CORROSION OF MOLYBDENUM ELECTRODES IN LEAD GLASS MELTS

PART 1 - REACTION PRODUCTS AND EFFECT OF ALKALIES

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Received January 18, 1996.

At a corrosion potential, layers of oxidic reaction products containing molybdenum, lead, potassium and small amounts of sodium occur on the surface of molybdenum electrodes in lead glass melts. The molybdenum valency of 3 corresponds best to the oxygen content in the products. The corrosion very probably proceeds in particular in areas which are not covered by the layer. When the potential is raised by 400 mV or more, the layers contain only molybdenum and oxygen whose ratio is close to the composition of MO_3. The corrosion rate of molybdenum expressed as the rate of precipitation of lead is proportional to the sum of molar concentration of both alkalies reduced by a constant value of approximately 10.5 mol.%, independently of the ratio of the two alkalies.

INTRODUCTION

The behaviour of electrodes supplying electric current to the glass melt may play a significant role in industrial glass melting. At temperatures between 1100 °C and 1600 °C, the electrodes are exposed to the effects of the glass melt which acts as an electrolyte. Moreover, alternating electric current passes through the electrodes into the melt at densities ranging from tenths to units of amperes per square centimeter. Under such conditions, considerable corrosion of the molybdenum electrodes may take place, in particular is the case of lead glass melting, with the consequential loss of expensive material and contamination of the melt with the reaction products. Two methods for protecting the electrodes from corrosion have been developed in the Czech Republic: anodic protection [1], and protection provided by using electric current of reduced frequency [2]. Both have been used for many years in the melting of lead glasses by means of molybdenum electrodes. In spite of this, the principle of the protection cannot be regarded as having been satisfactorily explained. This applies in particular to the reduced frequency method. It appears advisable to elucidate first the mechanism of the corrosion processes involved, and this was the aim of part I of the present paper. Part 2 will be focused on the effects of alternating current on the corrosion processes.

Corrosion of molybdenum electrodes in glass melts proceeds similarly to the corrosion of metals in aqueous solutions by the electrochemical mechanism where the basic process, oxidation of the metal, takes place at the expense of reduction of so-called corrosion depolarizers, i.e. substances whose equilibrium redox potential is more positive than that of the metal being dissolved. On the electrode, a corrosion potential is then established at which the rate of oxidation of the metal and that of the reduction of the depolarizer, characterized by the anodic and cathodic current, are identical but for their sign.

The sequence of redox potentials in glass melts does not differ much from the sequence known for aqueous solutions [3]. In agreement with this, a decisive part in the corrosion process is played by the presence of refining agents such as As_2O_3, Sb_2O_3 and CeO_2 and by that of colouring oxides [4]. Lead oxide is the only majority component of the melt which depolarizes the corrosion of molybdenum.

The study of molybdenum corrosion in strongly aggressive lead glass melts showed that similarly to the case of other types of glass, the corrosion rate can be substantially affected by the alternating current [5 through 9]. It was found that alternating current may not only accelerate the corrosion, but also slow it down significantly [7]. An interesting course is exhibited by the dependence of corrosion rate on frequency: At frequencies of the order of 10^3 to 10^4 Hz, the corrosion rate approaches the value corresponding to the current-free state. The corrosion rate increases with decreasing frequency up to a maximum, and then decreases to a minimum at frequencies of the order of 10^{-1} to 10^0 Hz, even below the value corresponding to the current-free state. These findings constitute the principle of protecting the molybdenum electrodes by using current of reduced frequency [2].

In all such instances, there is a close relation between dissolution of the metal and precipitation of lead. The respective relationships between molybdenum loss and the amount of precipitated lead, and current density as well as frequency show similar courses [7].

On the assumption that molybdenum is oxidized to a valency of 6, a comparison of the amounts of precipitated lead and molybdenum lost by corrosion yielded ratios of their equivalents lower than unity:In a model lead glass melt of composition A (cf. table 1), the ratio had an average value of 0.90 for the range of conditions of 7 to 48 hr and 0 - 2 A cm^{-2}. The values of the ratio showed no correlation with current density. However, lower values were established for the shortest period of 7 hr, on the average 0.79 [6]. Rudolph et al. [8] report for a 24 % lead glass melt a mean molybdenum valency of 5.1, calculated on the same principle, which corresponds to an equivalent ratio of 0.85. Using the method of cyclic voltammetry, the authors determined the normal potentials of the basic reactions involved in the corrosion of molybdenum: For oxidation of lead to Pb^{2+}, the potential amounts to -635 mV, for oxidation of molybdenum to valency 3, it is -830 mV, and for additional oxidation to valency 6, -560 mV. In view of these values, oxidation to a higher valency degree should be difficult. In agreement with the ratio of lead and molybdenum equivalents established, the authors assume existence of a two-stage reaction mechanism: Molybdenum is first oxidized to valency 3, a part of it in this valency is dissolved in the glass melt, and a major part is then oxidized to a higher stage.

At a corrosion potential affected by alternating current only, X-ray microanalysis of the layers of corrosion products in cold state revealed the presence of MoO_2 and $PbMoO_4$, and sometimes also of $K_2Pb(MoO_4)_2$. $PbMoO_4$ was not formed when Sb_2O_3 was present in the glass melt. An increase in the potential beyond -300 mV with respect to the oxygen electrode resulted in the formation of a compound which was probably $K_2Pb(MoO_4)_2$ [8].

