

Influence of process parameters on the formation of protective MoSi_x layers on molybdenum electrodes during electric melting of glass

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With the aid of laboratory experiments, the cathodic passivation of molybdenum electrodes during electrical melting of glass was studied. The formation of molybdenum silicide layers does not only depend on the cathodic passivation currents, but also on time and the AC heating current density. If the melt has freshly been prepared from raw materials, the molybdenum silicide layer is thinner than under otherwise same conditions. While at an AC heating current density of 1 A/cm^2 , a cathodic current density of 3.75 mA/cm^2 led to optimum layer formation, at a heating current density of 2 A/cm^2 , higher cathodic current densities are required.

Einfluß von Prozeßparametern auf die Bildung von MoSi_x -Schutzschichten auf Molybdänelektroden bei der Elektroschmelze von Glas

Die kathodische Passivierung von Molybdänelektroden bei der Elektroschmelze von Glas wurde mit Hilfe von Laborexperimenten untersucht. Die Bildung von Molybdänsilicidschichten hing nicht nur von den kathodischen Passivierungsströmen ab, sondern auch von der Zeit und der Heiz(Wechsel)-Stromdichte. Wurde die Schmelze frisch aus Rohstoffen hergestellt, war die Molybdänsilicidschicht dünner als unter sonst gleichen Bedingungen. Während bei einer Heizstromdichte von 1 A/cm^2 eine kathodische Stromdichte von $3,75 \text{ mA/cm}^2$ zu einer optimalen Schichtbildung führte, waren bei einer Heizstromdichte von 2 A/cm^2 höhere kathodische Stromdichten erforderlich.

1. Introduction

The corrosion of molybdenum electrodes during electric melting of glass is still a problem for many glass melt compositions [1 to 5]. While e.g. in borosilicate melts, metallic molybdenum possesses a high degree of chemical stability even at temperatures as high as 1600°C , high corrosion rates are observed, if the glass melts contain polyvalent compounds [6 and 7]. According to the electrochemical series of elements [6 and 7], many polyvalent compounds occurring in their oxidized state can be reduced by metallic molybdenum to the corresponding reduced state [8 and 9]. Especially, high corrosion rates are observed if this reduced state is the metal, e.g. in the case of NiO , CoO , PbO , SnO_2 , As_2O_3 or Sb_2O_5 . Then the metal is deposited on the electrode surface, may form alloys with molybdenum and also form local galvanic elements which may further enhance the corrosion process [7 and 10].

To minimize the corrosion of molybdenum electrodes, three techniques have been developed in the past decades. The first is the low-frequency passivation [5], which fundamentals, up to now, are not understood. Furthermore, both anodic [1] and cathodic [2] passivation have been introduced. Here DC currents are superimposed between the heating electrodes and a counter

electrode additionally inserted into the melt. In the case of the cathodic passivation, MoSi_x layers are formed if the current densities applied are high enough [10 to 12]. As recently pointed out, these layers increase in thickness with the current densities applied [12]. If the current density, however, exceeds a certain value, the layers become unstable and are dissolved into the melt as molybdenum silicide particles. In this paper, laboratory experiments are carried out which are fairly close to the technical system. This equipment has already been used in previous studies [12]. Up to now, solely the influence of the superimposed cathodic current densities on the formation of the MoSi_x layer has been reported. In this paper, the effect of further experimental parameters, such as time, temperature and heating current density is described.

2. Experimental procedure

A container fabricated from refractory was located inside an SiC-heated furnace. It contained about 800 g of a soda–lime–silica glass melt with the composition (in wt%): 72.11 SiO_2 , 13.27 Na_2O , 6.34 CaO , 3.47 MgO , 1.12 Al_2O_3 , 1.83 B_2O_3 , 1.7 K_2O and 0.15 Sb_2O_3 . The molybdenum electrodes were embedded in alumina tubes and additionally in a sleeve prepared from refractory to avoid a contact of the metal with air. Altogether, three electrodes were inserted: two of them acted as

Received November 6, 1997.

heating electrodes and the third one as counter electrode. Between the heating electrodes, an AC current density in the range of 0.5 to 2 A/cm² was supplied. Between these two heating electrodes and the counter electrode, a DC potential resulting in current densities in the range of 0 to 20 mA/cm² was supplied.

