

CATHODIC BEHAVIOR OF MOLYBDENUM ELECTRODE IN VARIOUS GLASS MELTS

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The cathodic behavior of molybdenum electrode has been investigated in model glass melt of the basic composition of 16Na₂O, 10CaO, 74SiO₂ (wt.%) with additions of SO₃ or Sb₂O₃ or without additions at 1400°C. There exists a range of cathodic potentials reduced by some hundreds millivolts against the rest state where the reduction of electroactive species acting as depolarizers of molybdenum corrosion may be suppressed. The potentials of the maximum suppression of lead or antimony precipitation correspond to potentials at which the anodic molybdenum oxidation finishes. The layers of molybdenum silicides have been not found on the electrode at those potentials. In glass melt containing sulfur trioxide, the sulfur depletion of glass in electrode vicinity takes place. At more reduced potentials, the subsequent formation of silicon and formation of the silicides Mo₃Si, Mo₅Si₃ and MoSi₂ occurs. The formation of silicon and silicides is impeded by presence of the electroactive glass components mentioned above. The overall cathodic current increases at the same time. That is probably due to the preferential reduction of the electroactive species by reduced alkali metal.

INTRODUCTION

The cathodic behavior of molybdenum electrode in glass melt plays an important role in electrochemical protection of heating electrodes and other molybdenum parts exposed to glass melt. The cathodic behavior is important not only in application of the cathodic protection itself, but also in anodic protection, where introduction of one or more auxiliary electrodes, which represent the cathodes, is necessary.

It is obvious that the anodic corrosion i.e. molybdenum oxidation is fully suppressed at a sufficiently negative potential without presence of any protective layers. On the contrary, the rate of depolarization reactions which are frequently associated with separation of metals (lead, antimony) should increase in that potential region. Results of some papers show, however, that the rate of depolarization reaction exerts a minimum at a certain potential. That was proved quantitatively for lead precipitation from 24% lead crystal glass [1,2]. A remarkably lower intensity of the glass blackening in the proximity of the electrode could be observed in soda–lime–silica glass refined by antimony oxide if the potential was reduced from the rest state by 250 mV [3]. No sulfide layer was found on the electrode in the same glass refined by sulfate if the potential was reduced by 200 mV [4]. The suppression of the anodic molybdenum oxidation at a sufficiently negative potential was confirmed in all the cases quoted.

The presence of protecting silicide layers may be an explanation for the suppression of both the corrosion and depolarizing reaction. Rüssel and Kämpfer [5,6] delimited the optimal conditions for the formation of compact silicide layers on the molybdenum electrode in glass refined by antimony oxide. The relation of the presence of silicide layers to molybdenum corrosion or to antimony precipitation was not studied directly. However, the occurrence of silicide layers on protected electrodes could not be demonstrated when a well functioning cathodic protection (the corrosion suppressed almost by 50%) was applied commercially [7,8]. Silicide layers were found in the region of suppressing corrosion processes neither in the papers quoted above [1-4]. A double silicide layer was formed if the potential was reduced by 600 mV with respect to the rest state. The composition of the layers corresponded well to that of MoSi₂ for the outer layer and to Mo₅Si₃ for the inner layer. It was found in the paper [6] that the quality of silicide layers was deteriorated after fresh raw materials were added to the glass melt. That may be associated with antimony precipitation prior to silicide formation, the silicide formation under given conditions taking place only after the reserve of antimony oxide becomes exhausted.

The cathodic formation of silicide layers on molybdenum in a soda-lime-silica glass melt was already investigated by Vander Poorten, Haan and Olivier [9]. The formation of the layer of silicide MoSi₂ was

described. A layer of silicide Mo_5Si_3 occurs under that layer. Characteristic course of the cathodic polarization curve with a local maximum of cathodic current was described. The authors explain this course by reduction on Na^+ cations taking place primarily. Metallic sodium then reduces silicates from the glass melt to silicon. At the beginning, the rate of those processes increases with potential decrease. In following potential region, a limited rate of the silicon diffusion into molybdenum starts to manifest itself, hence the reaction rate stagnates or starts to decrease. After the saturated concentration of silicon in molybdenum is attained, the reaction rate starts to increase again together with decreasing potential and formation of silicides starts. The observed increase of the height of the maximum of the cathodic current at mixing the melt is not in principal discrepancy with that mechanism. The relation of the silicides formation to the corrosion and depolarization reactions was not studied and neither the content of depolarizers in the glass melt used was specified more closely.