A quantitative analysis of the layers was performed only in study [5] where for glass A (cf. table 1) the composition of the layer was 60 Mo, 11 Pb, 4 K (wt.%), the rest being oxygen.

All the investigations of the layers of reaction products indicated that at least a part of the lead metal was formed inside the layer of reaction products.

The above data on normal potentials show that the oxidation of molybdenum can be sensitively influenced by even a small shift in the potential of the molybdenum electrode. Nishikata, Numata and Tsuru [10] pointed out the significant role of oxygen ion activity in the corrosion of metals in melts: If the metal ions are capable of forming a relatively insoluble oxide with the oxygen atoms, a layer of the oxide is formed on the surface of the corroded metal, and its potential is then that of the oxide electrode. The Me^{n+} ions formed by oxidation of the metal are bound by the reaction which can be written e.g. for even n as follows:

$$Me^{n+} + n/2\ O^{2-} \rightleftharpoons MeO_{n/2} \qquad (1)$$

As the activity of Me^{n+} ions is correlated with the activity of oxygen ions through the value of the product of dissolution, the potential of such an electrode will depend solely on the activity of oxygen ions:

$$\varepsilon_{ox} = \varepsilon_{0,ox} - RT/2F \ln a_{O^{2-}} \qquad (2)$$

The standard potential $\varepsilon_{0,ox}$ also includes the value of the dissolution product of the oxide. The behaviour of a metal in the melt then generally depends on the potential,

Table 1. Composition of the experimental glasses.

glass	content (wt.%) SiO_2	B_2O_3	Al_2O_3	PbO	BaO	ZnO	K_2O	Na_2O	As_2O_3	Sb_2O_3
A	65.00	-	-	21.00	-	-	14.00	-	-	-
B	58.78	-	-	25.27	-	1.50	12.06	1.75	0.20	-
1	59.89	-	-	24.80	0.62	-	9.28	4.90	0.20	0.04
2	60.72	-	-	24.41	-	1.52	6.99	5.86	0.22	-
3	60.98	0.52	-	24.14	-	1.66	6.96	5.52	0.22	-
4	60.20	-	0.05	24.20	-	2.10	10.1	2.55	0.21	-

but likewise on the activity of oxygen ions, expressed by its negative logarithm *pO* as demonstrated in figure 1. In dependence on potential and *pO* there exist three regions of corrosion behaviour: The stability region of the oxide (passivity), the metal stability region (immunity), and the ion stability region (activity). The horizontal line represents the boundary of reduction of the majority kation in the melt. The term passivity should be understood to mean that the passivating effect in the narrower sense of the word depends on the protective properties of the oxide layer.

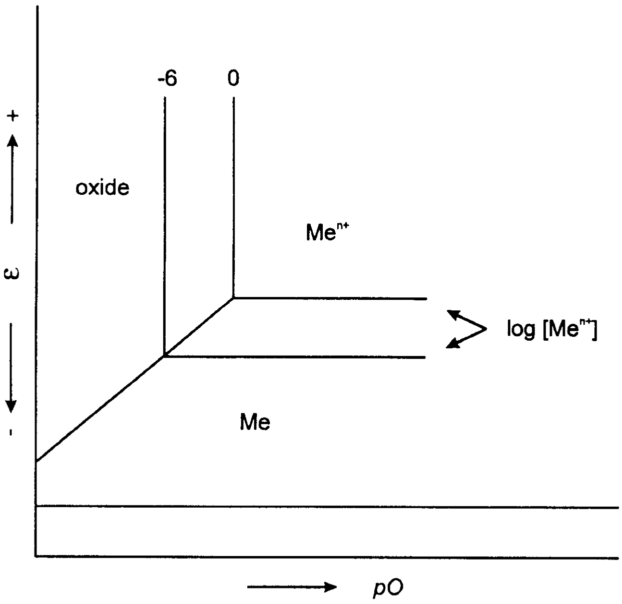

Figure 1. ε - *pO* diagram according to Nishikata, Numata and Tsuru [10].

The activity of oxygen ions may therefore affect corrosion of the metal in principle in both directions. It can contribute to a passive behaviour of the electrode, thus suppressing corrosion, but on the other hand may enhance the driving force of corrosion by shifting the potential towards its more negative values.

In silicate glass melts, the activity of oxygen ions O^{2-} is associated with the activity of non-bridging oxygens O^- and with the activity of bridging oxygens O^0 by means of the equilibrium

$$2\,O^- \rightleftharpoons O^{2-} + O^0. \qquad (3)$$

The equilibrium constant *K* of this reaction is given by the equation:

$$K = \frac{a_{O^0}\, a_{O^{2-}}}{(a_{O^-})^2}. \qquad (4)$$

The activity of oxygen ions should thus increase with increasing concentration of alkalies. The results of measuring oxygen ion activity in glass melts show that this is actually the case and it holds that $a_{O^{2-}} << [R_2O]$.