The experimental equipment as well as the procedure to introduce the electrodes into the melt has already been described in detail in [12].

After a certain corrosion time in the range of 20 to 50 h at which both constant AC and DC currents were supplied, the electrodes were drawn from the melt, embedded in resin and cross cut. After grinding and polishing, the cut was studied using a scanning electron microscope (SEM DSM 940 A, Carl Zeiss, Oberkochen (Germany)) and an energy dispersive X-ray analysis (EDX exl 10, Link, Oxford (UK)).

3. Results

3.1 Influence of time

In a series of experiments, the influence of time on the formation of the MoSi_x layer was studied. For that purpose, electrodes were drawn from the melt after corrosion times of 20, 30, 40 and 50 h. The experimental parameters were an AC heating current density of 1 A/cm² and a cathodic DC current density of 3.75 mA/cm². Figure 1a shows an SEM micrograph after a time of 20 h. The electrode possesses light appearance in the micrograph, the glass adherent at the electrode is of dark color. In between, a highly porous layer is observed consisting of metallic molybdenum, interpenetrated by a glassy phase. Silicon is not detected by EDX within the light regions of the micrograph and hence a molybdenum silicide layer is not formed. The metallic molybdenum is spread as particles into the melt. The state of the electrode is fairly similar to that of an electrode without any superimposed cathodic potential (see [12, figure 6a]). A longer corrosion time of 30 h leads to a different appearance, as shown in figure 1b. Here, at the surface, a layer slightly darker than the bulk electrode is seen. The mean thickness of this layer is around 15 μm and high quantities of silicon are detected by EDX. It is still porous and particles of light appearance consisting of molybdenum silicide are spread into the melt during corrosion. After 40 h (figure 1c), the layer possesses a thickness of around 50 μm and still contains some large pores with diameters in the range of 5 to 10 μm as well as notable smaller ones. After 50 h corrosion time, a further slight growth of the layer is observed. As shown in figure 1d, the thickness is now 60 μm and the porosity of the layer further decreased.

3.2 Influence of the AC heating current

In [12], the influence of the cathodic DC current density on the formation of the molybdenum silicide layer has already been described and DC current densities in the range of 2.5 to 5 mA/cm² have been reported to be op-

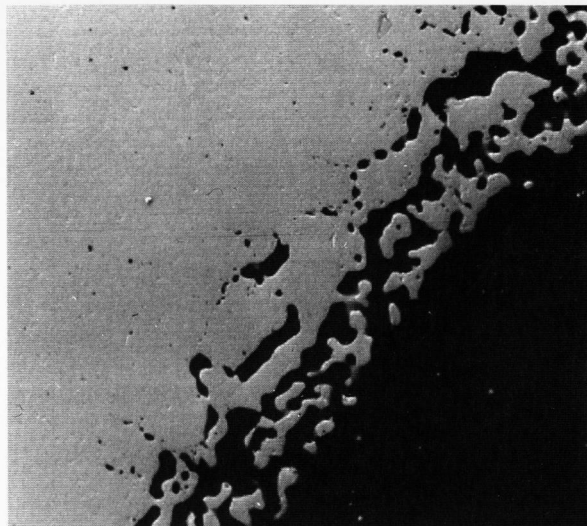
timum values for the formation of a strongly adherent molybdenum silicide layer. From studies in industrial glass furnaces as well as from laboratory experiments, it is well known that high heating current densities lead to stronger corrosion. Therefore, in this series of experiments, the heating current densities were adjusted to values of 0.5, 1 and 2 A/cm² while DC current densities of 2.5, 3.75 and 5 mA/cm² were supplied. Figure 2a shows an SEM micrograph of a molybdenum electrode corroded for 50 h using a DC current density of 2.5 mA/cm² and an AC current density of 2 A/cm². A porous layer possessing a thickness of around 80 μm is seen. This layer consists of metallic molybdenum, silicon is not detected using EDX. Some large particles of metallic molybdenum are seen in the adherent glass. By contrast, using an AC current density of 1 A/cm², a protective MoSi_x layer has been observed [12]. A DC current density of 3.75 mA/cm² led to the formation of molybdenum silicide layers with thicknesses of up to 60 μm, if AC current densities of 0.5 and 1 A/cm² (see figure 1d) were supplied. Figure 2b shows an SEM micrograph of a molybdenum electrode corroded using an AC current density of 2 A/cm² and a DC current density of 3.75 mA/cm². Also in this case, a porous layer consisting of metallic molybdenum and not of molybdenum silicide is observed. By analogy to figure 1b, also here metallic particles are found in the glassy phase. Figures 2c to e show SEM micrographs of electrodes corroded using a DC current density of 5 mA/cm² and AC current densities of 0.5, 1 and 2 A/cm², respectively. A DC current density of 0.5 A/cm² led to a molybdenum silicide layer possessing a thickness of around 40 μm which was strongly adherent and porous. Figure 2d shows a micrograph attributed to an AC current density of 1 A/cm². Here, a fairly similar layer was observed as in figure 2b. By contrast, in figure 2e which shows a sample corroded using an AC current density of 2 A/cm², the layer formed is much thinner (10 to 20 μm). However, it consists of molybdenum silicide as proved by EDX. Many molybdenum silicide particles possessing sizes of up to 20 μm in length are spread in the glass.