Recently [10], the cathodic suppression of the antimony precipitation from the glass melt refined by antimony trioxide was demonstrated directly. In accordance with the qualitative observation quoted above [3], the amount of precipitated antimony was reduced by the factor of three at the potential reduced by 200 mV against the rest state, increasing again at more reduced potentials. The same suppression of metal precipitation was also observed when the glass melt was repeatedly renewed.

The subject of the present paper is the relation of the rate of anodic molybdenum oxidation and the rate of depolarization reaction on one side and silicon and silicide layers formation on other side.

EXPERIMENTAL

The experiments were performed in three model soda-lime-silica glass melts of the basic composition of 16 Na_2O , 10 CaO , 74 SiO_2 (wt.%) modified by addition of 0.49 % SO_3 or 0.88 % Sb_2O_3 , the ratio of the major components remaining unchanged, or in basic glass melt without additions. The experiments were made at the

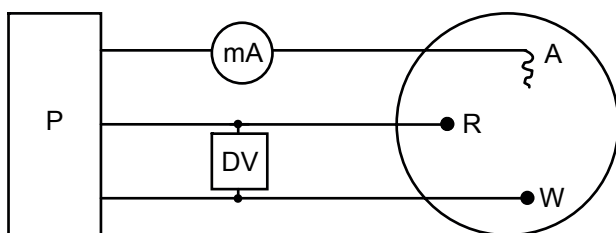


Figure 1. Wiring scheme for potentiostatic measurements. P - potentiostat, A - auxiliary electrode, R - reference electrode, W - working electrode, DV - digital voltmeter.

temperature of 1400°C at a constant potential maintained by means of potentiostat in the three-electrode arrangement (figure 1). The duration of the experiments was 5 h. The vertical working electrode made of molybdenum wire possessed an area of 0.765 cm^2 . The auxiliary electrode was made of the same material. The potential of the working electrode was fixed against the simple platinum reference electrode realized by a platinum wire passing through the surface of the melt. The glass content in the crucible was 68 g. More details concerning the experimental arrangement, preparation of model glasses and evaluation of the corrosion may be found in [4].

The overall current necessary to maintain the potential demanded was recorded during the experiments. Mean current densities were obtained by the integration of their time courses related to the electrode area at every potential. Based on those mean current densities, "stationary" polarization curves were obtained. The loss of electrode diameter was evaluated on sections cut perpendicular to electrode axis after finishing every experiment. The corrosion losses were expressed as corrosion current densities, considering molybdenum oxidation to Mo(VI). The polished electrode sections were analysed by methods of optical and electron microscopy completed by EDS and electron microprobe analysis (in sulphur containing glass). The results of the analysis of silicide layers (table 2 and 4) were re-calculated to pure Mo + Si.

RESULTS AND DISCUSSION

The rest corrosion potentials of molybdenum in the glass melts studied measured against the simple platinum reference electrode are given in table 1 and compared with the values obtained using the oxygen electrode with zirconium oxide and oxygen partial pressure given by the equilibrium in the Ni + NiO mixture. It may be seen that the corrosion potentials measured against both the reference electrodes increase at the addition of the corrosion depolarisers in the same order. The results given in following parts as dependent on electrode potential are given as the potential reduction related to the values given in the left column of the table 1.

Table 1. Rest corrosion potentials of molybdenum electrode in investigated glass melts.