Not much experimental data on the effect of changes in alkali content on corrosion of metals in silicate melts is available. In her study of the corrosion of Pt electrodes, Eden [11] reports an accelerating effect of alkalies depending on glass melt basicity. The same effect was found by Petzold and Kahl [12] in connection with the corrosion of molybdenum in glass melts free of depolarizing admixtures. The latter authors, in contrast to Eden, ascribe this effect solely to a decreased viscosity of the glass melt.

It cannot be ruled out that alkalies influence the corrosion process in some other way and the first part of the present study intends to explain the effects of reaction products on the surface of molybdenum electrodes in lead glass melts, and those of alkalies, on the corrosion rate.

EXPERIMENTAL PART

The experiments were carried out with glass melts the composition of which is given in table 1. The experimental conditions are specified at the respective results. The molybdenum electrodes were prepared of molybdenum wire 1.2 mm in diameter (in one case, figure 8.4 mm in diameter), made by Safina a.s. The molybdenum was protected from oxidation by a silica glass capillary of a slightly larger inner diameter. Its bottom end defined the working area of the electrode protruding from the capillary.

In the experiments using alternating current or no current at all, a pair of identical parallel vertical electrodes was immersed in a crucible with molten glass, placed in an electric furnace. In the case of the 50 Hz experiments, the electrodes were supplied with alternating mains current via a regulating and isolating transformer. In the lower-frequency experiments, the electrodes were supplied with rectangular current from a galvanostat controlled by a function generator.

The elevated potential experiments were carried out so that following establishment of the current-free corrosion potential during two hr, the potential was increased by the given value. The potential was set and measured against an oxygen reference electrode provided by a Pt wire passing freely above the melt surface. In that case, use was made of a divided crucible with a hole in the partitioning wall. The reference electrode was placed in one half, and the working and auxiliary molybdenum electrodes in the other. The surface area of the auxiliary electrode was larger several times than that of the working one.

Following conclusion of the experiment, the heating and power supply were switched off and the crucible allowed to cool down in the furnace. The crucible was

Table 2. Composition of reaction products formed at 1350 °C in glass melt B.

		content (wt.%)				indices in formula $K_xPb_yMoO_z$		
no.	conditions	Mo	Pb	K	O	x	y	z
1	$i = 0$	64.8	11.6	2.9	20.7	0.11	0.08	1.92
2	50 Hz	66.2	11.7	3.0	19.4	0.11	0.08	1.76
3	0.155 Hz	66.5	12.9	3.1	18.3	0.11	0.09	1.65
4	0.055 Hz	68.2	9.0	4.1	18.8	0.15	0.06	1.65
5	$i = 0$, 2.5 hr	87.1	0.7	7.4	4.8	0.21	0.00	0.33
6	Inclusion I	42.4	6.4	18.9	32.3	1.09	0.07	4.57
7	Inclusion II	34.9	24.1	14.4	26.7	1.01	0.32	4.59
8	Separ.particle	28.9	48.1	4.1	18.9	0.35	0.77	3.92

Duration of experiment (analyses 1 through 4): 7 hr, current density (analyses 2 through 4): 0.25 A cm^{-2}, analysis 5: 0.5 A cm^{-2} Analysis 8: cf. caption to figure 9.

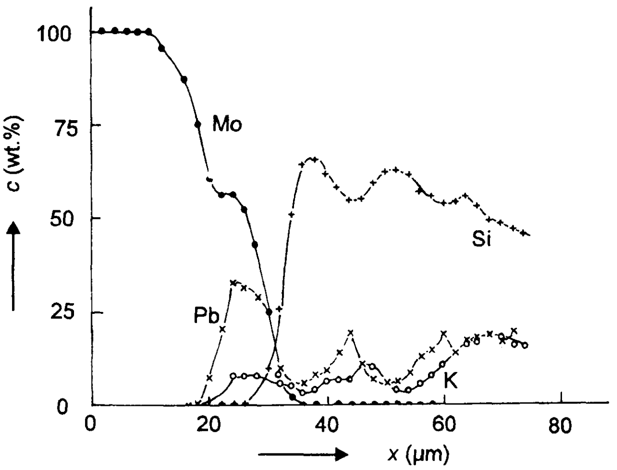

Figure 2. Concentration profile in the layer of reaction products. Glass B, 24 hr, 1250 °C, 0.5 A cm^{-2}, 50 Hz.

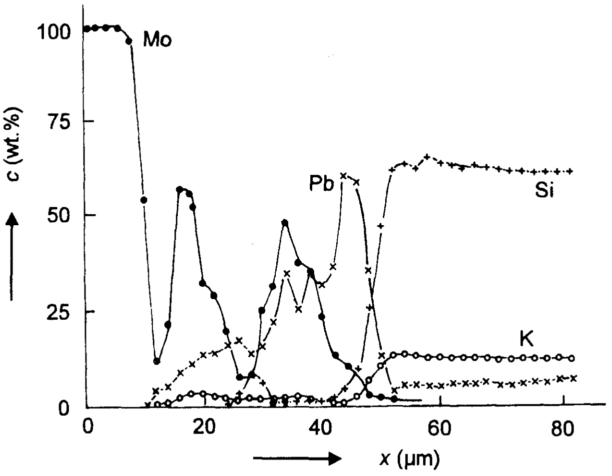

Figure 4. Concentration profile in the layer of reaction products. Glass B, 3.5 hr, 1350 °C, 0.5 A cm^{-2}, 0.8 Hz ($f>f_{min}$).