3.3 Influence of temperature

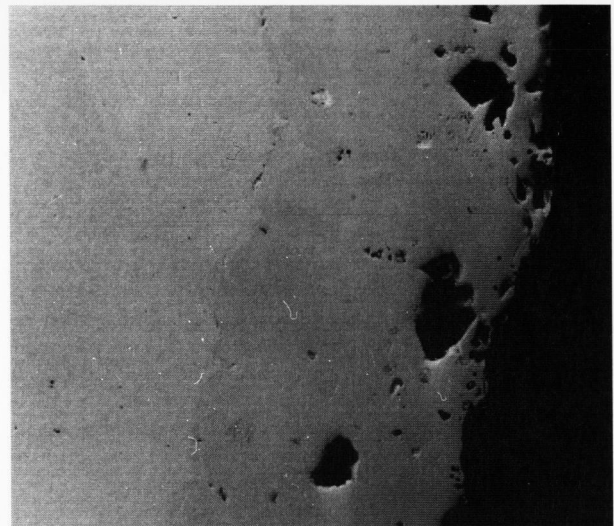
The experiments described up to now, were all performed using a temperature of 1450°C. Figure 3 shows an SEM micrograph of an electrode corroded at 1500°C. The AC current density was 1 A/cm² and the DC current density 3.75 mA/cm². The molybdenum silicide layer formed possesses a thickness of around 40 μm, i.e. 2/3 of that value obtained after corroding at 1450°C. Although the porosity is comparable to that obtained at 1450°C, the dissolution of the layer is somewhat stronger and more particles are spread into the melt during the corrosion process. Nevertheless, the layer formation is fairly good and comparable to that at 1450°C.

3.4 Influence of batch addition

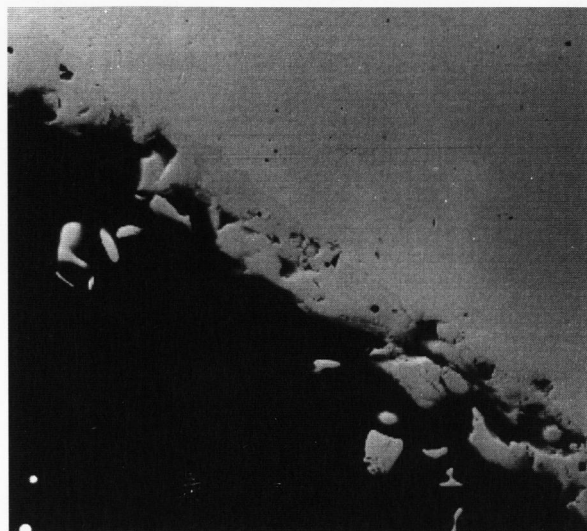
In the experiments described up to now, the glasses were melted from cullet and not changed during the corrosion