Glass melt	Potential (mV)	
	Pt, O_2 /melt	Pt, Ni+NiO/ZrO ₂ /melt
NCS	-808	-288
NCS+Sb ₂ O ₃	-793	-260
NCS+SO ₃	-704	-237.5
lead	-630	-164

NCS - soda-lime-silica glass (1400°C)
lead - 24 % PbO lead glass [2] (1380°C)

Behavior in sulfate refined glass melt

The goal of the measurements in this glass melt was to complete the results obtained in the same glass melt previously [4], especially by the analysis of reaction products in the narrower potential range. Similarly as it was found previously, no layer of oxidation products was found at the potential reduced by 200 mV where the oxidation stops. Penetration of silicon into the electrode down to the depth of about 5 μm could be demonstrated, however. Figure 2 shows the glass - electrode boundary at the potential reduced by 300 mV. It can be seen that a sharply distinguished layer about 5 μm thick of the composition given in table 2 forms on the electrode edge. The composition of this layer corresponds best to that of the compound Mo₃Si. A triple layer was observed at the potential reduced by 400 and 500 mV (figure 3): Towards from the electrode center to its edge, a layer of the similar composition as described at -300 mV occurs followed by a layer containing about 14.8 % Si (table 2). This composition is equal to that of the inner part of the layer described formerly at the potential reduced by 600 mV and corresponds to the

compound Mo₅Si₃. A thin layer of almost the same composition as the inner part occurs at the electrode - glass boundary. Hence, at shifting the potential towards more negative values, the molybdenum oxidation stops at first, the sulfide layer disappears at the same time and penetration of silicon (as a consequence of the reduction of sodium cations) starts. With the continued potential reduction, the layers of the compounds with lower and higher silicon content are subsequently formed. Concerning the outer, very thin layer, very rapid oxidation of the outer part of the Mo₅Si₃ layer immediately after switching off the potentiostat is likely to take place. The spongy appearance of this layer, very similar to that of the transformed layers in reaction of the protective silicide based coatings on molybdenum with glass melt [12] supports that assumption.

The analyses of the glass adjacent to the electrode as dependent on electrode potential and the distance from the electrode are listed in table 3. It may be seen that the sulfur concentration in the glass melt adjacent to the electrode at rest potential is practically independent of the distance from the electrode and only slightly lower than the concentration in original glass. On the

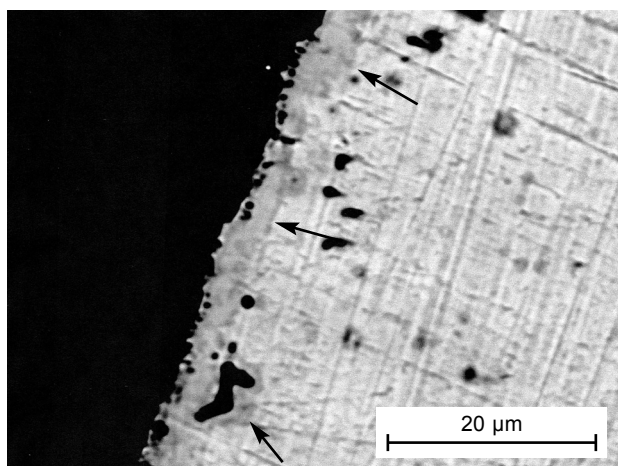


Figure 2. Beginning of the silicide formation in the glass melt containing SO₃ at a potential reduced by 300 mV. The layer/molybdenum boundary indicated by arrows.

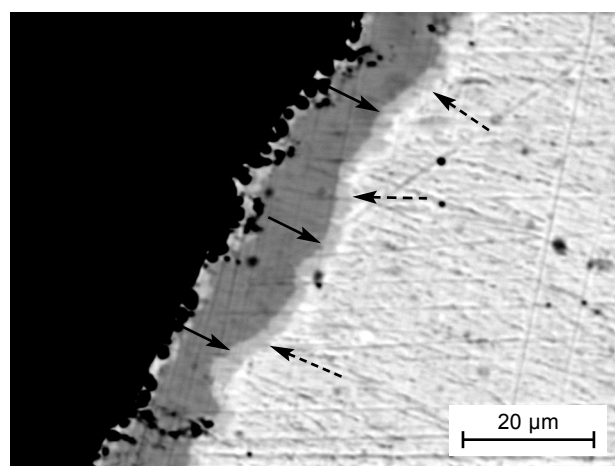


Figure 3. The triple layer formed in the glass melt containing SO₃ at a potential reduced by 400 mV. The inner layer/molybdenum boundary indicated by dashed arrows, the boundary between the inner and central layer indicated by full arrows.

