

CORROSION OF MOLYBDENUM ELECTRODES IN LEAD GLASS MELTS

PART 2 – EFFECT OF POTENTIAL AND TRANSFER OF ALTERNATING CURRENT BY THE ELECTRODE

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A comparison of the values of corrosion of molybdenum electrodes shows that the rest corrosion current is substantially lower than the mean value of alternating current over the current density range of 10^{-1} to 10^0 A cm⁻² considered. The efficiency of hypothetical alternating-current electrolysis amounts to only 12 to 24 %. The alternating current is probably for the most part transferred by a reversible reaction. The dependence of corrosion rate of molybdenum in glass melts containing PbO on frequency exhibits a twin minimum whose frequencies decrease with the total content of alkalis while being independent of the Na₂O : K₂O ratio. The corrosion rate, separation of lead and the total current all exhibit a substantial increase when the potential is reduced by 200 to 300 mV compared to the rest potential, i.e. at -840 to -940 mV with respect to the oxygen electrode. Oxidation of Mo occurs even under these conditions. The separation of lead ceases when the potential is increased by 100 mV. The reaction of the molybdenum oxidation products with the alkalis in the glass melt probably plays a significant role in the entire corrosion process as well as in the alternating current transfer between the molybdenum electrode and the glass melt.

INTRODUCTION

The first part of this communication [1] was concerned with describing the basic mechanism of corrosion of molybdenum electrodes in glass melt and the role of lead oxide as a corrosion depolarizer. Attention was also paid to the layers of oxidic reaction products on the electrode surface. It was proved that the composition of the reaction products changes very little with changing conditions, including the loading with alternating current. The only exception is exhibited by products arising at potentials increased by 500 mV above the rest value, since unlike the other corrosion products they comprise solely molybdenum and oxygen. The corrosion rate and the separation of lead in the rest state was found to be a linear function of the total content of alkalis expressed in molar percent.

The following part deals with an analysis of the effects of alternating current on the corrosion processes in glass melts, involving also data from the literature. The results are supplemented with an examination of the effects of alkalis on the frequency of the minimum rate of corrosion processes and by a detailed investigation of the effect of potential on the corrosion processes.

Influencing of corrosion processes by alternating current

Alternating current between the metallic electrode and the glass melt may be transferred: 1. by an anodic and cathodic reaction involving charge transfer (Faradayic current), 2. by alternate charging and discharging of the electric double layer (capacitive current). The share of the capacitive current increases with frequency.

Whereas the capacitive current does not affect the corrosion processes, Faradayic current may influence corrosion in two basic ways [2]:

1. In the rest state, corrosion does not proceed because no suitable depolarizing reaction is available. The transfer of alternating current then involves solely alternating oxidation and reduction of the material of the electrode (cf. figure 1). However, at an adequate amplitude of the alternating current the electrode potential may periodically attain such negative values that a different cathodic reaction can take place instead of re-reduction. The corrosion then starts at a certain current density. It is also important to what degree the oxidation products are removed

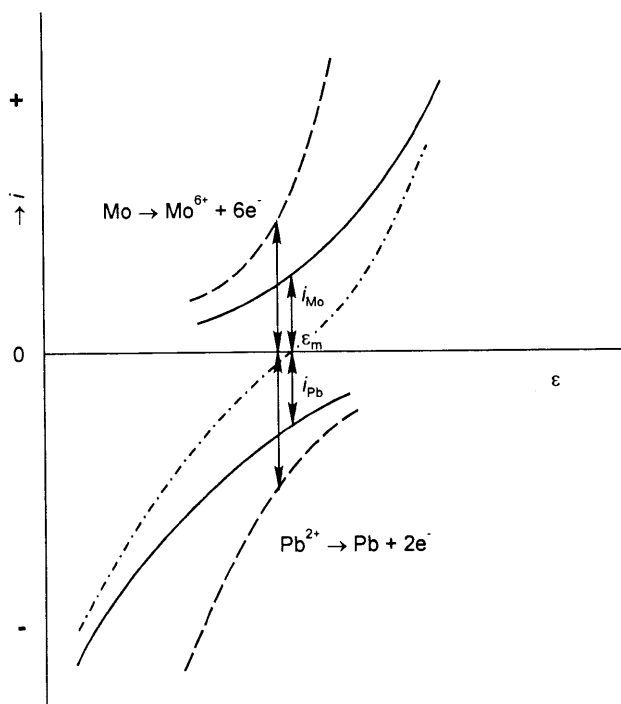


Figure 1. Establishing of corrosion potential ϵ_m for corrosion of molybdenum electrode in lead glass melt, and Dévay's concept of the mean value of corrosion current increased by the effect of alternating current.

— corrosion current and depolarizing reactions; — — — increase in mean value of corrosion and depolarization current; - · - · - overall electrode current

(by mixing, chemical reaction) from the action radius of the reverse reaction.