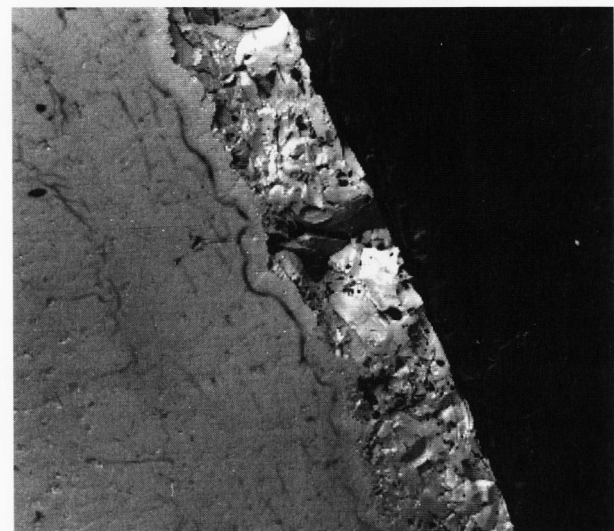
a) |————| 20 μm



c) |————| 20 μm



b) |————| 20 μm



d) |————| 50 μm

Figures 1a to d. SEM micrographs (backscattered electrons) of heating electrodes at an AC heating current density of 1 A/cm², a DC current density of 3.75 mA/cm² and a temperature of 1450 °C as a function of the corrosion time, a) 20 h; b) 30 h; c) 40 h, d) 50 h.

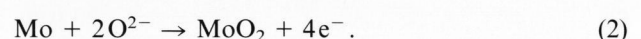
experiments. In a series of experiments, this was modified as follows: after inserting the electrodes into the melt and supplying an AC current density of 1 A/cm² and a DC current density of 3.75 mA/cm², within 8 h, altogether 400 g of raw materials were added to the batch (the overflowing glass was collected in a crucible [12]). After soaking for 16 h, another 200 g raw materials were added within 8 h. After another 18 h, i.e. after a total corrosion time of 50 h, the electrodes were drawn from the melt. Figure 4 shows an SEM micrograph of the molybdenum electrode. The molybdenum silicide layer observed possesses a thickness of 20 to 30 μm and is strongly fissured. Silicide particles spread into the melt were not observed.

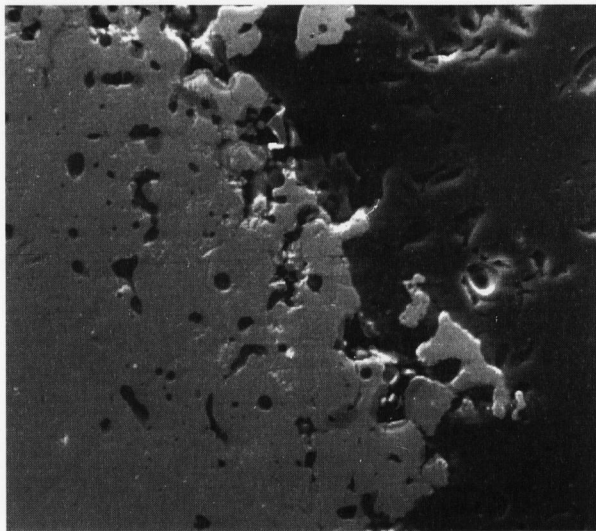
4. Discussion

Cathodic polarization of molybdenum heating electrodes may lead to the formation of molybdenum silicide layers at the surface. During this cathodic reaction, SiO₂ as component of the glass melt is reduced:

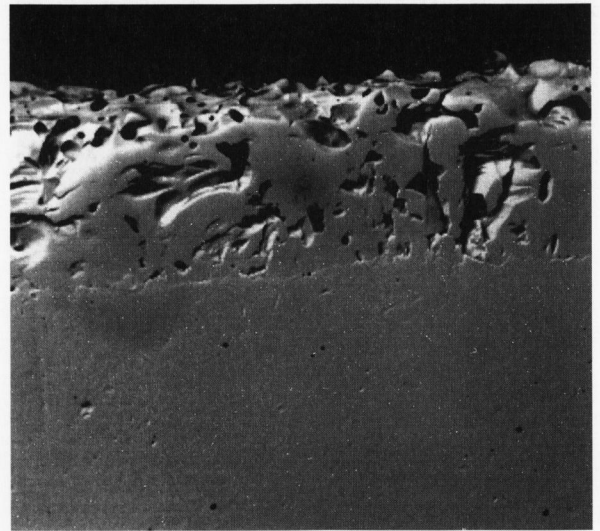


Simultaneously, polyvalent ions, such as Fe³⁺, Pb²⁺ or Sb⁵⁺ are also reduced. At the anode [12], at high current densities, the formation of MoO₂ layers is observed:

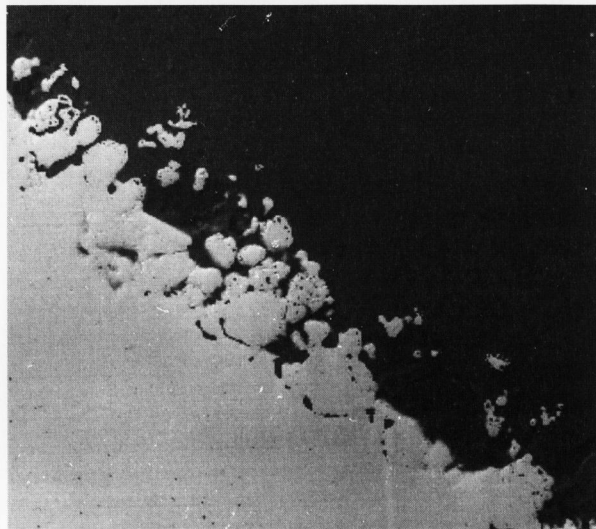




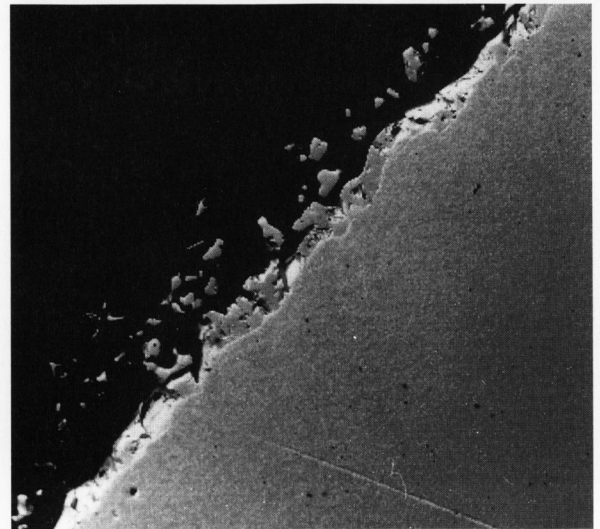
a) |————| 20 μm



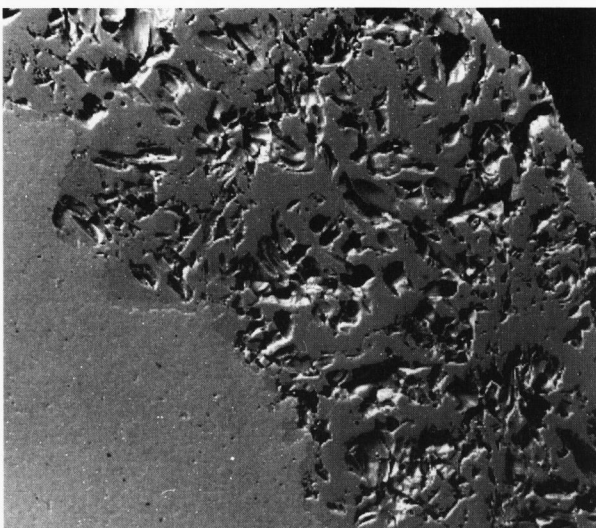
d) |————| 20 μm



b) |————| 50 μm



e) |————| 50 μm



c) |————| 20 μm

Figures 2a to e. SEM micrographs (backscattered electrons) of heating electrodes after a corrosion time of 50 h at a temperature of 1450 °C at different AC and DC current densities, a) $i(\text{DC}) = 2.5 \text{ mA/cm}^2$, $i(\text{AC}) = 2 \text{ A/cm}^2$; b) $i(\text{DC}) = 3.75 \text{ mA/cm}^2$, $i(\text{AC}) = 2 \text{ A/cm}^2$; c) $i(\text{DC}) = 5 \text{ mA/cm}^2$, $i(\text{AC}) = 0.5 \text{ A/cm}^2$; d) $i(\text{DC}) = 5 \text{ mA/cm}^2$, $i(\text{AC}) = 1 \text{ A/cm}^2$; e) $i(\text{DC}) = 5 \text{ mA/cm}^2$, $i(\text{AC}) = 2 \text{ A/cm}^2$.