Table 2. Composition of silicide layers on molybdenum electrode formed in soda–lime–silica glass melt with addition of SO₃ at various potentials. Re-calculated values given in brackets.

Element	Potential shift/site (mV)						Theoretical composition		
	-300	-400			-500			Mo ₃ Si	Mo ₅ Si ₃
		outer	central	inside	outer	central	inside		
Mo	86.66 (91.92)	88.74 (91.39)	82.02 (85.3)	87.17 (91.3)	87.89 (91.4)	80.92 (85.13)	82.88 (90.01)	91.11	85.06
Si	7.62 (8.08)	8.36 (8.61)	14.13 (14.70)	8.31 (8.7)	8.27 (8.6)	14.13 (14.87)	9.2 (9.99)	8.89	14.94
Na	0	0.113	0.10	0.06	0.00	0.02	0.35		
Ca	0.04	0.06	0.02	0.032	0.025	0.04	0.35		
O	5.68	2.73	3.73	4.43	3.81	4.89	7.22		

contrary, the glass in electrode vicinity is considerably sulfur depleted at potentials reduced by 200 mV and more. The migration of these anions towards the anode, i.e. auxiliary electrode is a possible explanation. The higher sulfur concentrations found at greater distances from the electrode at potential reduced by 200 mV as compared with those found at -400 mV are in accordance with this explanation.

Behavior in glass melt containing antimony trioxide

Figure 4 shows the "stationary" polarization curve of molybdenum electrode in glass melt containing antimony trioxide. It may be seen that the molybdenum oxidation stops at the potential reduced by about 200 mV also in this glass melt. The overall cathodic current course shows an increase at the beginning followed by a stagnation between -100 and -300 mV and another increase follows. This current course resembles that described formerly [2,3] under simultaneous effect of alternating current. Concerning the cathodic reaction products, the silicon penetration into the electrode was found at as low potential as -450 mV against rest state potential, namely to the depth of about 75 μm (figure 5). Only at the potential reduced by 500 mV a non-regular layer 2 to 3 μm thick appears on the electrode edge. Its content of 7.2 % Si does not differ considerably from that in Mo_3Si . At the potential reduced by 600 mV, a non-regular silicide layer 5 to 14 μm thick consisting

Table 3. Sulfur content in glass in wt. % in dependence on the distance from the electrode at various potentials. The original sulfur content was 0.196 wt.%.

Potential shift (mV)	Distance from the edge of the electrode (μm)				
	5	30	100	500	2500
0	0.220	0.152	0.163	0.176	–
-200	0.160	0.056	0.075	0.084	0.144
-300	0.057	0.044	0.052	0.056	–
-400	0.045	0.073	0.050	0.024	0.035

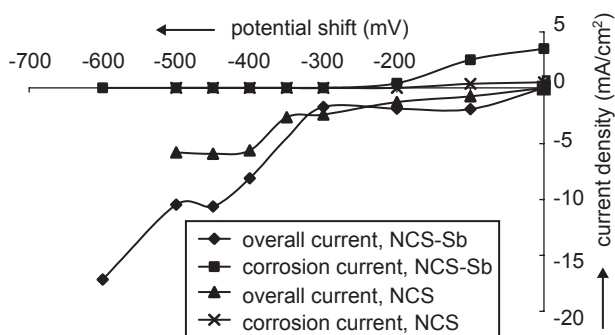


Figure 4. "Stationary" polarization curves and corrosion currents in soda-lime-silica glass melts with addition of Sb_2O_3 (NCS-Sb) and without additions (NCS).

again of two parts with higher and lower Si content appears (see table 4). Some bubbles could also be observed on the electrode at that potential.