2. The corrosion already takes place in the rest state. The corrosion current oscillates around the rest value. At increasing current density the increase in anodic current within the positive half-period is not compensated more by its decrease within the negative one. The cathodic current is affected in the same way.

The influence on corrosion taking place already in the rest state was dealt with by Dévay et al. who considered transfer of alternating current by the anodic (corrosive) reaction and by the cathodic one, as well as the capacitive current. Using mathematical derivation [3] and a physical model [4] the authors proved that with an exponential shape of the polarization curves corresponding to the transfer control of both reactions (figure 1), the alternating current raises the mean value of the anodic (corrosive) current along with increasing current density and decreasing frequency. The cathodic reaction is affected in the same way. This explanation assumes that the electrode surface is free of reaction products. With a different shape of polarization curves, such as for example that occurring in the case of the

control by diffusion [5a], corrosion may even be suppressed by the effect of alternating current [5b].

Specific conditions of conduction of alternating current by the electrode in glass melt

The present study will consider loading of the electrode by alternating current with a current density of the order of $10^{-1} - 10^0 \text{ A cm}^{-2}$, which corresponds to the loading of heating electrodes in electrical melting of glass. From previous chapter it follows that the electrode behaves as a resistor/capacitor combination. Both components depend on the passing current. When investigating the electrochemical effects of alternating current it is therefore useful to consider the following two limit cases: 1. The effects of alternating current of defined (imposed) course, where the course of the electrode potential is affected by its behaviour, and 2. the effect of alternating voltage of defined course, where, on the contrary, it is the course of the current which is affected. It was shown that the conditions of electrical glass melting approach the conditions involving the effects of forced current [6]. The quoted studies by Dévay et al. are likewise in general based on this concept. The forced-current conditions were therefore also considered in the theoretical analysis given below. The arrangement of the experiments with alternating current likewise meets the requirement pertaining to forced current.

Transfer of electrons in melts is usually a very fast process, controlled by mass transfer [5c]. This is at variance with the assumptions of Dévay's theory concerning the effects of alternating current, as well as with the presence of layers of reaction products on the electrode surface [1]. Silicate glass melts have the specific property of conducting current almost exclusively by the mediation of alkali ions [7].

The existing experimental findings on the influencing of corrosion of molybdenum electrodes in glass melts by the alternating current were summarized in the first part of the present study. The amount of corroded molybdenum was shown to be very roughly equivalent to the amount of separated lead even when alternating current is used. Further findings can be achieved by comparing the corrosion currents with the intensity of alternating current passing through the electrode.

EFFECT OF ALTERNATING CURRENT AND CORROSION CURRENTS ON MOLYBDENUM ELECTRODE IN GLASS MELT

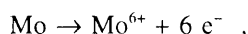
Table 1 lists the mean corrosion rates of molybdenum electrodes (taken over from table 3 and from [8, 9]), expressed as corrosion currents*.

* All the values specified here (except those in figure 6) are given per unit area, thus being in fact current densities.

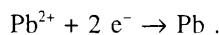
Table 1. Comparison of molybdenum corrosion rate with mean alternating current i_m passing through the electrode. Sinusoidal course, frequency 50 Hz.

source of data	glass melt and conditions	current densities (mA cm ⁻²)				
		i_{cf}	i_m	$\bar{i}_{Mo}$	$\bar{i}_{Pb}$	$\frac{2 \bar{i}_{Mo}}{i_m} (\%)$
table 3	24 wt.% PbO (As ₂ O ₃) 1380 °C, 7 hours	0	0	13.7	8.58	-
		500	450	54.1	45.5	24
ref. [9]	24 wt.% PbO (no refining agents), 1350 °C, 4 hours, rotation	1000	900	54.3	-	12
ref. [9]	24 wt.% PbO (Sb ₂ O ₃), 1350 °C, 4 hrs. rotation	1000	900	76.4	-	17
ref. [8]	78 SiO ₂ , 10 CaO, 16 Na ₂ O (wt.%), no refining agents, 7 hours, 1400 °C	0	0	0.295	-	-
		750	675	1.16	-	0.34

In the first given case, the rate of lead separation was also expressed on the basis of the known amount of separated lead. The following reactions were considered in the calculations:



and



The table shows that the rest corrosion current on an unloaded electrode in a lead glass melt amounts to only about 14 mA cm⁻², thus being incomparable with the alternating currents over the considered range of 10⁻¹ to 10⁰ A cm⁻² passing through the electrode. This disparity is still greater in the case of lead-free glass melts.

If the alternating current of defined course were conducted solely by means of the reactions mentioned above, that is according to the concept of Dévay et al., (and when so far neglecting the capacitive current), the mean value of the corrosion current should not obviously differ much from the mean value of alternating current passed during the anodic or anodic half-period, so that electrolysis by alternating current would in fact be in play.

