THE MECHANISM OF DISSOLUTION OF MOLYBDENUM IN GLASS MELT AND THE EFFECT OF ALTERNATING CURRENT

JIŘÍ MATĚJ, EVA KRUPKOVÁ, VÁCLAV HULÍNSKÝ*

Laboratory of Inorganic Materials Joint workplace of the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic and the Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague, Czech Republic E-mail: Jiri.Matej@vscht.cz

> *Department of Glass and Ceramics, Institute of Chemical Technology, Prague Technická 5, 166 28 Prague, Czech Republic

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The molybdenum corrosion and lead precipitation rates together with the overall electrode current were investigated in terms of the potential of the molybdenum electrode in three glass melts. Two of them contained 24 wt.% lead oxide, one of them containing also a small addition of arsenic oxide, and the third glass melt was free from lead oxide. The comparison of the rate of precipitating lead, of the corrosion rate and of the total electrode current in the melt free from arsenic oxide showed that molybdenum is for the most part transferred into the glass melt in the form of Mo(VI) even at potentials substantially more negative than the rest corrosion potential. The stationary polarization curves obtained for all the three glass melts exhibited courses typical of passivation. In the case of melts containing lead oxide the passivation already set in at the rest corrosion and lead precipitation rate in various glass melts in both directions. The accelerating effect always occurs in parallel with reduction of the mean electrode potential and vice versa. The effect of the electrode potential, of the alternating current and of the content of alkalies on the corrosion rate in the glass melts, can be explained by affecting the presence or layer thickness of molybdenum dioxide on the electrode.

INTRODUCTION

The behaviour of molybdenum as the most important material of electrodes used in electric melting of glass has been dealt with quite extensively in the literature. Descriptions have been presented in particular of the decisive role of corrosion depolarizers [1] and of the significant part played by alternating current which can both accelerate and slow down the corrosion processes [2]. However, no integral description of the phenomena involved in the transfer of the metallic material into the glass melt has so far been published.

Study of the mechanism of transfer of molybdenum into solution can be facilitated by investigating the behaviour of molybdenum in glass melts with a high content of lead oxide. The system allows the degree of corrosion of molybdenum to be determined as well as the amount of reacted depolarizer to be established. Rudolph et al. [3] have come to the conclusion that Mo^{3+} constitutes a transient oxidation degree of molybdenum. MoO_2 was determined by X-ray analysis in the layer of reaction products on an electrode in active state. The share of MoO_2 increases when antimony oxide has been added to the glass melt. Molybdenum is dissolved as Mo (VI). In contrast to this, the ratio of the amount of separated lead to that of dissolved molybdenum is indicative of a lower oxidation degree of Mo than 6. In the passive state, the main reaction product is the compound $K_2Pb(MoO_4)_2$, which is a liquid under the working conditions. A layer of reaction products containing molybdenum, lead, potassium, a small amount of sodium and oxygen whose composition corresponded to an oxidation degree of molybdenum lower than 6 was also found in a previous laboratory study [4] of the layers of reaction products on a molybdenum electrode in lead glass melt. No concentration gradients of lead nor molybdenum were determined in the layer. At a potential increased by 500 mV a layer corresponding to MoO₂ by its composition began to form. The corrosion rate and the amount of precipitated lead were further studied in terms of the electrode potential [5]. At the same time, the values of the overall (external) current required for maintaining the required potential, from which the stationary polarization curve was derived, were determined. Within the framework of this study, a distinct maximum of corrosion rate and lead seaparation was established at a potential more negative by about 200 -300 mV than the rest corrosion potential (cf. figure 2).

The rates of corrosion and of lead precipitation were decreasing in the direction towards more positive potential values. At potentials more negative by about 400 mV than the rest corrosion potential, both the corrosion rate and that of lead precipitation were found to decrease considerably. Further reduction of potential resulted in an increase in lead precipitation. A comparison of the amount of separated lead and that of dissolved molybdenum was indicative of a molybdenum oxidation degree lower than 6.