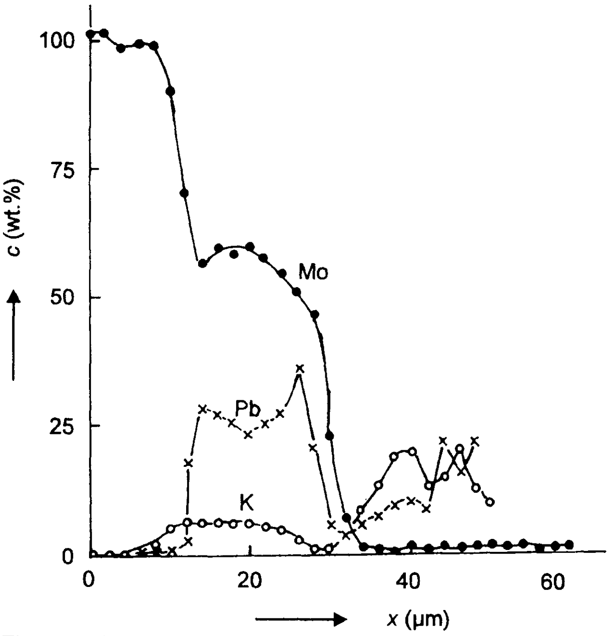

Figure 3. Concentration profile in the layer of reaction products. Glass B, 24 hr, 1250 °C, 0.5 A cm^{-2}, 14.3 Hz.

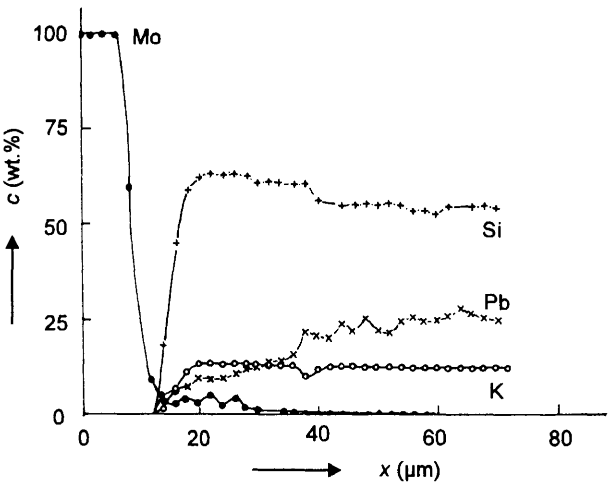

Figure 5. Concentration profile in the layer of reaction products. Glass B, 3.5 hr, 1350 °C, 0.5 A cm^{-2}, 0.3 Hz ($f<f_{min}$).

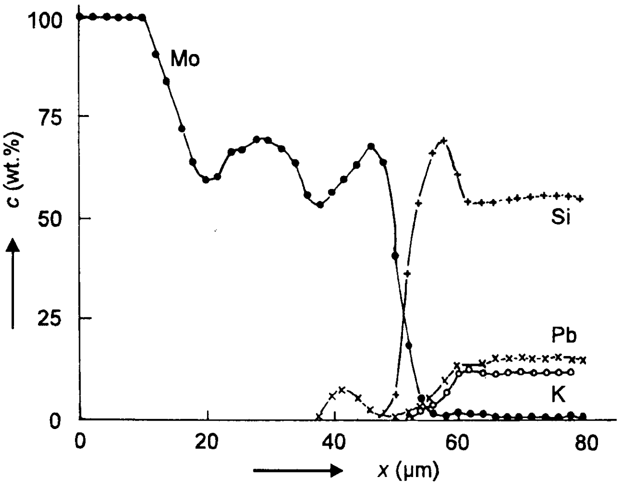

Figure 6. Concentration profile in the layer of reaction products. Glass B, 1250 °C, 2 hr at corrosion potential + 4 hr at potential raised by 500 mV.

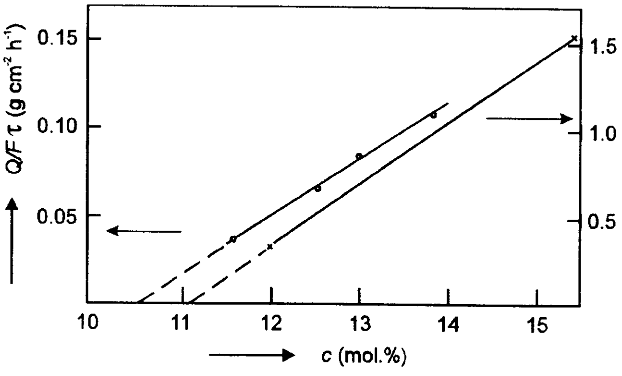

Figure 7. Lead precipitation rate vs. total molar concentration of alkalies in molten glasses containing 24 wt.% PbO (o) and > 30 wt.% PbO (x).