The efficiency of hypothetical alternating current electrolysis is given by the ratio of $\bar{i}_{Mo}$ or $\bar{i}_{Pb}$ currents calculated from the mean corrosion rate or from the separation of lead, to the current representing the maximum possible rate of electrolysis by alternating current. The latter is equal to one half of the mean value of alternating current i_m per one half-period (the supplementary process taking place in the other half-period). For a sinusoidal course of the current,

$$i_m = \frac{2\sqrt{2}}{\pi} i_{cf} \approx 0.900 i_{cf} [2].$$

The last column of table 1 lists the values of the efficiency of the electrolytical process calculated in this way. With glass melts containing PbO these values do not exceed 24 wt.%, whereas with lead-free melts this efficiency is lower by two orders of magnitude. It is therefore probable that under the conditions when the mean value of alternating current passing through the electrode is incomparably higher than the rest current, the major part of alternating current is transferred by some other than the corrosion and supplementary cathodic ("depolarization") process.

The small electrolytic effect of alternating current at its high density may in principle be due to:

1. A high share of the capacitive current. According to Nikitin and Esin, the capacity of the electrode double-layer for melts of silicate slags ranges from 11 to 115 μF cm⁻², while the majority of the values vary around 15 μF cm⁻² [10]. At a current density of 0.5 A cm⁻², a voltage of about 2 V, i.e. 1 V per half-cell, was measured on the electrodes at 1350 °C in a glass melt containing 24 wt.% PbO. On assuming that this entire voltage is loaded on the electric double-layer having a capacity of 15 μF cm⁻², then for a frequency of 50 Hz used in technical practice the capacitive current should amount to as little as 4.7 mA cm⁻². However, this current is equal to 470 mA cm⁻² for a frequency of 5000 Hz, that is virtually to the entire current passing through the electrode. This is in good agreement with the observed fading away of the

effects of alternating current on corrosion of molybdenum electrodes at frequencies of the order of 10^3 Hz. At 50 Hz, and the more at lower frequencies, the share of the capacitive current is not high enough to be regarded as the cause of the small electrolytic effect of alternating current.

2. An additional pair of different reactions competing with the corrosive reaction and the supplementary ("depolarization") one. In that case the reactions would yield products which should be found. The only alternative anodic reaction could be development of oxygen which, however, was not observed to take place in lead glass melts up to 2A cm^{-2} [11]. Apart from lead no other cathodic products were determined. This possibility may therefore also be ruled out with the exception of extremely high current densities or extremely low frequencies (below the frequency of the minimum rate of corrosion processes [1]).
3. A sole single reaction running during passage of alternating current in both directions. Only alternating oxidation and reduction of molybdenum comes into consideration. The overall reaction may be reversible, or only its first or second stage, as described by Rudolph et al. [9]. Alternating oxidation and reduction of depolarizers is improbable, in particular in glass melts with their minute contents. As alkalis are the carriers of current in melts, their possible reverse reaction with the electrode as a carrier of Faradayic current should also be considered. The probable participation of alkalis in the corrosion process is also indicated by the distinct effect of their content on corrosion rate in the rest state, as established earlier [1].

EXPERIMENTAL PART

The experiments were carried out in two different arrangements: Examination of corrosion of a pair of electrodes fed by alternating current of defined course from a galvanostat (table 2 and figure 2), and study of the dependence of corrosion on the potential of the electrode in potentiostatic three-electrode arrangement.

Both the experiments under the influence of alternating current and those at a defined potential, including the evaluation of the corrosion, are described in communication I [1]. In the case of experiments with a defined potential and involving assessment of the corrosion, however, use was made of a crucible of Al_2O_3 -based material, of the same type as that used in the alternating-current experiments. The lead collecting under the working electrode was separated from the lead separating from the auxiliary (also molybdenum)

electrode by a low partition at the crucible bottom. The entire experiment proceeded at the potential required without using preliminary equalization.

Table 2. Effect of total content of alkalis on frequency of minimum rates of corrosion processes at 1350 °C (glasses 1 - 4), and at 1380 °C (glasses 5, 6).

glass melt	<i>c</i> (mol.%)	<i>i</i> _{ef} (A cm ⁻²)	<i>f</i> _{min} (Hz)
1	13.77	0.6	0.25
2	12.91	0.6	0.42 0.47
3	12.47	0.6	0.53 0.59
4	11.54	0.6	0.76 0.87
5	15.46	0.5	0.56
6	12.02	0.5	0.635