From equation (1) it is clear that the growth of the layer is directly attributed to the current density and hence, increasing layer thickness at increasing current densities are not surprising. As pointed out in [12], high current densities $i(\text{DC}) > 10 \text{ mA/cm}^2$ led to rapidly growing layers which are not fully stable and molybdenum silicide particles are spread into the glass melt as particles. The formation and dissolution of the molybdenum silicide layer, however, are not solely functions of the DC current density applied. First, the layer needs some time to be formed. At the beginning, the electrode behaves in

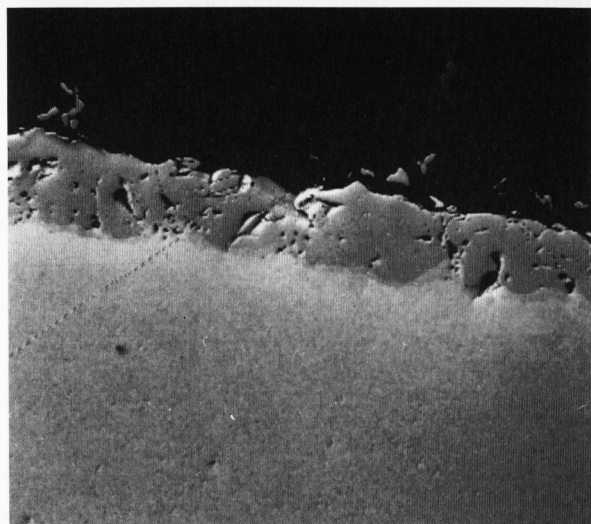


Figure 3. SEM micrograph (backscattered electrons) of a heating electrode after a corrosion time of 50 h at a temperature of 1500 °C ($i(\text{DC}) = 3.75 \text{ mA/cm}^2$, $i(\text{AC}) = 1 \text{ A/cm}^2$).

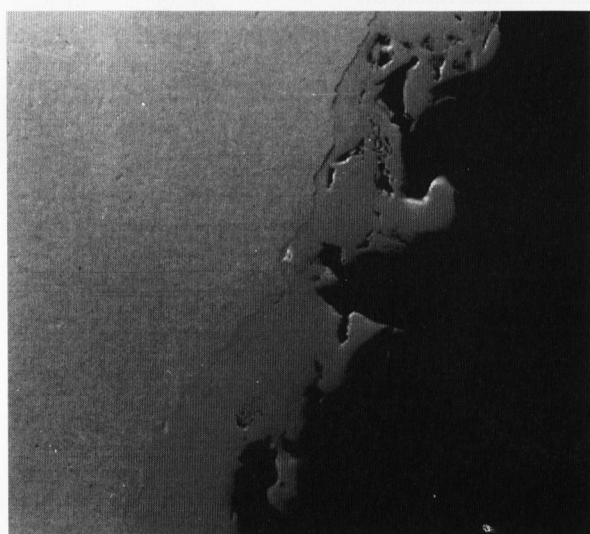


Figure 4. SEM micrograph (backscattered electrons) of a heating electrode after a corrosion time of 50 h at 1450 °C ($i(\text{DC}) = 3.75 \text{ mA/cm}^2$, $i(\text{AC}) = 1 \text{ A/cm}^2$) after addition of batch.