The studies [4 and 5] referred to above were carried out on 24 wt.% lead crystal refined with 0.2 wt.% arsenic oxide. It could have been expected that at the considerable excess of lead oxide as depolarizer the behaviour of the electrode will not be affected by the presence of small amount of arsenic oxide. However, a comparison of the corrosion behaviour in glass melts containing 24 wt.% PbO and various amounts of arsenic oxide showed that even small additions of arsenic oxide suppressed significantly both the corrosion rate and the amount of separated lead [6]. Alternating current interferes with this effect, as has also been confirmed by study [5]. The separated lead was found to contain several weigh percent of As.

Study [5] also dealt with a discussion of the possible effect of alternating current on the corrosion of molybdenum in the glass melt. It was concluded that a significant share of the alternating current is probably transmitted by a reversible reaction between the layer of reaction products and the alkali ions.

The present study had the aim to compare the behaviour of molybdenum at various potentials established in [5] with the behaviour in a glass melt with the same content of lead oxide but free from arsenic oxide, and also with that in a simple model glass melt free from lead oxide, and in this way to contribute to the explanation of the corrosion mechanism under various conditions. Another aim was to contribute to the explanation of influencing the molybdenum corrosion processes by alternating current.

EXPERIMENTAL

The compositions of the glass melts employed are listed in table 1. The arrangement used in measuring the precipitation of lead and the corrosion at various potentials in lead glass melts was described in [5]. The potential of the working electrode was maintained by a potentiostat at the required value with respect to the Pt reference electrode. The required current was supplied to the glass melt by means of an auxiliary molybdenum electrode. Mean values of this current comparable with the currents calculated from mean corrosion and lead precipitation rates also yielded the "stationary" polarisation curves. The measurements at a given potential under simultaneous loading by alternating current were essentially carried out in the same way. A couple of identical electrodes with an overhang of 2 cm and an area of 0.765 cm² were supplied with alternating current. At the same time, direct current was supplied from a controlled source, and maintained at a value suitable for attaining the chosen potential with respect to the reference electrode (figure 1).



Figure 1. Introduction of direct current and measurement of mean electrode potential (drawn in only for W2 electrode) under a.c. conditions. ACS - adjustable alternating current source; DCS - adjustable direct current source; DV - digital voltmetr; W1, W2 - working electrodes; R - reference electrode; A - auxiliary electrode.

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glass content (wt.%)											
	SiO ₂	B_2O_3	Al_2O_3	CaO	PbO	BaO	ZnO	K ₂ O	Na ₂ O	As_2O_3	Sb_2O_3
В	58.78	-	-	-	25.27	-	1.50	12.06	1.75	0.20	-
NCS-Sb	73.35	-	-	9.91	-	-	-	-	15.86	-	0.88
Neutrál	70.2	7.0	7.5	1.8	-	3.0	-	1.0	9.5	0.02	-

The extent of corrosion in both glass melts was determined as the loss of electrode diameter on transverse sections. In the case of the lead glass melt, use was made of sections cut through the crucible containing the embedded electrodes. The lead precipitated at the crucible bottom was mechanically separated and weighed when the rests of the glass have been removed by etching. The much smaller corrosion losses in the soda-lime-silicate melt were measured on electrodes removed from the crucible jointly with a layer of glass. After casting in epoxy resin and cutting the specimens were lapped with fine emery paper and measured while immersed in water. Some of the cut specimens were used for preparing polished sections for electron microanalysis. In all the instances the losses of molybdenum and the amount of lead separated from lead glass melts were expressed in terms of mean current densities corresponding to oxidation of molybdenum to degree +6 and to reduction of bivalent lead to metal similarly as described in study [5].