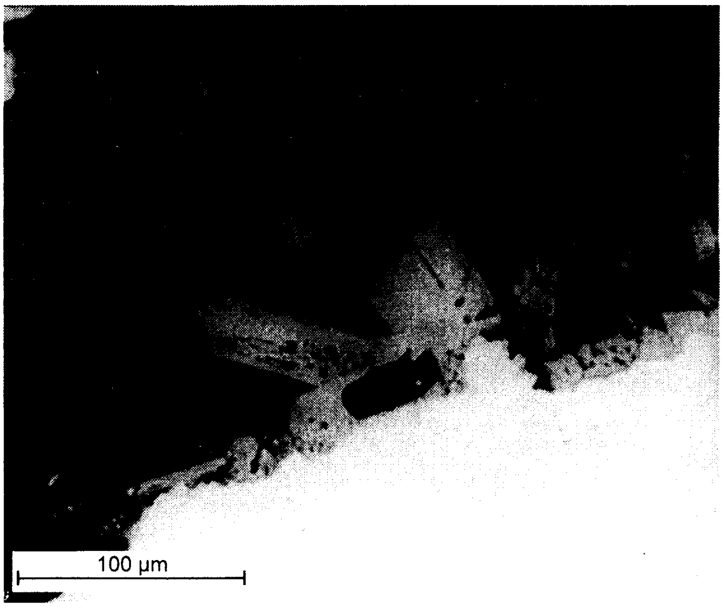

Figure 8. Separation of reaction products from Mo electrode (electrode at bottom right).
Glass A, 48 hrs., 1 A cm^{-2}, 50 Hz. Electron microprobe, composition.

then cut perpendicularly to its axis with a diamond saw, and polished sections for electron microanalysis were prepared. The electron microprobe was then used to display the overall composition in the neighbourhood of the electrode (figures 8 and 9) or a quantitative X-ray microanalysis at selected points (table 2, figures 2 through 6). was carried out.

The corrosion was characterized as the amount of precipitated lead collected at the crucible bottom, as this method allowed the process to be evaluated more precisely than by direct determination of corrosion or of the molybdenum dissolved. The lead was weighed directly following mechanical separation and removal of the remaining glass by dissolving in HF.

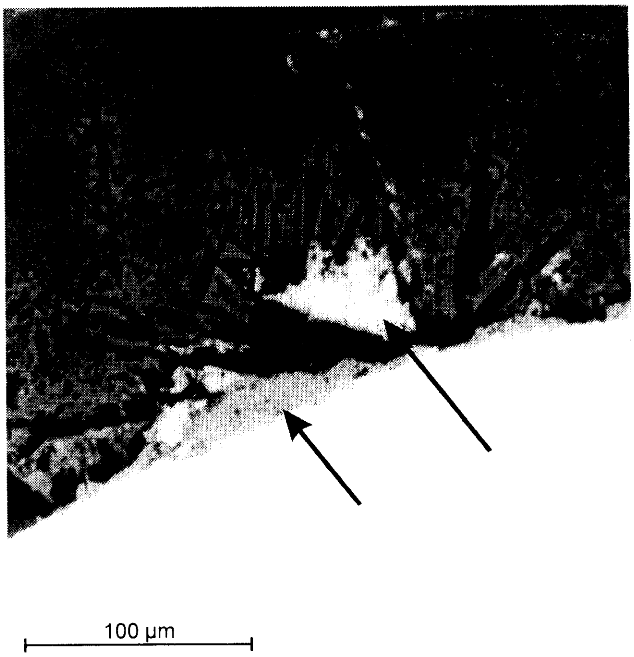

Figure 9. Particle detached from the layer and new layer of different composition within 3 hrs. of raising the potential by 500 mV. Electrode at bottom right, strongly crystallized glass higher up. Glass B, 1350 °C. Electron microprobe, composition.

A divided crucible was likewise employed for measuring the differences in potential in pairs of different glass melts. For this purpose, the crucible was of silica glass and the opening was placed at the top of the partitioning wall. Each half contained one of the glasses being compared, a platinum (oxygen) electrode and a molybdenum electrode.

RESULTS AND DISCUSSION

Layers of reaction products on the molybdenum electrode

It should first be pointed out that the electrode-glass melt interfaces show a considerable qualitative diversity. Examination of a large number of specimens indicate the existence of four types of interfaces: 1. The metal of the electrode adheres directly to the glass (possibly with a very thin intermediate layer containing oxygen, as shown below), 2. The electrode is coated with a layer of oxidic reaction products tenths to hundreds µm in thickness. 3. Precipitated lead adheres to the electrode. 4. A bubble of gas adheres to the electrode. The representation of these types of boundaries varies from place to place so that documenting the behaviour of an electrode at a "typical" point is a very difficult task. Moreover, the examinations were made on cooled-down specimens. As far as the layer of oxidic products is concerned, direct examinations show that in agreement with [8] the layer is probably at least partially in liquid form. Even under loading with symmetrical alternating current of mains frequency the layer may become detached (figure 8), and observation of load-free full-size operation electrodes showed that this can also occur when the electrodes are not in functional use [13]. As already mentioned in the introduction, the representation and thickness of the layer increase with decreasing frequency down to the frequency of the corrosion minimum.

Although glass B used in the experiments contained 12.06 wt.% K_2O as well as 1.75 % Na_2O, potassium only was determined in all of the analyses given below. The electron microanalysis established also sodium in concentrations of several tenths of percent, which is at the detection limit of the method in the given matrix. Sodium was likewise determined in analyses of inclusions carried out after their dissolving by atomic absorption. It may therefore be assumed that the reaction products contained both alkalies in proportions roughly corresponding to those in the glass.