Behavior in soda-lime-silica glass without refining agents

The experiments in this glass melt should show the influence of the presence of refining agents acting as corrosion depolarizers on the formation of the silicon containing layers on the electrode. Figure 4 shows also the "stationary" polarization curve of molybdenum electrode in this glass melt. As it may be expected, the corrosion rate is considerably lower in this glass melt where dissolved oxygen represents the only corrosion depolarizer. The molybdenum oxidation stops also in this glass melt at the potential reduced about by 200 mV against the rest state. The overall cathodic current course exerts an increase up to -300 mV, a stagnation between -300 and -350 mV followed by a steep increase and by another stagnation.

Table 4. Composition of silicide layers on molybdenum electrode in soda-lime-silica glass melt with addition of Sb_2O_3 at various potentials. Re-calculated values given in brackets. For theoretical silicides compositions cf. table 2.

Element	Potential shift/site (mV)		
	-500	-600	
		outer	inside
Mo	92.77	80.89 (86.15)	84.49 (91.52)
Si	7.23	13.00 (13.85)	7.83 (8.48)
Na	–	0.12	0.08
Ca	–	0.00	0.07
O	–	5.67	7.49

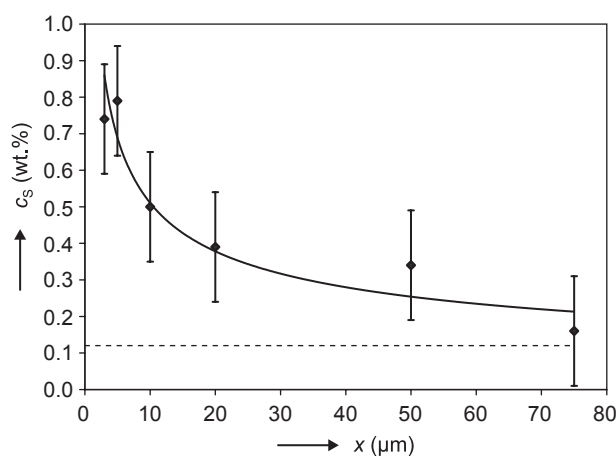


Figure 5. Silicon concentration c_s (wt.%) vs. penetration depth x (μm) at a potential reduced by 450 mV in soda-lime-silica glass with Sb_2O_3 addition. Dashed line: "background", cf. figure 6 and the corresponding text.

Penetration of silicon into the electrode has been found in both the foregoing glass melts. It is necessary, however, to check the reliability of the data with respect to the presence of the glass with high content of 74 wt.% SiO₂ (34.6 wt.% Si) on the contact with the analyzed thin layers. Figure 6 shows the concentration profiles of silicon in molybdenum found in glass without refining agents at three different potentials including the rest potential where no silicon reduction takes place. The concentrations found at the rest potential show no gradient, they fluctuate, however, around an average value of 0.125 %. A considerably higher value found at a very low depth of 1.5 μm represents an exception. This is in accordance with the distortion that may be expected down to the depth of 2 to 2.5 μm with respect to the volume excited at the used accelerating voltage. The values found in greater depth at that potential should be attributed to the effect of fluorescence. With respect to this "background", the silicon penetration found at -100 mV cannot be considered as fully demonstrated. A conclusive silicon penetration down to the depth of 50 to 75 μm occurs at the potential reduced by 300 mV.

Formation of a compact layer of MoSi₂ 16 μm thick and similar to that described recently [4] has been found already at the potential reduced by 400 mV in this glass melt. An amply occurrence of great bubbles on the electrode could be observed at a potential reduced by 350 mV.

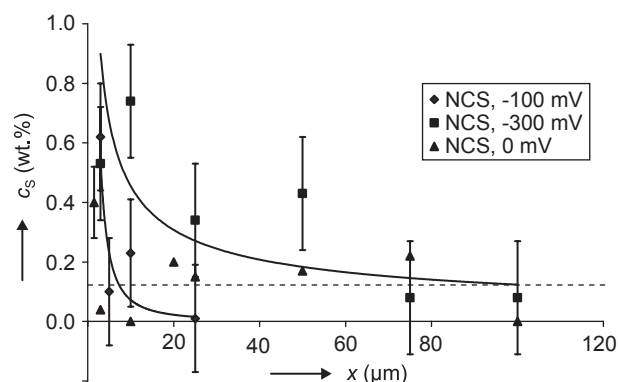


Figure 6. Silicon concentration c_s (wt.%) vs. penetration depth x (μm) at potentials reduced by 100 mV and 300 mV in soda–lime–silica glass without additions as compared with the "background" data found at rest potential.