The changes in potential are related to a value corresponding to the spontaneously established corrosion potential without passage of the direct current. In the case of electrodes loaded with alternating current these were the mean potential values established on the RC filter. The DC circuit indicated by dashed lines (figures 5 - 8) was of course not applied when measuring the dependence of mean electrode potential on AC density or frequency. In all the instances use was made of the simple platinum oxygen-function reference electrode represented by Pt wire passing freely through the surface. This type has minimum demands in terms of the space required.

RESULTS AND DISCUSSION

Figure 2 shows the dependence of lead precipitation and molybdenum corrosion rates (expressed as current density) and the total current passing through the electrode on the potential of electrodes in a lead glass melt corresponding to composition B (table 1) but prepared without the addition of arsenic oxide. For the sake of comparison, the corrosion and lead precipitation rates in the same glass melt refined with arsenic oxide found formerly [5] are also plotted in the same figure. The plots show that the courses for both glass melts are similar. Both the rates of lead precipitation and corrosion attain a maximum at a potential more negative by 100 -200 mV with respect to the rest potential, whereas in the glass melt containing arsenic oxide the maximum occurred at potentials more negative by about 200 - 300 mV. Towards more positive values, an abrupt decrease occurs and later on all three currents do not exhibit any greater changes. A decrease also takes place in the direction towards the more negative values, the cathodic currents pass through a minimum and then increase again. The difference in the behaviour in the two melts is based on the fact that rest state rates of molybdenum oxidation and of lead precipitation in the glass melt refined with arsenic oxide are substantially lower. This is in full agreement with the findings on the effect of arsenic oxide established earlier [6].

An additional difference follows from a comparison of partial currents i_{Pb} and i_{Mo} at various potentials (table 2): The Table indicates that in this glass melt the rates of lead precipitation and molybdenum oxidation at the rest potential are identical. At the more negative potentials the differences in these currents do not differ much (with deviations in both directions) from the total current passing through the electrode. There holds therefore an equivalence between Mo(VI) and Pb(II) for the total process of molybdenum dissolution in the glass melt over the wide range of 0 to -400 mV with respect to the rest potential. Anodic dissolution of molybdenum probably does not take place at the more negative potentials. The deviation from this equivalence in the glass melt containing arsenic oxide can partially be attributed to preferential precipitation of arsenic at the expense of the precipitation of lead [6]. The definitive explanation would need additional experimental data.

Table 2. Corrosion and lead precipitation rates expressed as current densities i_{Mo} and i_{Pb} and mean overall current density *i* at different potentials ε .

$\epsilon(mV)$	$\Delta\epsilon \left(mV\right)$	$i_{\rm Pb}$ (mA cm ⁻²)	i_{Mo} (mA cm ⁻²)	$i_{\rm Pb}$ - $i_{\rm Mo}$ (mA cm ⁻²)	<i>i</i> (mA cm ⁻²)	$i_{ m Pb}$ / $i_{ m Mo}$
-1230	-600	78.27	1.88	76.39	-82.85	41.63
-1130	-500	72.70	2.01	70.69	-74.77	36.17
-1030	-400	77.91	6.31	71.60	-66.11	12.35
-930	-300	158.80	51.84	107.00	-99.96	3.06
-830	-200	88.26	63.80	24.46	-33.16	1.38
-630	0	61.56	61.35	0.21	0.00	1.00
-530	100	35.59	36.42	-0.83	13.79	0.98
-430	200	11.49	11.37	0.12	11.07	1.01
-130	500	1.25	4.06	-2.81	9.78	0.31



Figure 2. Corrosion rate i_{Mo} , lead precipitation rate i_{Pb} and mean overall electrode current *i* vs. electrode potential at 1380 °C in 24% lead crystal glasses with and without As₂O₃.



Figure 3. Corrosion rate expressed as current density and overall electrode current vs. potential at 1400 °C in model glass NCS - Sb.



Figure 4. Oxidic layer formed in glass NCS - Sb at potential raised by 500 mV. Electron microprobe, composition.