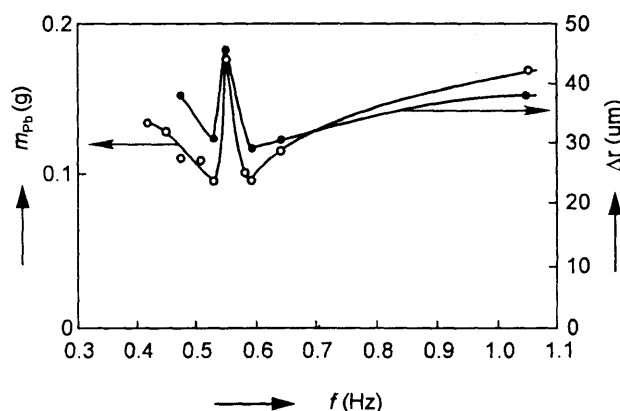


Figure 2. Corrosion loss Δr and the amount of separated lead m_{pb} vs. frequency in glass melt no.3.

● - Δr ; ○ - m_{pb}

Dependence of the frequency of minimum corrosion rate on the content of alkalis in the glass melt

Table 2 lists the frequencies at which the dependences of the amount of separated lead and of the corrosion established for various glass melts on the content of alkalis attained a minimum. The glasses, already described in communication [1], had variable ratio of Na_2O to K_2O and contained 24 wt.% PbO (Nos. 1 - 4), and 31 - 32 wt.% PbO (Nos. 5 and 6) respectively. In some instances the courses exhibited two relatively close minimums with a relatively sharp peak inbetween (figure 2). The occurrence of the twin minimums is probably general but we did not succeed in distinguishing them in all the cases.

From table 2 it follows that the frequency of both minimums decreases with increasing total content of alkalis, so that the charge transferred during the half-period increases. It therefore appears that in the region of frequencies higher than the frequency of the (higher) minimum (under which a new process has to be considered) the alkalis from the melt take part in the charge transfer between the electrode and the melt.

The effect of molybdenum electrode potential on the rate of corrosion processes

The results of the study of corrosion of molybdenum electrodes in a glass melt containing 24 wt.% PbO (cf. glass B in communication [1]) in dependence on potential are summarized in table 3 and in figure 3. In the latter diagram, the shift of electrode potential against the rest state is plotted on the horizontal axis. The mean value of rest potential with respect to the oxygen electrode is -640 mV. The vertical axis represents the mean rates of lead separation and of corrosion, expressed as the mean values of anodic and cathodic current $\bar{i}_{\text{Mo}}$ and $\bar{i}_{\text{Pb}}$ for the entire duration of the experiment. In the calculation based on the total loss of the electrode and on the amount of separated lead, oxidation of molybdenum up to the valency of 6 was considered. The diagram also shows the

mean value of total current $\bar{i}$ (compare to figure 1), obtained by integrating the time courses of current supplied by the potentiostat. A comparison of these currents with currents i_t determined at the end of the experiment and listed in the last but one column of table 3 shows that at the more negative potentials the values do not much differ, which is indicative of a comparative equalization of the current in the course of the experiment. In contrast to this, at the end of the experiment the anodic currents are substantially lower so that a permanent decrease of the current occurs; this can be explained by gradual migration of alkali ions away from the electrode. The difference in the time courses at the more positive and more negative potentials is illustrated by figure 4.

Figure 3 shows that the corrosion rate and that of lead separation attain a maximum at a potential reduced with respect to the rest state by 200 to 300 mV, i.e. at -840 to -940 mV with respect to the oxygen electrode. The overall electrode current likewise attains its maximum at -940 mV. At a potential reduced by 400 mV (to -1040 mV) the rate of corrosion and that of lead separation fall to a minimum. The overall electrode current also has its minimum at -1140 mV. At still more negative potentials the overall electrode current shows again a considerable increase, and the corrosion rate of molybdenum and that of lead separation are also somewhat higher.

Table 3. Mean rates of corrosion and "depolarizing" reactions and of overall electrode current vs. electrode potential.

ϵ (mV)	$\Delta\epsilon$ (mV)	m_{Pb} (g)	$\bar{i}_{\text{Pb}}$ (mA cm ⁻²)	Δr (mm)	m_{Mo} (g)	$\bar{i}_{\text{Mo}}$ (mA cm ⁻²)	$\bar{i}_{\text{Pb}} - \bar{i}_{\text{Mo}}$ (mA cm ⁻²)	$\bar{i}$ (mA cm ⁻²)	i_t (mA cm ⁻²)	$\frac{\bar{i}_{\text{Pb}}}{\bar{i}_{\text{Mo}}}$
-640	0	0.1340	8.58	0.0598	0.0331	13.74	-	0	0	0.63
	0*	0.7152	45.50	0.2928	0.1303	54.10	-	0	0	0.84
-740	-100	0.7336	47.00	0.2216	0.1036	43.00	4.00	-60.22	-59.47	1.09
-840	-200	1.6832	107.83	0.3417	0.1419	58.88	48.95	-172.45	-189.26	1.83
-940	-300	1.8955	121.43	0.4080	0.1522	63.18	58.25	-264.18	-237.93	1.92
-1040	-400	1.4125	26.43	0.0365	0.0202	8.38	18.05	-82.31	-91.92	3.15
-1140	-500	0.8400	53.81	0.0608	0.0331	13.73	40.08	-52.00	-48.53	3.92
-1240	-600	0.6363	40.76	0.0097	0.0555	23.04	38.46	-173.46	-189.26	17.7
-540	+100	0	0	0.0253	0.0141	5.87	-	3.48	3.12	0
-440	+200	0	0	0.0152	0.0086	3.57	-	3.98	2.95	0
-340	+300	0	0	0.0388	0.0214	8.89	-	5.71	3.29	0
-240	+500	0	0	0.0605	0.0330	13.73	-	7.26	4.77	0