the same manner as an electrode without any superimposed cathodic current. After a corrosion time of 30 h, the silicide layer is observed and further grows over the whole duration of the experiments. If the formation of stoichiometric MoSi₂ is assumed, x in equation (1) is equal to 2 and from the current flow, a theoretical thickness of the layer, d , can be calculated from the density of MoSi₂ (6.31 g/cm³):

$$d = C \cdot t \cdot i \quad (3)$$

with $C = 1.136 \mu\text{m} \cdot \text{h}^{-1} \cdot \frac{\text{cm}^2}{\text{mA}}$ and t in h,

and i in $\frac{\text{mA}}{\text{cm}^2}$.

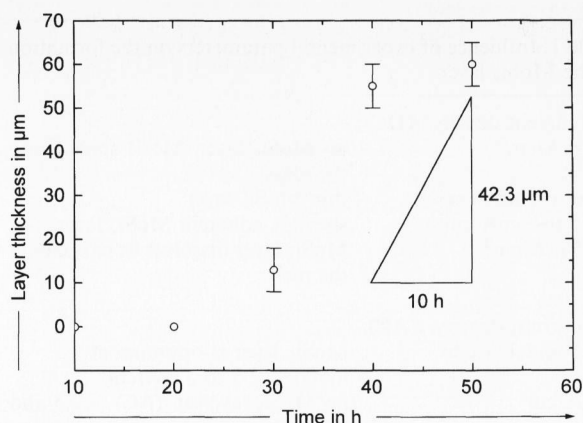


Figure 5. Thickness of the molybdenum silicide layer as a function of time.

According to this calculation, the thickness of the layer should increase by 42.6 μm every 10 h at a current density of 3.75 mA/cm², if the only cathodic reaction is that according to equation (1). In figure 5, the layer thickness is drawn against the corrosion time. It is seen that between 30 and 40 h, the layer grows by around 42 μm which is in total agreement with the theoretical calculation above. After supplying the cathodic current, first polyvalent ions, such as Fe³⁺ which occur in the vicinity of the electrode are reduced, because these compounds possess less negative standard potentials than the reaction according to equation (1) [10]. During 10 h at 3.75 mA/cm² and a total electrode area of 16 cm², a charge flow of 2.16 kA s occurs. This is attributable to a quantity of e.g. 1.08 g Sb₂O₃, if it is assumed that all antimony occurs as Sb³⁺ and is reduced within a three-electron step to the corresponding metal or, however, to e.g. 1.6 g Fe₂O₃. By comparison with the chemical composition and the quantity (800 g) of the melt, 1.08 g Sb₂O₃ and 1.6 g Fe₂O₃ correspond to concentrations of 0.135 and 0.2 wt%, respectively. Since in the white glass melt used, iron occurs in much lower concentration, mainly Sb₂O₃ should contribute to the current flow. Within the first 20 h, i.e. that corrosion time which does not yet lead to the formation of a silicide layer, a higher charge flow (4.32 kA s) occurs than that of 2.40 kA s attributed to a quantitative reduction of Sb₂O₃ to metallic antimony. Two reasons may be responsible: first, reduced ions may be oxidized again at the anode or at the surface of the melt and secondly, other polyvalent elements, such as Fe³⁺ or sulfur compounds may also contribute.

However, the formation of the molybdenum silicide layer does not solely depend on DC current density and time, but is also influenced by temperature and the AC current density. An increase in temperature enhances both diffusion and convection and hence may lead to a stronger participation of the polyvalent ions in the electrode reactions as described above. Besides, also the dissolution of the layer as silicide particles into the melt

Table 1. Influence of experimental parameters on the formation of the MoSi_x layer