Figure 3 shows the dependence of molybdenum corrosion rate and the mean total current on potential in the model soda-lime glass melt refined with antimony oxide (NCS-Sb in table 1) under loading with alternating current. The plot also includes the value corresponding to the rest potential without loading with alternating current. In this case the alternating current has obviously a very small effect on the corrosion. The relationship established has the shape of a typical polarization curve having the maximum at a potential increased by 200 mV and followed by passivation.

A comparison of the courses for all the three glass melts in figures 2 and 3 indicates that their shape differs only in the position of the maximum with respect to the corrosion potential. It must therefore be assumed that in a lead glass melt containing arsenic oxide the passivation already occurs in the rest state, and that in the same glass melt free from the refining agent the passivation occurs closely above the rest potential, whereas in the soda-lime glass melt refined with arsenic oxide the setting in of passivation requires an increase in potential by about 200 mV. It may therefore be assumed that passivation associated with the presence of an oxide layer on the electrode surface can already occur in the rest state. On the basis of thermodynamic considerations, Gohlke and Pfeiffer [7] have come to the assumption that the corrosion of molybdenum is already in the rest state inhibited by the presence of a thin layer of MoO₂ oxide at the molybdenum-glass melt interface. There is no doubt about the formation of a compact and relatively thick layer of oxides at potentials increased by the order of hundreds mV: Existence of a layer composed of molybdenum and oxygen corresponding by its composition to MoO₂ in lead glass melt B at a potential increased by 500 mV was already described in our previous study [4]. A layer of similar composition was also found in the NCS-Sb melt at a potential raised by the same amount (figure 4). The molybdenum content of 79% corresponds again best to MoO₂. An incompact oxide layer begins to form from +200 mV with respect to the rest potential. This corresponds well to the maximum of corrosion and total current in figure 2. At the rest potential, when no passivation took place in the glass melt, no layer of reaction product was observed except for antimony adhering to a part of the electrode surface. As far as the lead glass melt with a content of arsenic oxide is concerned, in which corrosion is inhibited in rest state, the possible presence of a thin layer consisting only of molybdenum and oxygen under the thicker multicomponent layer described in Introduction was indicated in [4]. However, we have not succeeded in providing firm evidence of this layer even by repeated analyses. Regardless of the content of arsenic oxide, only an abovementioned multicomponent layer was determined in the two lead glass melts. Within the framework of limit deviation of the individual analyses, the character and composition of the layers did not differ from the layers described earlier [4]. It should be taken into account, however, that electron microanalysis of such a type of sample allows layers more than about 50 nm thick to be distinguished. If the electrode surface in the two glass melts differed only in the layer thickness of the product it is not surprising that that no distinct difference of potentials in rest state between the two glass melts was established. It has been repeatedly found that the electrode potential in a glass melt containing arsenic oxide is even by several mV more negative than in the same glass melt free from arsenic oxide.

An indirect evidence for the presence of a layer of oxides which inhibits corrosion in rest state, is provided by the effect of alternating current. Table 3 demonstrates that alternating current (0.5 A cm⁻²) accelerates several times the lead precipitation and corrosion in rest state in glass melt B containing arsenic oxide to the val-



Figure 5. Weight loss Δm [8] and mean electrode potential vs. alternating current density at 1400 °C in soda-lime-silica glass without refining agents.



Figure 6. Lead precipitation Q [6] and mean electrode potential vs. alternating current density in 24 wt.% lead glass without refining agents.

ues corresponding roughly to the glass melt free from arsenic oxide given in table 2. On the other hand, the corrosion processes are relative little affected at potentials shifted towards the more positive and the more negative values. Such a phenomenon can be hardly explained otherwise than by elimination of the oxide layer which has been inhibiting the corrosion processes in rest state.

Table 3. Effect of alternating current (0.5 Acm^2) on corrosion and lead precipitation expressed as respective current densities in lead glass containing As_2O_3 .

