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4. Electrochemical Study on the Corrosion of Molybdenum Electrodes in TV Glass Melts Containing Antimony

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The electrochemical corrosion of molybdenum electrodes in TV glass melts with the components of SiO_2-Al_2O_3-Na_2O-K_2O-SrO-BaO-ZrO_2 containing antimony ions was investigated at 1350 or 1450 . The corrosion rate of the molybdenum electrodes increased with increasing antimony concentration and temperature. When the alternating current (AC) of 50Hz was applied to the electrodes, the corrosion rate of the electrodes increased with increasing current density. Any corrosion of the electrodes could not be observed up to 1 A/cm^2 in the antimony-free glass melt. The corrosion rate of electrodes increased linearly with the antimony concentration in the glass melt. From these results it was suggested that the primary corrosion process was the oxidation of the molybdenum electrodes by antimony ions in the glass melt both with and without AC supply under our experimental conditions. The AC supply accelerated the corrosion of the electrodes by formation of molybdenum ions during the anodic polarization, followed by the reduction of antimony ions in the glass melt in preference to the molybdenum ions during the cathodic polarization.

1. Introduction

Molybdenum is commonly used as an electrode material for electrical melting and electrical heating in industrial glass making tanks because of its good chemical and mechanical durability in glass melts at high temperature. Polyvalent ions, which have more positive normal potentials than molybdenum, such as antimony, arsenic, lead or nickel, accelerate the corrosion of the molybdenum electrodes [1] [8]. It is also known that the AC supply induces the corrosion of molybdenum electrodes [5] [9]. As increase the current density, the corrosion of molybdenum electrodes increases. To reduce the corrosion of electrodes, cathodic or anodic polarization have been investigated by making protective layers on the electrode surfaces [10] [14]. For the needs of industry it is important to optimize the concentration of polyvalent ions and

electrical conditions of electrodes to achieve both the reduction of corrosion of the electrodes and good fining in the glass melt. In this study the influence of the antimony concentration, which is used as a fining agent, temperature and the alternating current density on the corrosion of electrodes in the TV glass melt were investigated.

2. Experimental

Figure 1 represents a schematic drawing of an apparatus for electrochemical experiments. In order to prevent the oxidation of the electrodes, the furnace was purged with nitrogen gas during the experiments. An alumina crucible was placed on the bottom of the furnace that could be rotated by an electric motor. The speed of alumina crucible was set to be 0.22cm sec^{-1} at the middle of electrodes. A molybdenum rod (purity: >examined.

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99.95%, diameter: 4.9mm, length: 30mm, PLANSEE) was connected with a platinum wire at the top of it and embedded in alumina tube except 10mm of the bottom end of it. The connected part was sealed with ceramic cement to prevent the oxidation of the electrode. The current density in the range of 0 2 A/cm² was supplied between the electrodes by a potentiostat (Husou Seisakusho Ltd., HECS9077). The basic glass composition was $72SiO_2$, $1Al_2O_3$, $9Na_2O$, $6K_2O$, $6SrO$, $5BaO$, $1ZrO_2$ (in mol%) modified by Sb_2O_3 in the range of 0 0.080 mol% (0 0.34 mass%). The commercial glass cullet was used for the glass containing 0.080 mol% of Sb_2O_3. The other glasses with 0 0.037 mol% of Sb_2O_3 were prepared from raw materials of reagent grade. The raw materials were melted at 1550 in a platinum-rhodium crucible and stirred with a platinum stirrer for homogenization. After the experiment, the electrodes were cut at the cross section and the diameter was estimated from the optical photograph of the cut out surface. An electron
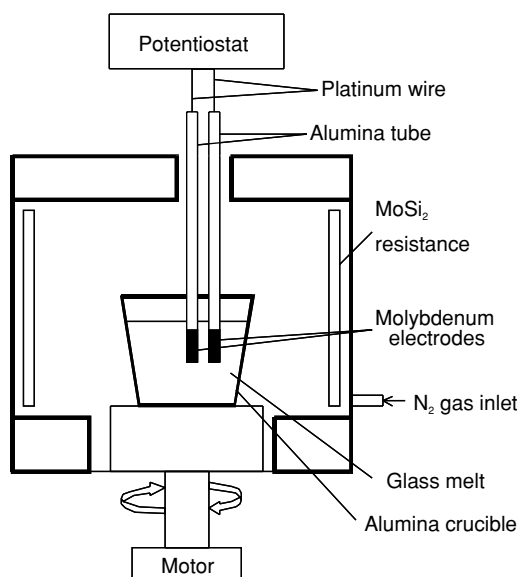

Fig. 1 Schematic drawing of an apparatus for electrochemical experiments of molybdenum electrodes in glass melts.

microprobe analyzer (EPMA, Shimadzu EPMA 1600) was used to observe the electrode/glass interface.