Table 2 shows the composition of reaction products on the molybdenum electrode formed in glass B under the various conditions. The results were obtained by X-ray microanalysis. The concentration data on the left-hand side of the Table indicate that the compositions of typical reaction product layers do not show any significant differences (cf. analyses nos. 1 through 4), and also do not differ much from the composition found in glass A as mentioned in the introduction. Their composition is not substantially affected by the passage of alternating current, which also applies to the frequency lower than that of the corrosion minimum (analysis no. 4). A different composition is exhibited by the layer during the initial stage (analysis no. 5).

On the right-hand side of table 2, the compositions have been expressed as those of hypothetical binary molybdate. This part of the table is indicative of a considerable deficit in the content of alkalies and lead in analyses 1 and 4, but in particular a deficit in the content of oxygen. Even at an excess of free molybdenum oxide these products cannot contain mostly hexavalent molybdenum, and the oxygen content does not correspond to even tetravalent molybdenum. This finding is in good agreement with the assumption that trivalent molybdenum is formed [8]. According to the data on the ratio of equivalent amounts of precipitated lead and dissolved molybdenum, mentioned in the introduction, the overall process includes for the most part oxidation of molybdenum to valency 6 at the expense of reduction of lead. The bottom lines of table 3 give the composition of so-called molybdenum inclusions [13] whose samples were taken after passage through a production electric melting furnace with molybdenum electrodes and were at least several hr in contact with the glass melt. The variable colouring of these samples from dark grey to light shades is indicative of their gradual oxidation. The recalculated results listed in the right-hand side of the table show that the products have oxygen enough for forming molybdates with excess MoO_3. (The apparent excess of oxygen is probably due to an error in the analysis where the oxygen content was calculated as the difference from 100 %. Even at the maximum attainable accuracy of relative ±1 % for the majority components (Mo, Pb), the possible error in the determination of oxygen may be several times higher.) Additional oxidation of molybdenum may thus take place by contact with the glass melt of the products in the layer adjacent to molybdenum.

Figure 9 gives the composition of the region at the edge of the electrode for a sample from which particles were probably detached following an increase in potential by 500 mV, and on which formation of a new layer has started. Whereas the newly formed layer adhering to the electrode comprises only molybdenum and oxygen, the separated particle has a composition (analysis no. 8 in table 2) which is much closer to the composition of inclusions than to that of the typical layer of reaction products. Molybdenum is therefore oxidized to valency 6 at the latest immediately after separation of the original layer from the electrode. The remaining layer on the electrode has ample oxygen corresponding to molybdenum valency 6. It cannot therefore be ruled out that the separated particle becomes oxidized by the increased potential already before its becoming detached from the electrode.

The data given above were obtained by point analyses of selected places having surfaces of the best possible quality, and located approximately halfway the thickness of the reaction products. To obtain information on the course of concentrations within the layer and in the adjacent glass, point analyses on another series of specimens were made along a line perpendicular to the electrode-glass interface (figures 2 through 6). There was the disadvantage that the analyses could not avoid points with lower-quality surfaces and inhomogeneities, including crystallized glass melt and lead droplets. It may be pointed out that the concentrations of none of the samples were in disagreement with the results of analyses listed in table 2, with the exception of a higher mean content of lead.

The courses of concentrations in specimens loaded with alternating current are shown in figures 2 through 5. The courses at 1250 °C in figures 2 and 3 support the earlier finding [6] in that thicker layers of reaction products arise in the region of very low frequencies than at the mains frequency. At 1350 °C, when the corrosion proceeds at a significantly higher rate, the course of concentration, despite certain irregularities, shows an increase in lead concentration from the electrode towards the outer edge of the reaction product layer. In all the cases of reaction products being formed under the effect of alternating current (i.e. in figures 2 through 4), the concentration of lead at the layer-glass interface is higher than that in the adjacent glass. This indicates existence of a chemical bond of lead in the layer. A decrease in molybdenum concentration from the electrode towards the glass can also be observed in figures 2 through 4. On the other hand, the course of potassium concentration in all of the layers described is flat, decreasing at both sides of the layer. Figure 5 shows the courses of concentrations at the point where at the frequency lower than that corresponding to the minimum corrosion rate, there is no layer of corrosion products. The adjacent glass layer was found to be depleted of lead to a distance of about 50 μm from the interface, and enriched with dissolved molybdenum. The lead depletion of glass is associated with SiO_2 enrichment, the latter being responsible for crystallization of glass close to the electrode (compare with figure 9). Of interest is the constant concentration of potassium in the glass, reaching up to the region where even the apparent concentrations of the other components change abruptly, possibly by the effect of surface topography in the region. A similarly flat course of potassium concentration can be observed in figure 4 where a layer of corrosion products is present.