*Under the influence of sinusoidal a. c. at current density of 0.5 Acm⁻² and frequency of 50 Hz

Meaning of the symbols:

$\epsilon, \Delta\epsilon$ - electrode potential and potential shift

m_{Pb} - amount of lead separated

Δr - loss of electrode radius

m_{Mo} - weight loss of a molybdenum electrode

$\bar{i}_{\text{Pb}}, \bar{i}_{\text{Mo}}$ - mean lead separation and corrosion rates expressed as mean current densities and calculated from m_{Pb} and m_{Mo} , respectively

$\bar{i}$ - mean total electrode current density

i_t - total electrode current density at the end of the experiment

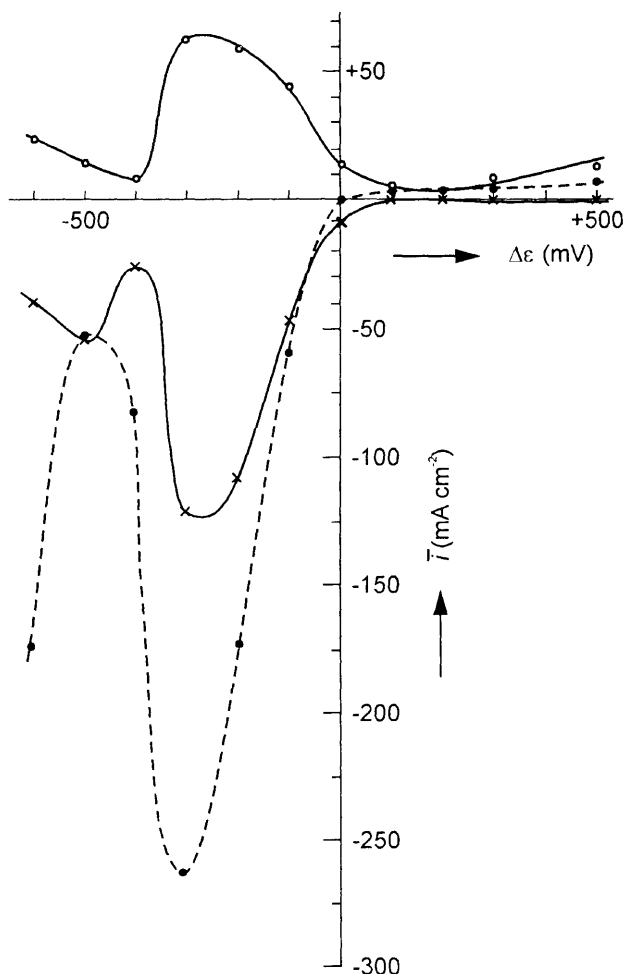


Figure 3. Corrosion rate $\bar{i}_{\text{Mo}}$, lead separation rate $\bar{i}_{\text{Pb}}$ and mean overall electrode current $\bar{i}$ vs. electrode potential at 1380 °C in glass melt containing 24 wt.% PbO. The rest potential corresponds to -640 mV with respect to the oxygen electrode.
 ○ - $\bar{i}_{\text{Mo}}$; × - $\bar{i}_{\text{Pb}}$; ● - $\bar{i}$

At the rest potential the corrosion rate and the separation of lead are comparably low. A shift of the potential to more positive values by 100 mV and more brings about complete suppression of lead separation. The corrosion rate decreases further when the potential is raised by 200 mV, then increasing again.