$\Delta \epsilon (mV)$	$i_{\rm Pb}$ (mAcm ⁻²)	i_{Mo} (mAcm ⁻²)
-100	85.5	59.6
0	45.5	54.1
+100	0	1.5
+400	0	2.7



Figure 7. Lead precipitation Q [6] and mean electrode potential vs. alternating current density at 1380 °C in 24 wt.% lead glass containing As_2O_3 .



Figure 8. Radius loss Δr and mean electrode potential vs. frequency at alternating current density of 1Acm² at 1475 °C in special lead glass containing 12 wt.% PbO.

Alternating current is known to be capable of affecting the corrosion rate in both directions. Figures 5 through 8 show the dependence of corrosion rates on current density or frequency (figure 8) together with the affecting of the mean electrode potential. It can be seen that in all the cases the accelerating effect of alternating current acts in parallel with the shift of the mean electrode potential towards the more negative values and vice versa. This again supports the concept of influencing the rates of corrosion processes by the presence of a layer of oxides on the electrode supposing that the layer is removed at adequately negative potentials in the cathodic half-period.

Apart from the effects of alternating current, the presence of the oxide layer may also eplain the effect of the content of alkalies in the glass melt on the rate of corrosion processes. On taking into account that over the entire process the molybdenum is transferred into the glass melt as Mo (VI), while the composition of the reaction products on the electrode corresponds to a substantially lower oxidation degree, oxidation of the transient products to degree 6 appears to represent a very probable stage in the process of molybdenum corrosion. As in this oxidation degree molybdenum probably exists as molybdate or oxocomplex of molybdenum, it may be assumed that the dissolution of molybdenum proceeds essentially according to the scheme

I Mo
$$+ 2O^{2-} \rightarrow MoO_2 + 4e^{-}$$

II MoO₂ $+ 2O^{2-} \rightarrow MoO_4^{-2-} + 2e^{-}$

Then the rate of dissolution of the oxide layer will probably increase with the concentration of oxygen ions. If formation of this layer proceeds simultaneously at the metal interface, its resulting thickness will be the lower the higher is the rate of its dissolving. The noteworthy effect of the total molar concentration of alkalies on the rate of lead precipitation and corrosion in rests state was described in work [4]. The rate of the corrosion processes increased linearly with total concentration of alkalies from its certain value, without any influence of the representation of sodium or potassium ions. On the basis of the concept of dissolution of the oxidic layer this behaviour may be explained by influencing the concentration of oxygen anions required for dissolving the layer of oxides. This concentration is determined by the equilibrium between non-bridging oxygens O[°], bridging oxygens O[°] and oxygen ions

$$2O^{-} \leftrightarrows O^{\circ} + O^{2-}$$

where the concentration of O^{\cdot} is given by the content of alkalies in the glass melt.

According to the above considerations, the presence of a relatively thick layer of oxide in the rest state can be expected to form in glass melts with a low content of alkalies. Gohlke and Pfeiffer [7] have documented the presence of such a layer, unfortunately without specifying the composition of the glass melt. Holzwarth, Rüssel and Tomandl [9] describe occurrence of an oxygen-containing layer in an aluminosilicate glass melt, unfortunately again without specifying the content of alkalies. Figure 9 illustrates the presence of such a layer in the rest state in glass Neutral, which is a glass melt containing only 10.5 mol.% R_2O . Under the effect of alternating current, only an incompact layer was formed (figure 10).

CONCLUSION

In glass melts with a high content of lead oxide and probably also in other glass melts, molybdenum is for the most part dissolved as Mo(VI). Passivation was observed to set in all the instances studied. In the case of glass melts containing 24 wt.% lead oxide the passi-



Figure 9. Oxide layer on molybdenum electrode in glass Neutrál at 1360 °C without current load. Electron microprobe composition.



Figure 10. Non-compact layer in glass Neutrál at 1360 °C formed under a.c. load of 1Acm².

vation starts already at the rest corrosion potential, or even at slightly more negative potentials in the presence of arsenic oxide.