There is the question as to what part is played by the presence of reaction product layers in the kinetics of the corrosion process. A higher representation and layer thickness in the region where corrosion is suppressed by lower-frequency current indicate that contrary to the assumption by Rudolph et al. [8], the layers of reaction products formed at the corrosion potential or in its proximity actually protect the electrode at least to some extent, even though the corrosion is not by far suppressed to the degree corresponding to the region of higher potentials. Evidence for the protective effect of the layers was already presented in study [14] which succeeded in detecting and investigating a major area freed of reaction products, unfortunately not in a lead glass melt. A higher corrosion rate of the region was established, even though the effect of a local electric cell may also have been involved.

Different properties are exhibited by the layer of corrosion products formed at a potential raised by 400 mV over the current-free one (figure 6). Except for the outer skin, the layer does not contain potassium nor lead. The composition of the internal zone approaches that of MoO_3. This finding is in agreement with the results of examination and point analyses of products formed at a potential increased by 500 mV over the current-free one. Figure 6 illustrated a decrease of molybdenum content in the direction towards the outer face of the layer, and comparatively high concentrations of lead in the glass adjacent to the layer of reaction products. This indicates that the precipitation of lead was suppressed.

Steep increases in molybdenum concentration up to 100 % at the inner face of the reaction products can be observed in figure 2 and in particular in figure 6. This seems to indicate the existence of still another layer in which the very low mean molybdenum valency is subject to a stepless change. Existence of such a layer is also supported by some micrographs of the electrode-glass interface; however, the small differences in brightness did not permit adequate reproduction.

The discussion of the given part of products may be concluded by pointing out that even layers of reaction products formed under no-current corrosion potentials or in their proximity do protect the electrode to some extent and that corrosion takes place in particular over the denuded areas. Additional information may be provided by an investigation of the effect of alkalies in the glass melt.

Effect of alkalies on the rate of corrosion of electrodes

The effect of the content of alkalies on the rate of corrosion of molybdenum electrodes in the unloaded state was studied on six commercially produced glass melts, of which four contained 24 wt.% PbO and two 30 wt.% PbO. The results are summarized in table 3 and in figure 7. The figure and the table show a linear course of the relation between corrosion rate (expressed as the rate of lead precipitation) and the sum of molecular concentrations of both alkalies in glasses 1 through 4. The ratio of the two alkalies does not play any role in the relationship. In the case of glasses 5 and 6 the corrosion rate also increases with the total content of alkalies. The linear relation for glasses 1 through 4 intersects the horizontal axis at a concentration of about 10.5 mol.%. The straight line passing through two points for the remaining two glasses intersects the horizontal axis at a concentration of about 11 mol.%, i.e. relatively close to the more reliable value for glasses 1 through 4.

The corrosion rates in glasses 5 and 6, which are higher by order of magnitude, cannot be explained by a higher working temperature. The results of measuring the temperature dependence of the corrosion rate [15] indicate that an increase in temperature from 1350 °C to 1380 °C of a similar glass melt containing 24 wt.% PbO would raise the corrosion rate by a factor of about 1.5. The much higher corrosion rates in glass melts 5 and 6 must therefore be also due to a higher content of lead oxide, but in particular to the different effect of arsenic and antimony trioxides in combination with lead oxide. Such combined effects would deserve a separate study.

Table 3. Effect of alkali content on rate of lead precipitation.

glass	c (mol.%)			$Q/A\tau$ ($\mathrm{g\,cm^{-2}\,h^{-1}}$)
	K_2O	Na_2O	Total	
1	7.64	6.12	13.77	0.1072
2	5.69	7.22	12.91	0.0808
3	5.66	6.81	12.47	0.0642
4	8.34	3.19	11.54	0.0355
5	8.68	6.77	15.46	1.55
6	8.81	3.21	12.02	0.336

Glasses 1 through 4: 24 % PbO, refined with As_2O_3 (overall composition listed in table 1), 7 hr, 1350 °C.
Glasses 5 and 6: 31-32 % PbO, refined with Sb_2O_3, 5 hr (no. 5) and 7 hr (no. 6), 1380 °C.

Table 4. Comparison of potential differences of molybdenum and oxygen electrodes (0.021 MPa) in pairs of glass melts showing the greatest differences in the concentrations of alkalies (cf. table 3).

glass pairs	potential difference (mV) Pt electrodes	Mo electrodes
4 vs. 1	64.4	18.9
6 vs. 5	108.9	24.2

According to the relationship plotted in figure 7 one can expect that at a total alkali concentration lower than about 10.5 mol.%, the corrosion rate would decrease almost to zero. This behaviour can be explained by the following possible mechanisms:

1. The content of alkalies affects the activity of oxygen ions in the glass melt, and thus, in the sense of equation (2), also the potential of the oxide electrode. The concentration limit established is then related to the fact that the corrosion potential also approaches the equilibrium potential of the depolarizer.
2. The content of alkalies affects the rate of dissolution of the layer of reaction products on the electrode.
3. The content of alkalies affects the viscosity and the transport rate in the glass melt.