The last column in table 3 lists the ratio of lead separation rate to that of molybdenum corrosion. In the rest state its value amounts to 0.63, or to 0.84 when alternating current is involved. These values are lower than unity, as has already been established earlier [1]. This can be explained by a mean oxidation degree lower than 6, at which the molybdenum is dissolved in the glass melt [9, 12]. Another possibility is based on participation of another depolarizer in the corrosive reaction, for example As^{5+} or As^{3+} . The ratio of corrosion and lead separation rates changes in terms of potential:

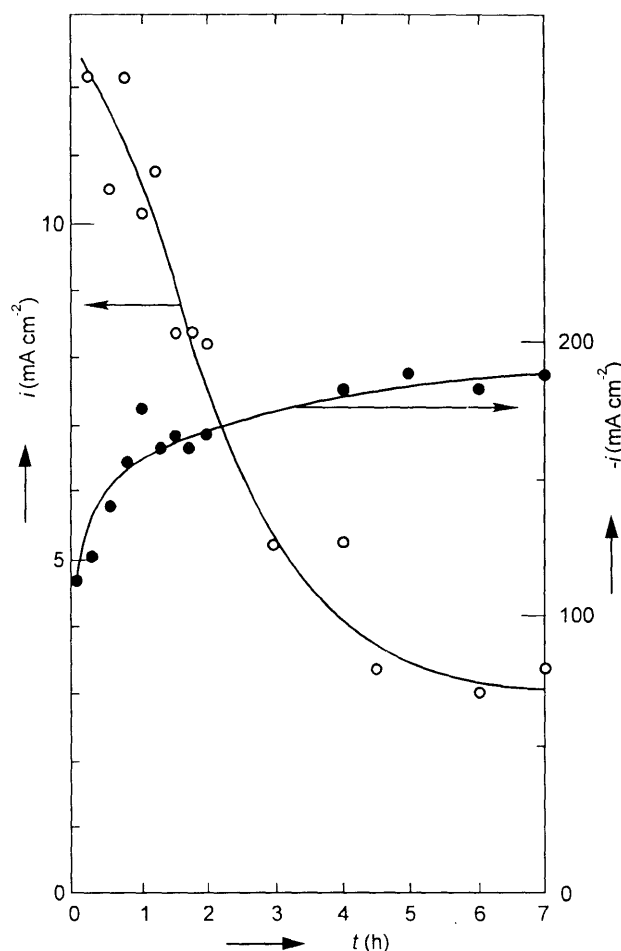


Figure 4. Overall electrode current vs. time.
 ● - at potential decreased by 200 mV against rest state
 ○ - at potential increased by 300 mV against rest state

from zero value at +100 mV and more, it increases continuously in the direction towards the more negative potentials.

On comparing the rate of lead separation with the overall electrode current in the cathodic region one sees that within the maximum corrosion region the overall (cathodic) electrode current is substantially higher than the rate of lead separation. This difference is even more marked when anodic current $\bar{i}_{\text{Mo}}$ is subtracted from current $\bar{i}_{\text{Pb}}$ (table 3). An additional process thus takes a considerable part in the transfer of cathodic current in this region. In the region of potentials more positive than the rest potential the overall electrode current is comparable to the corrosion current.

In table 4 the established limit values of potentials according to figure 3 are compared with normal potentials of the basic corrosion reactions according to

Table 4. Comparison of experimentally established limit values of potential with normal potentials of basic reactions involved in corrosion of molybdenum in lead glass melt.

normal potentials according to ref [9]		limit values in figure 5.	
reaction	potential (mV)	effect	potential (mV)
$\text{Mo}^{3+}/\text{Mo}^{6+}$	-560	Pb separation limit	-640 to -540
Pb/Pb^{2+}	-635	Maximum corrosion and lead separation rates	-840 to -940
Mo/Mo^{3+}	-830	Assumed end of molybdenum oxidation	-1040

Rudolph et al. [9]. The range of potentials over which separation of lead ceases, from -640 mV to -540 mV, overlaps the normal potential of the Pb/Pb^{2+} reaction. The potential of -1040 mV, at which both the lead separation rate and the corrosion rate pass through a minimum, can be regarded as a limit at which oxidation of molybdenum ceases. The oxidation probably does not occur at still more negative potentials, and the corrosion loss established (although still expressed in figure 3 as anodic current) should rather be attributed to cathodic corrosion. With respect to the normal potential of the Mo/Mo^{3+} reaction this limit is shifted towards significantly more negative values. This implies that the equilibrium has been shifted by some subsequent reaction in favour of oxidation. As shown in communication [1], formation of oxide layer may be such a reaction. Another possible reaction is that of oxides with alkalis, as indicated by the correlation of the rate of corrosion processes with the maximum of the cathodic current. In view of the normal potential of the $\text{Mo}^{3+}/\text{Mo}^{6+}$ reaction, there arises the possibility of interpreting the end of lead separation as passivation involving oxidation of molybdenum to degree 6, as assumed by Rudolph et al [9]. Against this explanation stands the fact that the reaction products in rest state (where a strong deceleration should already be expected in view of the courses in figure 3) correspond by their composition best to molybdenum of oxidation degree 3 [1].