3. Results and Discussion

3.1 Corrosion without AC supply

The degree of corrosion were measured at 1350 or 1450 for 24h without AC supply with rotation of the crucible. The results are summarized in **Table 1**. The corrosion rate was calculated from the decrease in electrode diameter, the surface area of 4.9mm diameter of rod and the corrosion time (i.e. 24h). As shown in **Table 1** the degree of corrosion, i.e. the decrease in diameter of electrodes, was increased with increasing temperature and antimony concentration. The corrosion rate at 1450 was double of that at 1350 in the glass melt containing 0.080mol% of Sb_2O_3. **Figure 2** is the image of the BEM (backscatter electron micrograph) of molybdenum/glass interface after dipping the electrodes in the glass melt containing 0.080 mol% of Sb_2O_3 at 1450 for 24 h with rotation of the crucible. And the image of EPMA distribution of elements is shown in **Fig. 3**. Several phases are observed at the molybdenum/glass interface in **Fig. 2**. The main constituent of the brightest phase ((a) in **Fig. 2**) was antimony, and a small amount of oxygen was also detected. The dark phase, i.e. thin layers and particles around the molybdenum electrode surface ((b) in **Fig. 2**), could not be identified accurately. However, barium, molybdenum, oxygen and a small amount of antimony were detected by EPMA analysis. On the other hand, it was difficult to find any damage on the molybdenum surface after dipping in the antimony-free glass melt at 1450 for 24h with rotation of the crucible as shown in **Fig. 4**.

The BEM image of molybdenum/glass interface and concentration profiles of the molybdenum and antimony after dipping in the glass melt containing 0.080mol% (0.34 mass%) of Sb_2O_3 at 1450 for 3h

Table 1 The Degree of Corrosion of Molybdenum Electrodes in Glass Melts at 1350°C or 1450°C for 24h without AC Supply and with Rotation of the Crucible.

Sb_2O_3	Temperature	Time	Diameter of Mo (initial)	Diameter of Mo (after corrosion)	Corrosion rate
mol %	°C	h	mm	mm	mg cm^{-2} h^{-1}
0.080	1350	24	4.9	4.8	2.3
0	1450	24	4.9	4.9	
0.037	1450	24	4.9	4.8	2.3
0.080	1450	24	4.9	4.7	4.6

without rotation of crucible are demonstrated in **Fig. 5** and **Fig. 6**, respectively. Less than 1.5 mass% Sb_2O_3 was detected inside the electrode up to $20\mu m$ from the surface. And the diffusion of molybdenum into glass phase was observed over the range of 80 μm from the molybdenum surface. Most antimony ions are in the trivalent state in TV-glass melts melted at 1550 [15], [16]. Therefore, the redox reaction of molybdenum electrode with antimony ions in the glass melt is described by the following equation.

$$Mo + n/3\,Sb^{3+} \qquad Mo^{n+} + n/3\,Sb^0 \qquad (1)$$

The free energy change of eq. (1) is negative, therefore, the equilibrium shift to the right side resulted in the formation of molybdenum ions (Mo^n), such as Mo^3, Mo^4, Mo^5 and Mo^6, and metallic antimony (Sb^0) at the electrode/glass interface[1] [14]. In the binary system of molybdenum and antimony, the only stable phase is Mo_3Sb_7[17], [18].

Fig. 4   **BEM image of molybdenum/glass interface after dipping in the glass melt without Sb₂O₃ at 1450°C for 24h with rotation of the crucible.**
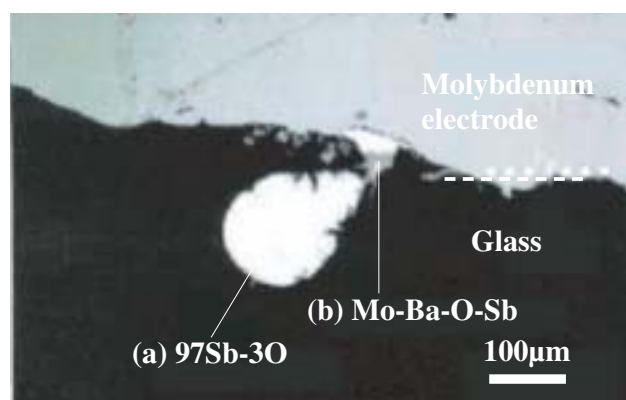