Table 4 demonstrates the difference between the potentials of molybdenum electrodes placed in glass melts having the largest difference between the concentrations of alkalies, and for comparison, also the difference between the potentials of oxygen electrodes in the same pairs of glasses. The difference between equilibrium potentials of oxide electrodes operating at various activities of oxygen ions follows from equation (2) and depends on the ratio of oxygen ion activities in the two glass melts. It can be readily proved that the same relationship holds for the difference between the potentials of the oxygen electrodes, insofar as they operate under the same partial pressure of oxygen. The table shows that the difference in the potentials of molybdenum electrodes determined is much smaller than the difference in the potentials of the oxygen electrodes. Although the corrosion potential of the molybdenum electrode is shifted, with respect to the equilibrium potential of the oxide electrode, towards more positive values (and the shift may differ at different potentials), the established difference between the potentials of the molybdenum electrodes seems to be very small. Moreover, all of the experimental values include the diffusion potential at the joint of the two electrolytes, which increases the potential difference for both types of electrodes.

These facts will appear in a different light on considering the increased corrosion of denuded areas, or of surfaces coated with a thin layer containing solely oxygen. The potential of such an area with respect to the glass melt will obviously differ from that covered with a layer having the composition described in table 2. Whereas the potential of the coated area will probably depend very little on the composition of the glass melt, influencing of the potential according to equation (2) can be expected to occur just at the denuded point. The potential measured will then acquire values somewhere between the potentials of the denuded areas and those of the coated ones. For this very reason the potential will be affected by the glass composition significantly less than would correspond to equation (2). It cannot be ruled out that the role of the insoluble compound binding the metal ions is not played by the oxide, but by some more complex compound of molybdenum, oxygen, alkalies and lead. Inadequate knowledge of the high-temperature properties of such compounds has so far prevented this possibility from being examined. The effects of microcells resulting from non-uniform coating of electrodes should also be considered.

Influencing of the glass melt transport is improbable in particular because on this principle it would hardly be possible to explain the decrease of the corrosion rate down to zero below a certain limit concentration of alkalies.

The last remaining explanation is based on a reaction of the layer of reaction products with the glass melt, where the rate of the reaction (depending on the content of alkalies) determines the thickness of the layer, and thus also the rate of the entire process.

CONCLUSION

1. Corrosion of molybdenum electrodes in lead glass melts, both under load of symmetrical alternating current and without current, results in the formation of a layer of oxidation products containing molybdenum, oxygen and a small amount of alkalies and lead. The molybdenum to oxygen ratio corresponds best to molybdenum valency of 3. The layer protects to some degree the electrode and the corrosion affects mostly the denuded areas. It cannot be ruled out that under this layer the metal is covered by still another thin layer comprising just molybdenum and a small amount of oxygen whose concentration decreases in the direction towards the molybdenum metal.
2. At a potential increased by 400 mV or more over the current-free one, the layer consists only of molybdenum and oxygen. It contains no potassium and little or no lead. The molybdenum to oxygen ratio corresponds to a molybdenum valency of 6.
3. The dependence of corrosion rate on the sum of molar concentrations of the two alkalies is linear, with corrosion onset at about 10.5 mol.%. The ratio of the two alkalies is of no consequence here. A possible explanation of this behaviour was proposed.

Acknowledgements

The authors wish to thank Ing. J. Lubas for the design and preparation of direct observation of reaction products on the molybdenum electrode.

This work was supported by Czech Grant Agency for Science (Grant no. 106/93/1205).

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Translated by K. Němeček.

KOROZE MOLYBDENOVÝCH ELEKTROD V OLOVNATÝCH SKLOVINÁCH

ČÁST I - REAKČNÍ PRODUKTY A VLIV OBSAHU ALKÁLIÍ

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Cílem práce je přispět k mechanizmu koroze molybdenových elektrod v olovnatých sklovinách. V úvodu jsou shrnuty poznatky o vztahu mezi vylučováním olova a korozí molybdenu, podle nichž je molybden pravděpodobně oxidován nejprve do mocenství 3 a dále z větší části do mocenství 6. Je ukázána role kyslíkových iontů ve sklovině, jejichž aktivita rozhoduje o tvorbě vrstvičky oxidu na povrchu kovu. Tím může být jednak koroze brzděna, naproti tomu se však může uplatnit zvýšení hnací síly korozního procesu.

V experimentální části jsou uvedeny výsledky analýz vrstev reakčních produktů na molybdenové elektrodě. Podle nich se na povrchu elektrody při korozním potencionálu vytváří vrstva kyslíkových reakčních produktů obsahujících molybden, draslík, olovo a malé množství sodíku. Svým obsahem kyslíku odpovídá tato vrstva nejlépe mocenství molybdenu 3. Je ukázáno, že tato vrstva se může samovolně odlučovat a že k největší korozi dochází pravděpodobně na místech, která touto vrstvou nejsou pokryta. Při zvýšení potenciálu o 400 mV nebo více obsahují vrstvy na molybdenu pouze molybden a kyslík v poměru blízkém složení MoO_3.

Byla dále vyšetřována závislost rychlosti koroze vyjádřené jako rychlost vylučování olova na obsahu alkálií ve sklovině. Bylo zjištěno, že rychlost koroze je úměrná součtu molárních koncentrací obou alkálií sníženému o hodnotu, která činí přibližně 10,5 mol.%. Na poměru obou alkálií přitom nezáleží. Je navržen výklad tohoto chování založený na tom, že alkálie, které zvyšují obsah nemůstkových kyslíků ve sklovině a tím i koncentraci iontů 0^{2-}, přispívají ke zvýšení hnací síly koroze na místech zbavených vrstvy reakčních produktů.