The comparison of the cathodic behavior in various glass melts

Table 5 summarizes the occurrence of various processes and reaction products in the above three glass melts as dependent on electrode potential. The table is completed by the data involving determination of precipitated antimony in the same glass melt as dealt in previous paper [10] and cathodic behavior of molybdenum electrode in lead glass melt containing 24% PbO [1,2]. Some data concerning the sulfate refined glass melt have also been overtaken from [4]. It is obvious that the oxidation of molybdenum always stops at potentials reduced by 200 to 250 mV in all the soda-lime-silica glass melts and by 400-500 mV in lead glass melt. Simultaneously, minima of the amount of precipitated metals demonstrate themselves at those potentials in glass melts containing lead and antimony oxides. (In glass melt containing SO₃, the sulfide formation stops at that potential). Beginning with or below that potential, the silicon penetration into molybdenum starts that may be followed by formation of silicide layers at the most negative potentials. Hence, the suppression of the lead and antimony precipitation is not associated with the presence of detectable silicide layers on the electrode surface. This is in accordance with what was found in the application of the cathodic electrode protection [7]. The found correlation of the maximum suppression of metal precipitation with finishing of the anodic molybdenum oxidation may be explained in two ways: 1. The metal precipitation at potentials not very remote from the corrosion one is enhanced in presence of a layer of oxidation products (with composition different from that of the passivation layer). The high lead concentration found in the layer of oxidation products on molybdenum electrode in lead glass melt at potentials corresponding to maximum corrosion and lead separation rate [2] seems to support this explanation. 2. The presence of silicon in the surface layer increases the metal precipitation overvoltage. The solubility of silicon in molybdenum amounts only 1.0 wt.% at 1820°C [11]. Still lower solubility may be expected at 1400°C. The silicon occurrence found only at potentials substantially

Table 5. The occurrence of reaction products in dependence on the glass composition and on the shift of the potential. The meaning of the glass designation is the same as in table 1.

Glass melt	Phenomenon/Potential shift (mV)					
	End of Mo oxidation	Minimum point of depolarizer precipitation	Beginning of silicon penetration	Beginning of formation		
				Mo ₃ Si	Mo ₅ Si ₃	MoSi ₂
NCS+Sb ₂ O ₃	-200 ÷ -300 (-125 ÷ -250 [3])	-200 [10]	-450	-500	-600	Not found
NCS+ SO ₃	-200	-200*	-200 ? (a hint)	-300	-400	-600 [4]
NCS	-200	-	-100 ÷ -300	Not found	Not found	-400
lead	-400 ÷ -500 [2]	-400 ÷ -500 [2]	Not found	Not found	Not found	Not found

* Mo₂S₃ layer not observed beginning with that potential

more negative than those of the minimum antimony precipitation in the glass melt containing antimony trioxide is also in discrepancy with the second explanation. On the other hand, the limited accessibility of the layers in the closest vicinity of the glass-metal boundary to analysis shown above does not enable to exclude fully the effect of silicon formation. The migration of sulfate anions from the cathode takes place as a phenomenon specific for the glass melt containing SO_3 .

As for the presence of silicide layers on the electrode, it was demonstrated in accordance with the paper [9] that the formation of those layers is preceded by silicon precipitation. Only then the formation of sharply limited layers of Mo_3Si , Mo_5Si_3 and MoSi_2 subsequently follows. The formation of the silicide layer of the composition corresponding to Mo_3Si , not mentioned in [9] but described in phase diagram of the system Mo-Si [11], has already been observed in the paper [4] in glass melt containing SO_3 . It has been found now also in glass melt containing antimony trioxide. It may be seen from the figures 2 and 3 that silicide layers with lower silicon content grow from outside towards the inside of the electrode. That is also in accordance with the idea expressed in [9] according to that the silicides form only after the solubility limit of silicon in molybdenum is attained. It is also obvious from Table 5 that the silicon precipitation and subsequent silicide formation take place far more easily in absence of depolarizers, i.e. in soda-lime-silica glass melt containing no depolarizers or in sulfate refined glass melt where the sulfate anions are removed to a greater extent from the electrode vicinity. This is in accordance with the observation of Rüssel and Kämpfer [6]. The probably cause of this behavior is the competition of both the processes as it will be discussed below.

