in the glass melt and by dissolution kinetics. If the dissolution rate increases with increasing temperature more strongly than the corrosion rate, the thickness of the layer will decrease with increasing temperature.

4. Conclusions

The presence of various polyvalent elements having different standard potentials leads to redox reactions with metallic molybdenum. At first, a layer of molybdenum oxide is formed at the electrode surface. Later, it is redissolved in the glass melt and finally evaporates into the furnace atmosphere. Some polyvalent elements, such as Sb³⁺ or Ni²⁺, are reduced to the metal. Since the thickness of the oxide layer decreases with increasing temperature, the dissolution of this layer is presumed to be the step which
determines the rate of the corrosion process. Anodic passivation does not seem to be a promising way to minimize the corrosion rate.

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5. References