Fig. 2   **BEM image of molybdenum/glass interface after dipping in the glass melt containing 0.080mol% of Sb₂O₃ at 1450°C for 24h with rotation of the crucible.**
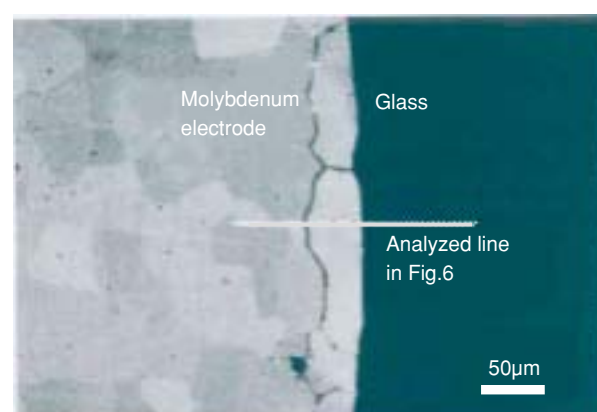

Fig. 5   **BEM image of molybdenum/glass interface after dipping in the glass melt containing 0.08mol% of Sb₂O₃ at 1450°C for 3h without rotation of the crucible.**
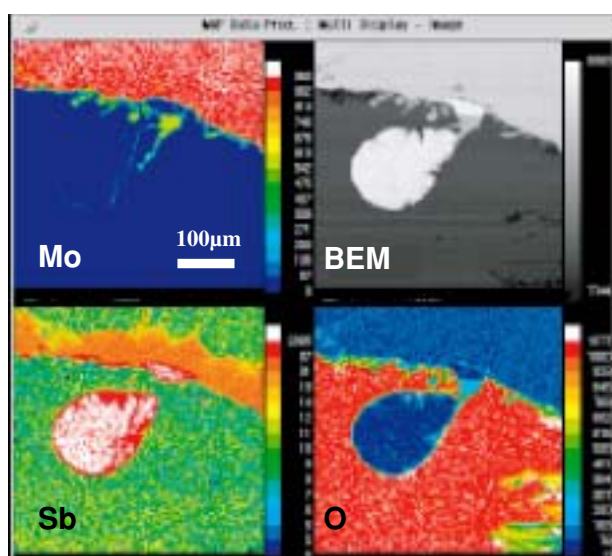

Fig. 3   **Image of EPMA distribution of elements at molybdenum/glass interface after dipping in the glass melt containing 0.080mol% of Sb₂O₃ at 1450°C for 24h with rotation of the crucible.**
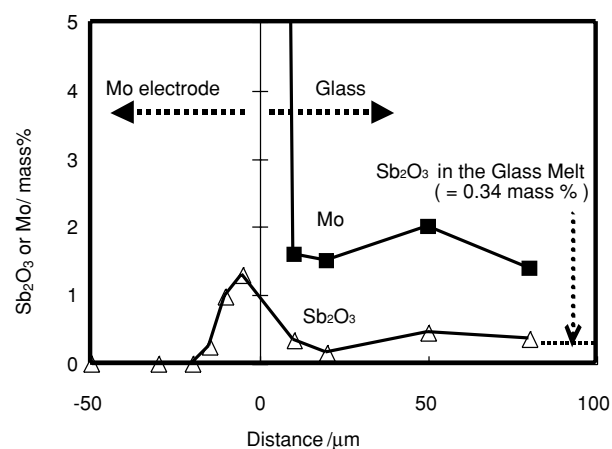

Fig. 6   **Concentration profiles of Mo and Sb₂O₃ at the molybdenum/glass Interface (Analyzed line was shown in Fig.5) after dipping the molybdenum electrodes in the glass melt containing 0.080mol% (0.34 mass%) of Sb₂O₃ at 1450°C for 3h without rotation of the crucible.**

This Mo_3Sb_7 phase melts and decomposes at approximately 780 . From **Fig. 6** up to 1.5 mass% of Sb^0 seems to be soluble in the molybdenum electrode at 1450 . The solubility of Sb^0 in the TV glass melt wasn't identified in this study. However, it can be assumed that the content of Sb^0 in the glass melt becomes progressively larger as the examination and finally exceeds the solubility, which results in the precipitation of Sb^0 particles in liquid at the electrode/glass interface (see **Fig. 2**). On the other hand the molybdenum ions generated at the electrode/glass interface moved away from the electrode surface and remain as the ionic state in the glass melt.