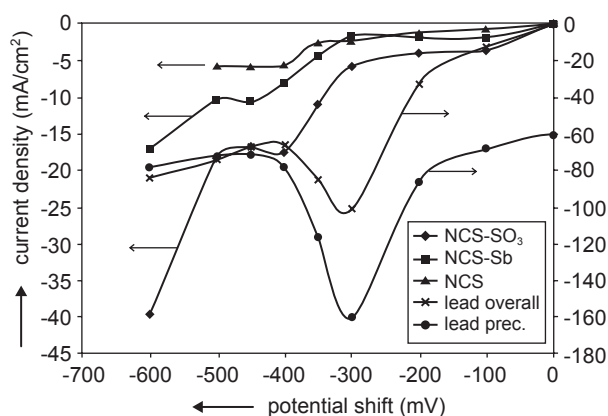


Figure 7. Comparison of "stationary" polarization curves in soda-lime-silica glass melts with additions of Sb_2O_3 (NCS-Sb) and SO_3 (NCS- SO_3) without additions (NCS) and that found in 24% PbO lead glass melt (lead overall) completed by the course calculated from the amount of precipitated lead (lead prec.).

The courses of the "stationary" polarization curves in soda-lime-silica glass melt containing various depolarizers completed by that obtained in glass melt containing 24% lead oxide [2] are compared in figure 7. It may be seen that the courses are similar in all the modifications of the soda-lime-silica glass melt: Up to the potential reduced by 100 to 200 mV, the overall cathodic current increases, then its stagnation follows. Another increase occurs only at -300 to -350 mV, followed by another stagnation or minimum of cathodic current and by the third increase at about -500 mV. The similar course shows also the far higher cathodic current in the glass melt with high content of lead oxide. The comparison of the polarization curves for the three modifications of the soda-lime-silica glass melt shows that the overall magnitude of the cathodic current is associated with the content of the electroactive components (corrosion depolarizers) in the glass melts. The comparison of the overall cathodic current with the current corresponding to the lead separation in the lead containing glass melt (and also other data given in the paper [2]) show that practically all the cathodic current in that glass melt is equivalent to the reduction of lead cations to metallic lead. It is probable that the analogous equivalence applies to a great extent also in soda-lime-silica glass melts. An assessment of the current densities necessary to form the layers of MoSi_2 confirms that statement: Taking into the calculation the density of MoSi_2 equal to 6310 kg/m^3 [8], the current density of 4.8 mA/cm^2 results for the layer $38 \mu\text{m}$ thick found in [4] after 7 h. For the layer $16 \mu\text{m}$ thick formed during 5 h in the glass melt without refining additions as described above, that current density amounts 2.8 mA/cm^2 . Both the values are comparable with the actual mean current density of 5.6 mA/cm^2 at -400 mV for the glass melt without additions in figures 4 and 7. They are, however, many times lower than the corresponding current densities in both the glass melts containing electroactive additions. (The formation of inside layers of lower molybdenum silicides that would somewhat increase the resulting values was not taken into account in the above calculation). It may hence be stated that the prevailing share of the cathodic current in the potential range studied is not transferred by reduction of alkali cations and by succeeding equivalent silicide formation at the presence of those electroactive species. The majority is transferred either by the direct reduction of those electroactive species, or, more likely, the alkali metal reduces those species prior to silicates. Both the dependence of the height of the cathodic peaks on stirring rate described in [9] and the deteriorated formation of silicide layers in presence of those components of glass melt may be well explained in this way. For the sake of completeness, the reduction of OH^- groups bound in glass melt to hydrogen described in [4] should also be considered. The bubble formation was also observed in the present paper as described above.