A polished section for electron probe microanalysis was prepared from a specimen exposed to a potential reduced by 200 mV. A layer of oxidic products about 50 μm in thickness was found (figure 5), that is a thicker one than in the cases reported in communication [1]. Its quantitative analysis showed the products to contain (in wt.%) 31.95 K, 44.18 Mo, 9.30 Pb and 14.62 O. From the case of oxidic layers formed at rest potential and by the effect of alternating current, the given layer differs in

a substantially higher content of potassium. On expressing its composition as compound $\text{K}_x\text{Pb}_y\text{MoO}_z$, one obtains for $x = 1.87$, $y = 0.1$ and $z = 1.995$, that is a similar or higher value for z than in the layers analyzed earlier. The presence of silicon was not found. However, at a potential reduced by 500 mV no layers of oxidic products were determined, but the results indicated the beginning of formation of an irregular layer containing silicon, lead, potassium and molybdenum.

The relationship between the mean corrosion rate and potential, and the analyses of the products thus show that even at significantly negative potentials (according to the courses of curves in figure 3, probably as low as -1040 mV with respect to the oxygen electrode) the process involved is actually oxidation of molybdenum and not cathodic corrosion. Alkalies probably take part in the corrosion mechanism. The layer of reaction products does not protect the electrode, or provides only limited protection.

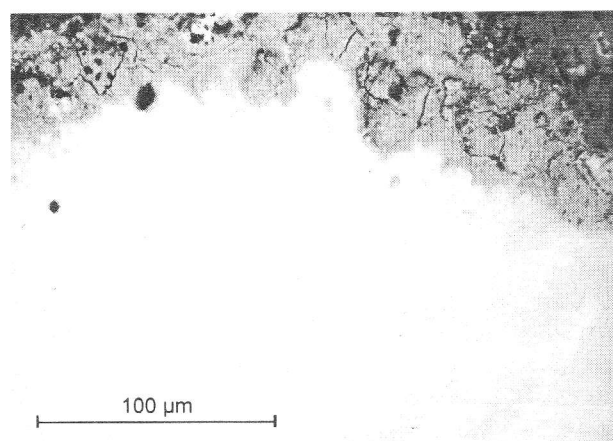


Figure 5. Layer of reaction products on molybdenum electrode at a potential reduced by 200 mV. Reflected electrons

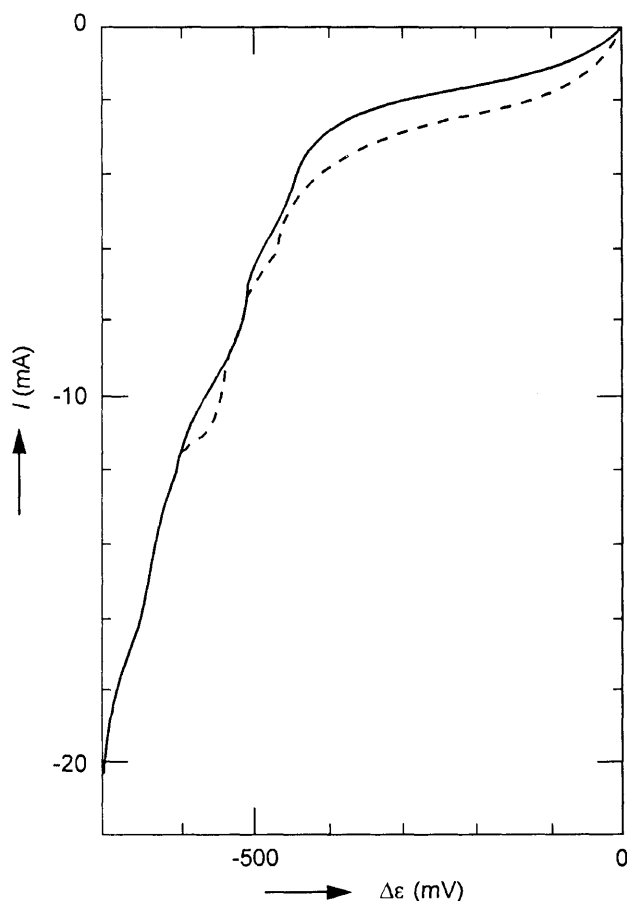


Figure 6. Cathodic polarization curves of molybdenum electrode, in glass melt containing 74 SiO₂, 10 CaO and 16 Na₂O (wt.%) and no refining agents. 1400 °C, 50 mV min⁻¹, electrode area 0.2 cm².