DC current density, $i(\text{DC})$:	
0 mA/cm ²	no MoSi _x layer, Mo is spread into the glass
up to 2 mA/cm ²	thin MoSi _x layer
2.5 to 5 mA/cm ²	strongly adherent MoSi _x layer
>5 mA/cm ²	MoSi _x layer dissolves as particles in the melt
AC current density, $i(\text{AC})$:	
0.5 and 1 A/cm ²	MoSi _x layer is optimum at $i(\text{AC}) = 2.5$ to 5 mA/cm ²
2 A/cm ²	no MoSi _x layer at $i(\text{AC}) = 2.5$ and 3.75 mA/cm ²
	thin MoSi _x layer at $i(\text{AC}) = 5$ mA/cm ²
temperature increase:	the MoSi _x layer formed is thinner
batch addition:	the MoSi _x layer formed is thinner
time ($i(\text{DC}) = 3.75$ mA/cm ²):	
up to 20 h	no MoSi _x layer, Mo is spread into the glass, same appearance as without cathodic passivation
20 to 50 h	the MoSi _x layer is formed and grows with time up to 60 μm thickness after 50 h

should be higher at higher temperatures. Therefore, it is not surprising that at a higher temperature a thinner molybdenum silicide layer is observed.

Obviously, an increase of the AC current density to a value of 2 A/cm² drastically influences the formation of a protective MoSi_x layer. At DC current densities of 2.5 and 3.75 mA/cm², the formation of a silicide layer is not achieved, while at lower AC current densities of 0.5 and 1 A/cm², strongly adherent layers are formed. By increasing the DC current density to 5 mA/cm², also at an AC current density of 2 A/cm², a molybdenum silicide layer is formed. By contrast to lower AC current densities, the layer is not as strongly adherent and notably thinner. In principle, however, it can be stated that higher DC current densities also require higher AC current densities superimposed. In this context, it should be noted that in industrial glass tanks, current densities are usually around 1 A/cm² and current densities as high as 2 A/cm² are avoided, because otherwise the corrosion rate increases drastically.

The effect of AC current density on the layer formation is supposed to be fairly complex. In principle, an increase in the AC current density leads to an increase in temperature because the energy input (mainly localized to the vicinity of the electrodes) increases. In the model system used, however, this should not be the main reason, because of the more effective heat transfer by comparison to industrial glass furnaces. An additional reason should be that using a heating current with a frequency of 50 s⁻¹, during the anodic half-wave, oxidation of the electrode and during the cathodic half-wave, a re-

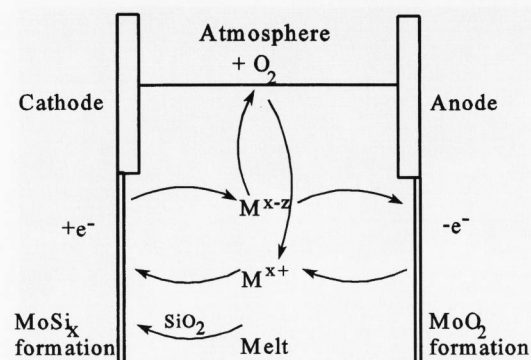


Figure 6. Schematic drawing of the redox processes during cathodic passivation of molybdenum electrodes.

duction process takes place. Higher currents should enhance the process and not all oxidized products formed during the anodic process will rediffuse to the electrode and hence will be reduced again during the cathodic process (see also figure 6).

A not as good formation of the molybdenum silicide layer is also observed, if raw materials are added during the corrosion process. This should mainly be caused by the polyvalent components of the raw materials, which in the case of the glass composition used should mainly occur in their oxidized states if the melt is freshly prepared from the raw materials but occur in the reduced state after many hours. Thus, as in the case of the time dependence of the layer formation discussed above, this can explain the thinner layers observed.

5. Conclusions

During cathodic passivation, a layer of molybdenum silicide grows on the molybdenum electrodes after a time lag of more than 20 h. The layer observed is thinner if the temperature is increased, the melt is freshly prepared from raw materials or the DC current is increased. While at an AC current of 1 A/cm², a DC current superimposed of 3.75 mA/cm² is optimum, an AC current of 2 A/cm² requires higher DC currents (e.g. 5 mA/cm²), otherwise, an MoSi_x layer is not formed.

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These investigations were conducted with the kind support of the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF), Köln (AiF-No. 10043), by agency of the Hüttentechnische Vereinigung der Deutschen Glasindustrie (HVG), Frankfurt/M, through the resources of the Bundesminister für Wirtschaft. Thanks are due to all these institutions.

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