The potentials of the plateau on cathodic current in glass melt without additions (-400 to -500 mV) and those of the local maximum in glass melt modified by Sb_2O_3 (-450mV) and by SO_3 (-400mV) in figure 7 do not differ substantially each other. When reduced by the corresponding rest state value of about -800 or -700 mV (cf. table 1), they also do not differ very much from the value of the local maximum of -1100 mV related directly to oxygen electrode given in the paper [9] for a glass melt of similar composition. The presence of electroactive specimens (acting as depolarizers of molybdenum corrosion) affects then in principle just the magnitude of the overall cathodic current as it has been substantiated above. In addition to that comparatively expressive effect associated with the reduction of alkali cations, the effect of decreasing anodic current on the resulting overall cathodic current manifests itself in the potential region between the corrosion potential and that corresponding to the finishing anodic molybdenum oxidation. Concerning the soda–lime–silica glass melts, that effect is most expressed in the glass melt containing SO_3 . The courses in the lead containing glass melt with its quite different composition are naturally not comparable with those in the above glass melts.

CONCLUSION

1. There exists a range of cathodic potentials reduced by some hundreds millivolts against the rest state where the reduction of electroactive species acting as depolarizers of molybdenum corrosion may be suppressed.
2. The potentials of the maximum suppression of lead or antimony precipitation correspond to potentials at which the anodic molybdenum oxidation finishes. The layers of molybdenum silicides have been not found on the electrode at those potentials. In glass melt containing sulfur trioxide, the sulfur depletion of glass takes place.
3. At more reduced potentials, the subsequent formation of silicon and formation of the silicides Mo_3Si , Mo_5Si_3 and MoSi_2 occurs.
4. The formation of silicon and silicides is impeded by presence of the electroactive glass components mentioned above. The overall cathodic current increases at the same time. That is probably due to the preferential reduction of the electroactive species by reduced alkali metal

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KATODICKÉ CHOVÁNÍ MOLYBDENOVÉ ELEKTRODY V RŮZNÝCH SKLOVINÁCH

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Cílem práce bylo zejména zjistit, jaký je vztah mezi potlačením anodické koroze a depolarizačních reakcí a přítomností vrstev silicidů na elektrodě v katodické oblasti. Katodické chování molybdenové elektrody bylo vyšetřováno v modelové sklovině o základním složení $16\text{Na}_2\text{O}$, 10CaO , 74SiO_2 (hmot.%) modifikované přísadami SO_3 nebo Sb_2O_3 , případně bez přísad při teplotě 1400°C . Bylo použito potenciostatické tříelektrodové uspořádání s molybdenovou pracovní a pomocnou elektrodou a jednoduchou platinovou referenční elektrodou. V tomto uspořádání byly získány stacionární polarizační křivky spolu s velikostí koroze při daném potenciálu. Byly dále vyšetřeny reakční produkty vznikající na elektrodě. Získané výsledky byly porovnány s dříve publikovanými výsledky pro sklovinu s obsahem 24 % PbO . Z výsledků a jejich diskuse plyne, že existuje oblast katodických potenciálů snížených vůči klidovému koroznímu potenciálu o několik stovek mV, v níž je potlačena nejen anodická oxidace molybdenu, ale i redukce elektroaktivních látek působících jako depolarizátory koroze molybdenu. Potenciály, při nichž je maximálně potlačeno vylučování antimonu a olova, přitom odpovídají potenciálům, při nichž končí oxidace molybdenu. Za těchto podmínek nebyly na elektrodě nalezeny vrstvy silicidů. Ve sklovině s obsahem oxidu sírového bylo zjištěno ochuzení skloviny v okolí katody na síru. Teprve při dalším snížení potenciálu dochází k průkaznému vylučování křemíku a následně se tvoří vrstvy silicidů Mo_3Si , Mo_5Si_3 a MoSi_2 . Tvorba křemíku a silicidů je ztížena za přítomnosti výše uvedených oxidů včetně oxidu olovnatého. Současně vzrůstá celkový katodický proud. Pravděpodobnou příčinou je přednostní redukce těchto oxidů vyredukovaným alkalickým kovem před redukcí oxidu křemičitého.