— — — with a layer of oxides
 ————— without this layer

To prove the assumption of a reaction of the oxides with alkalis, a layer of oxides was produced on the electrode by exposing it for two minutes to air at 650 °C before immersing it in the melt. The oxidation resulted in the formation of a smooth dark-grey layer. Such conditions may yield MoO₂, MoO₃ and several oxides of the Mo_xO_{3x-1} homologous series [13]. Figure 6 shows a comparison of the cathodic polarization curve of the treated electrode in the glass melt containing (in wt.%) 74 SiO₂, 16 Na₂O, 10 CaO and free of refining agent, with the polarization curve of an untreated electrode. The diagram indicates that up to -450 mV with respect to the rest state the cathodic current of the treated electrode is higher than that of the electrode with an untreated metallic surface. The subsequent course is virtually identical. It is therefore probable that at a cathodic polarity alkalis react with the oxidic layer if this is present on the electrode. One cannot rule out that under the effect of alternating current this reaction proceeds

reversibly. Since oxidation of molybdenum takes place conclusively even at substantially more negative potentials with respect to the rest state, under the effect of alternating current a re-reduction of molybdenum within the cathodic half-period is improbable. In order to elucidate further the problem, it will be necessary to evaluate the changes in potential caused by alternating current. It is not yet clear at what point molybdenum is oxidized to the higher degree, but it is probably at the interface between the reaction products and the glass melt.

CONCLUSION

1. The dependence of the lead separation rate and the corrosion rate in glass melts containing lead oxide on the frequency of alternating current exhibits a minimum which may be twinned. The frequency of this minimum decreases with the total content of alkalis in the melt, the Na₂O to K₂O ratio being not pertinent.
2. The rate of corrosion of the molybdenum electrode as well as the rate of separation of lead in a glass melt containing 24 wt.% lead oxide increase considerably with a relatively small shift of potential from the rest value to more negative potentials, and attains a maximum between -840 and -940 mV with respect to the oxygen electrode. An increase in the potential by 100 mV with respect to the rest value completely inhibits separation of lead.
3. Between the molybdenum electrode and the glass melt, alternating current with densities of the order of 10⁻¹ to 10⁰ A cm⁻² is probably transferred to a significant degree by a reversible reaction between the layer of oxidation products and alkali ions. The reaction of oxidation products with alkalis from the melt probably plays an important part also in the overall corrosion process.

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KOROZE MOLYBDENOVÝCH ELEKTROD V OLOVNATÝCH SKLOVINÁCH

ČÁST 2 - VLIV POTENCIÁLU A PŘENOS STŘÍDAVÉHO PROUDU ELEKTRODOU

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V úvodu této části práce navazující na sdělení I [1] je podán přehled poznatků o obecných příčinách ovlivnění korozních dějů střídavým proudem. Jsou pak vymezeny specifické podmínky molybdenové elektrody ve sklovině zatížené střídavým proudem definovaného průběhu o hustotě řádu 10^{-1} - 10^0 A cm⁻².

Z porovnání různých experimentálních dat (Tab.1) vyplývá, že klidové korozní proudy ve sklovinách s obsahem oxidu olovnatého jsou podstatně nižší než střední hodnota proudu v anodické nebo katodické půlperiodě za uvažovaných podmínek. Pak by v podstatě mělo docházet k elektrolýze střídavým proudem. Je ukázáno, že účinnost předpokládané elektrolýzy ve vybraných případech sklovin s 24 hmot.% oxidu olovnatého činí jen 12 - 24 %, ve sklovině bez obsahu PbO a jiných depolarizátorů je ještě o dva řády nižší. Střídavý proud mezi molybdenovou elektrodou a sklovinou proto pravděpodobně není přenášen pouze oxidací molybdenu a doplňkovou katodickou reakcí. Při frekvencích 50 Hz a nižších se ve větší míře neuplatní ani kapacitní proud.

Byla vyšetřena frekvenční závislost rychlosti vylučování olova a koroze v několika olovnatých sklovinách s různým obsahem alkálií, která vykazuje minimum mezi 0,25 - 0,87 Hz (Obr. 2, Tab. 2). Bylo zjištěno, že frekvence tohoto minima klesá s celkovým obsahem alkálií ve sklovině, přičemž nezáleží na poměru Na₂O a K₂O. Tento poznatek nasvědčuje účasti alkalických iontů na přenosu střídavého proudu mezi elektrodou a sklovinou. Navíc bylo zjištěno, že zmíněné minimum může být dvojité.

Dále byla v potenciostatickém tříelektrodevém uspořádání proměřena závislost rychlosti koroze, vylučování olova a celkového proudu elektrody na jejím potenciálu (Obr. 3, Tab. 3). Bylo zjištěno, že nejvyšší rychlosti dosahuje koroze i vylučování olova při potenciálu sníženém vůči klidové hodnotě o 200 - 300 mV. Při tomto potenciálu dosahuje maxima i celkový proud elektrody. Tento proud je podstatně vyšší než by odpovídalo rychlosti vylučování olova. Při posunu potenciálu do kladných hodnot o pouhých 100 mV vylučování olova zcela ustává. Také toto měření doplněné o analýzu reakčních produktů za podmínek maximální rychlosti koroze potvrzuje předpoklad o účasti alkálií na korozním procesu a na vedení střídavého proudu.