3.2 Corrosion with AC supply

The change of the molybdenum electrodes diameter for different current densities after dipping in the glass melts with various antimony concentrations were shown in **Fig. 7**. Here, the experimental conditions, such as temperature, time and AC frequency, are kept constant (1450 , 24h, 50Hz). As shown in **Fig. 7** the diameter of the electrode decreased with increasing current density and antimony concentration. The degree of corrosion of electrodes under the fixed current density of $0.53A/cm^2$ for various Sb_2O_3 concentrations (0 to 0.080 mol%) can be estimated from **Fig. 7**. And the corrosion rate was calculated from the decrease in the diameter, the surface area of 4.9mm diameter of rod and corrosion time (i.e. 24h). The results were summarized in **Table 2** and the dependence of the corrosion rate on the antimony concentration was plotted in **Fig. 8**. The corrosion rate of the electrode increased linearly with the Sb_2O_3 concentration both with and without AC supply. It was assumed that there were enough amounts of antimony ions in the glass melts to reduce the molybdenum electrode for all experimental conditions as shown in **Table 2**. It may be concluded that the corrosion process of molybdenum electrodes is controlled by the redox reaction with antimony ions in the glass melts. Moreover, the linear relationship between the antimony concentration and the corrosion rate indicates that the molybdenum electrode is oxidized to Mo^{3+}, which can be oxidized to higher valence state (such as Mo^{4+}, Mo^{5+} and Mo^{6+}), by Sb^{3+} at electrode/glass interface. This first reaction stage at electrode/glass interface can be described by the following equation (2).

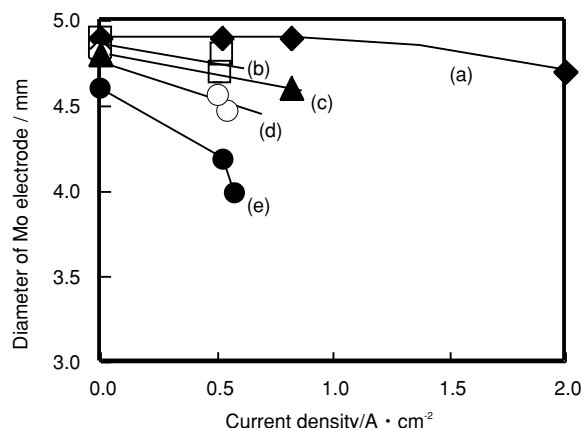$$Mo^0 + Sb^{3+} \quad Mo^{3+} + Sb^0 \quad (2)$$

Fig. 7 Change of the diameter of molybdenum electrodes as a function of current density after dipping in TV glass melt with various antimony concentrations (a) Sb_2O_3=0 mol% ( ), (b) 0.019 ( ) , (c) 0.031 ( ), (d) 0.037( ), (e) 0.080( ) at 1450°C for 24h with rotation of the crucible.
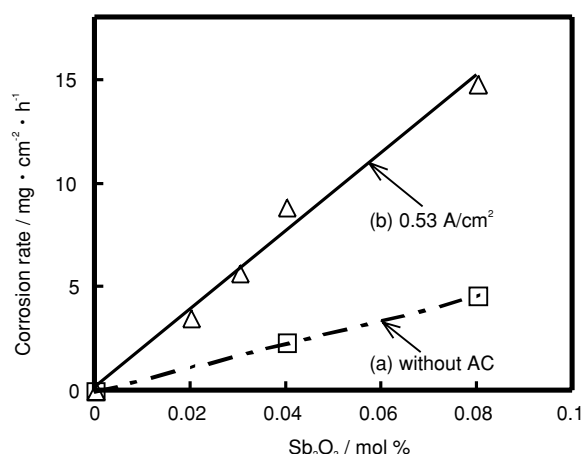

Fig. 8 Dependence of corrosion rate of molybdenum electrode on the antimony concentration in the TV glass melt at 1450°C for 24h (a) without AC supply or (b) with current density of $0.53A/cm^2$.