Alternating current can affect the rate of corrosion processes in various glass melts in both directions. The accelerating effect always manifests itself in parallel with a shift of the mean electrode potential towards the more negative values and vice versa.

The effects of the electrode potential, of alternating current and the concentration of alkalies in the glass melt can all be explained by the presence or thickness of a layer of molybdenum dioxide on the electrode.

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References

- Hierl G., Hanke K., Scholze H.: Glastechn.Ber. 52, 55 (1979).
- 2. Matěj J., Bernard V.: Glastechn. Ber. 66, 307 (1993).
- Rudolph T., Balazs G.B., Rüssel C., Tomandl G.: Glastechn.Ber. 61, 177 (1988).
- Matěj J., Freivolt Š., Hulínský V.: Ceramics Silikáty 40, 1 (1996).
- Matěj J., Hulínský V., Mamo K.: Ceramics Silikáty 42, 132 (1998).
- 6. Matěj J., Pecháček T., Klaška J., Hulínský V.:
 a) Proc.5th ESG Conf. June 21-24 1999, Prague, CD-ROM Design @ Publishing
 a.s., p. A4-40 A4-47 1999.
 b) Sklář a keramik 50, 337 (2000) (in Czech).
- Gohlke D., Pfeiffer T.: Korrosion von Molybdän im Kontakt mit der Glasschmelze, Seminar für die Glasindustrie, Plansee AG, 8.10.1999 Reutte.

- 8. Matěj J., Staněk J.: Glastechn.Ber. 61, 1 (1988).
- 9. Holzwarth S., Rüssel C., Tomandl G.: Glastechn. Ber. 64, 195 (1991).

MECHANISMUS ROZPOUŠTĚNÍ MOLYBDENU VE SKLOVINĚ A VLIV STŘÍDAVÉHO PROUDU

JIŘÍ MATĚJ, EVA KRUPKOVÁ, VÁCLAV HULÍNSKÝ*

Laboratoř anorganických materiálů Společné pracoviště Ústavu anorganické chemie Akademie věd České republiky a Vysoké školy chemicko-technologické v Praze Technická 5, 166 28 Praha

*Ústav skla a keramiky Vysoká škola chemicko-technologická v Praze Technická 5, 166 28 Praha

Byly vzájemně porovnány závislosti rychlosti koroze, případně vylučování olova na potenciálu molybdenové elektrody nalezené ve dvou sklovinách s obsahem 24% oxidu olovnatého, které se navzájem lišily přísadou malého množství oxidu arsenitého a v jedné sklovině neobsahující oxid olovnatý. Z porovnání rychlostí vylučování olova a koroze vyjádřených jako proudové hustoty a celkového proudu procházejícího elektrodou ve sklovině neobsahující oxid arsenitý vyplývá, že molybden je z převážné části převáděn do skloviny jako Mo(VI), a to i při značně negativnějších potenciálech než je klidový korozní potenciál. Ve všech třech sklovinách vykazují získané stacionární polarizační křivky průběhy typické pro pasivaci, přičemž ve sklovinách s obsahem oxidu olovnatého dochází k nástupu pasivace již při klidovém korozním potenciálu, za současné přítomnosti oxidu arsenitého dokonce již při potenciálu zápornějším. Dále bylo vyšetřeno ovlivnění středního potenciálu molybdenové elektrody střídavým proudem v různých sklovinách. Výsledky byly porovnány s ovlivněním koroze resp. vylučování olova za stejných podmínek. Střídavý proud může rychlost koroze případně vylučování olova ovlivňovat v obou směrech. Ve všech případech se urychlující účinek střídavého proudu projevuje souběžně s posunem středního potenciálu elektrod k zápornějším hodnotám a obráceně. Ovlivnění rychlosti koroze potenciálem elektrody, působením střídavého proudu i koncentrací alkálií ve sklovině je možné vysvětlit ovlivněním přítomnosti resp. tloušťky vrstvy oxidu molybdeničitého na elektrodě.