3.3 Corrosion mechanism

A schematic drawing of corrosion mechanism is demonstrated in **Fig. 9 (a)** and **Fig. 9 (b)**. It is known that the normal electrode potential of molybdenum is much lower than that of antimony[1], [2], [5]. Therefore, molybdenum electrodes can be oxidized easily by antimony ions in glass melts. As described above the metallic antimony particles were observed around the electrodes after dipping in the glass melt containing antimony ions (**Fig. 2**) and the dissolved molybdenum ions were detected in the molybdenum/glass interface over the range of 80μm from the electrode surface (**Fig. 6**).

Table 2   Conditions and Results of Corrosion Test in TV Glass Melts at 1450°C for 24h with the Current Density of 0.53A/cm^2 and with Rotation of the Crucible.

Sb$_2$O$_3$	Sb$_2$O$_3$	Temperature	Time	AC supply	Mo diameter (initial)	Mo diameter* (after corrosion)	Mo dissolved in glass** (after corrosion)	Corrosion rate*
mol %	mass%	°C	h	A/cm^2	mm	mm	mol%	mg cm^{-2} h^{-1}
0	0	1450	24	0.53	4.9	4.9		
0.019	0.080	1450	24	0.53	4.9	4.8	0.014	3.5
0.031	0.13	1450	24	0.53	4.9	4.7	0.022	5.7
0.037	0.16	1450	24	0.53	4.9	4.5	0.035	8.9
0.080	0.34	1450	24	0.53	4.9	4.2	0.058	15

* Estimated from Fig.7

** Calculated from the decrease in Mo electrode diameter and weight of glass (i.e.,750g)

Additionally the linear relationship between the corrosion rate of electrodes and the antimony concentration in the glass melt was observed (**Fig. 8**). These results indicate that the main reason of corrosion is the oxidation of molybdenum electrode by antimony ions in glass melts (**Fig. 9 (a)**). The influence of AC supply is shown in **Fig. 9 (b)**. When the AC voltage is applied to the electrodes, molybdenum electrode is oxidized to the ionic state during anodic part of the AC cycle. The molybdenum ions generated during the anodic polarization are reduced again to the metallic state during the cathodic polarization in antimony-free glass melt. On the contrary if antimony ions exist in the glass melt, these antimony ions are reduced to the metallic state in preference to molybdenum ions during cathodic polarization, which lead to the acceleration of the corrosion of electrodes.

4. Conclusions

The corrosion mechanism of the molybdenum electrodes in the TV glass melt composed of SiO$_2$-Al$_2$O$_3$-Na$_2$O-K$_2$O-SrO-BaO both with and without Sb$_2$O$_3$ was investigated by the electrochemical experiments. The corrosion rate of electrodes was proportional to the antimony concentration in the glass melts both with and without AC supply. It was elucidated that the dominant factor of corrosion was the redox reaction of the molybdenum electrodes with antimony ions in glass melts. The AC supply accelerated the corrosion by the formation of the molybdenum ions during anodic polarization, followed by the reduction of antimony ions in preference to the molybdenum ions during the cathodic polarization.
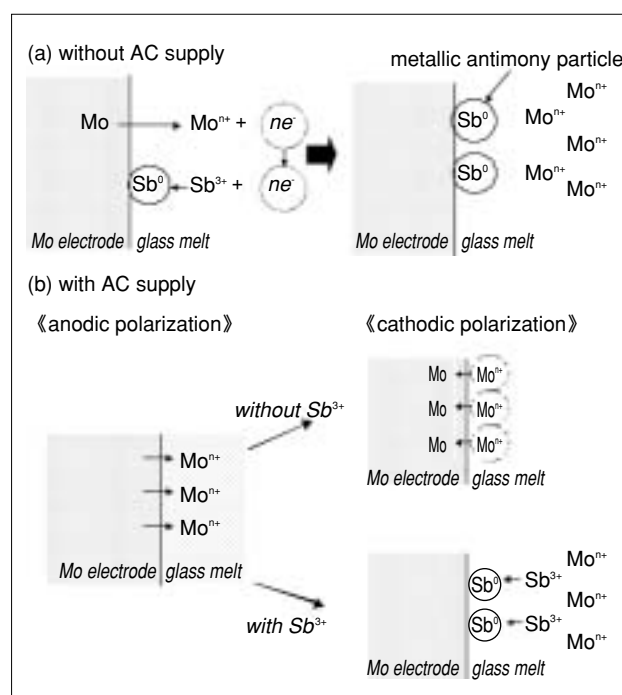

Fig. 9 Corrosion mechanism of molybdenum electrodes in glass melts (a) without AC supply or (b) with AC supply.

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